APPENDIX F

Supporting Documentation for Case Studies and Remediation

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Managing Hydroblast Water During Turnarounds

By Hiram Perez

A case study

A turnaround at a refinery or chemical plant is typically a major event involving numerous plant and contractor personnel, all performing a variety of activities under strict budgets and timelines. These activities usually include the disassembly, cleaning, refurbishing, and reassembly of all feed lines, storage tanks, process towers, and associated equipment. One technique that is commonly used to clean surfaces of residual products such as scale, sludge, and polymer buildup is hydroblasting.

Hydroblasting

Hydroblasting uses specialized equipment to clean surfaces by "blasting" them with water at an elevated pressure of around 10,000 PSI. Compared to other cleaning techniques, hydroblasting is relatively quick and cost-effective. However, a typical hydroblaster uses anywhere from 30 to 60 gallons of water per each minute of use. Assuming it takes one 10-hour shift to clean a typical distillation tower, that's up to 36,000 gallons of contaminated wastewater that now has to be dealt with. With water disposal costs ranging anywhere from $0.50 per gallon for non-hazardous contaminants to over $2.50 per gallon for hazardous contaminants, you'd be looking at disposal costs of anywhere from $18,000 to over $90,000 for this one piece of equipment alone. Provision for this is frequently overlooked in the turnaround budget.

Case Study

This case study examines ways that one refinery essentially eliminated their disposal costs of hydroblast water during a recent major turnaround by proactively managing and tracking waste generation, storage, and disposition.

The Setting: North to Alaska

Williams Alaska Petroleum, Inc. owns and operates the largest petroleum refinery in Alaska with crude oil processing capability of 220,000 barrels per day. Located outside of Fairbanks in North Pole, Alaska, the refinery produces about 75,000 barrels per day of various petroleum products including gasoline, naphtha, jet fuel, heating fuel, diesel fuel, and asphalt. During May 11-27th of this year, the refinery shut down production to begin a $6 million scheduled turnaround of one of its main crude units. Turnaround specialist AltairStrickland West Inc. was brought in to provide overall project management as well as to coordinate the many contractors that would be required. Along with other specialized contractors, CAM Environmental Services was brought in to play a small but important role in this major event.

Before the Turnaround: Planning is Key

As with most turnaround activities, success is directly linked to the amount of planning that is performed. In many cases, environmental and waste issues are seen as something to be dealt with after the turnaround, not something to be planned for before the turnaround. Fortunately, this was not the case here. Technicians from CAM Environmental Services arrived the week before work actually began in order to familiarize themselves with the plant and to evaluate and finalize the waste management plans that would guide the tracking, testing, storage, and final disposition of all waste streams generated during the turnaround. Particular emphasis was placed on strategies to minimize the total volume of hydroblast water as well as ways

of keeping contaminant levels (primarily Sulfolane) low enough so it could be treated by the plant's own bioponds instead of having to be shipped for outside disposal.

During the Turnaround: Directing the Flow

CAM Technicians worked 12-hour shifts during the turnaround functioning as waste stream staging officers directing the flow of hydroblast water and other waste products to appropriate tanks or containers. Each tank or container was manifested for tracking purposes, analyzed to determine contaminant levels, and then segregated to avoid cross-contamination. As the analytical results were received, it was then possible to determine which tanks or containers could be combined before being discharged to the plant's bioponds for routine treatment as the turnaround progressed.

After the Turnaround : Conclusions and Lessons Learned

During a similar turnaround in 2002, the waste management plan in place underestimated the impact of Sulfolane-contaminated wastewater on the overall management of turnaround wastewater, and the burden of managing turnaround-related environmental issues severely taxed the environmental staff. As a result, a large quantity of hydroblast water was generated that had to be stored in rail cars until it could be processed. In contrast, during the 2003 turnaround, all of the hydroblast water was handled in-house with no need for outside disposal. Also, since the water was treated as the turnaround progressed, there was no need for any type of long-term storage. Lessons learned from this experience are included in the following list.

Williams. CAM

1 **Have a plan before you need one.** Know how you will handle waste streams before they are generated. Otherwise, you are always in reaction mode trying to catch up. Involve an environmental firm during the planning stage of any turnaround.

2 **Segregation of waste keeps small problems from growing into big ones.** It only takes a small amount of hazardous waste accidentally mixed in with a large tank of water to make it all hazardous. Track the source of all waste streams and keep them separated by hazard type.

3 **Analyze your options.** Perform an analysis of each storage tank so you know the contaminant level of each. You can then decide whether to recycle, combine, dilute, or dispose.

4 **Process as you go.** Have a system in place for processing waste as it is being generated instead of waiting until you have a huge quantity to try to get rid of all at once. Waste management is part of the turnaround process, not something separate from it.

5 **Augment key support functions.** Turnaround operations can put a heavy burden on environmental staffing levels appropriate for routine operations. Augmenting the regular environmental staff with additional qualified environmental professionals provides additional support to manage large, non-routine projects.

About the Author

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For more information, please visit www.cam-enviro.com.

SULFOLANE IMPACTED SOIL AND GROUNDWATER TREATABILITY STUDY

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ABSTRACT

During the long-term groundwater quality monitoring, elevated concentrations of dissolved organic carbon (DOC) were reported at two of the gas processing plants located in Alberta. The concentrations of petroleum hydrocarbons (PHC) were several orders of magnitude less than the DOC concentrations, or were not detected. Glycols and amines were included in the analytical schedule to observe if the analytical results of any of these could be correlated to the DOC concentrations detected. They returned non-detectable concentrations. A plant site historical product inventory was conducted to determine if the presence of any other products at the site could cause elevated DOC concentrations. The result of the review detected that, in 1992, existing amine process replaced the Sulfinol® process. The Sulfinol® gas sweetening method involves a combination of chemical and physical processes. It also utilizes diisopropanolamine (DIPA) as a chemical solvent. DIPA interacts with sour gas via its central nitrogen atom.

In 2000, sulfolane analyses were added to the existing groundwater quality analytical schedule to address the results of the historical plant operations. More than a half of the groundwater monitoring wells reported concentrations of sulfolane above the background concentrations. There were no guidelines for the maximum allowable concentrations (MAC) of sulfolane in soil and groundwater at that time. In 2004, EBA, conducted several laboratory treatments trials for the remediation of the soils and groundwater impacted by sulfolane in preparation for the site remediation. In 2005, Canadian Council of ministers of Environment (CCME), and Alberta Environment (AENV) adopted the Canadian Association of Petroleum Producers (CAPP) guidelines.

The soil treatability study investigated potential for bio-cell or bioreactor option. The bio-treatability trial conducted at the Hydroqual Laboratories showed that significant decrease in the sulfolane concentrations in soil occurred after 78 days of treatment.

The groundwater treatability trials were conducted at TIPML and the Ecoterra Solutions Inc. facilities. The TIPML conducted three trial utilizing mineralization, UV treatment and combination of both of the methods. The combination of mineralization and UV irradiation achieved 95% sulfolane removal ratio. Ecoterra conducted an aeration trial utilizing micro bubbles technology (GLR) in conjunction with slurry mixing and nutrient amendments and achieved 73% of sulfolane removal ratio.

tomographic Imaging and Porous Media laboratory

INTRODUCTION

In the last 20 years, soil and groundwater quality assessments, monitoring and remediation programs were conducted on numerous oil and gas facilities in Alberta. During that time, several thousands of analytical results were reviewed and compared against regulatory guidelines and standards. The most common compounds for compliance monitoring are petroleum hydrocarbons (PHC) and salts (produced formation water). The PHC with established guidelines for benzene, toluene, ethylbenzene and xylenes (BTEX) and four product group fractions. Chloride concentration is the best indicator parameter to monitor formation water impacts. In addition, there are a few other general indicator parameters, which are regularly monitored to determine if other site-specific parameters should be included in the analytical schedule. One of these is Dissolved Organic Carbon (DOC), which is an indicator parameter of the presence of hydrocarbons in soil and/or groundwater.

During the long-term monitoring, elevated concentrations of DOC were reported at two of the gas plants located in Alberta where the soil and groundwater quality was monitored for over one decade. The concentrations of PHC were several orders of magnitude lower than DOC concentrations or not detected. Glycols and amines were included in the analytical schedule to observe if the analytical results of these compounds could be correlated to the DOC concentrations, but returned non-detectable concentrations. The plant site historical product inventory review was conducted to determine if the presence of other products at the site could cause elevated DOC concentrations. The result of the review detected that, in 1992, existing amine process replaced the Sulfinol® process. The Sulfinol® gas sweetening method involves a combination of chemical and physical processes. It also utilizes diisopropanolamine (DIPA) as a chemical solvent. DIPA interacts with sour gas components via its central nitrogen atom.

In 2000, sulfolane was added to the existing analytical schedule to address the results of the historical plant operations. More than a half of the monitoring wells reported concentrations of sulfolane above the background concentrations. There were no guidelines for the maximum allowable concentrations (MAC) of sulfolane in soil or groundwater at that time.

BACKGROUND

The purpose of the annual groundwater quality monitoring program is to determine if the plant activities are affecting the local groundwater quality. Since the installation of the initial groundwater monitoring well network (1991), groundwater samples have been collected and analyzed for the following compounds: Chloride, Nitrite + Nitrate as Nitrogen (NO_2 + NO_3 as N), Dissolved Organic Carbon (DOC), Dissolved Kjeldahl Nitrogen (DKN), Total Dissolved Solids (TDS), Total Petroleum Hydrocarbons (TPH), and Benzene, Toluene, Ethylbenzene and Xylenes (BTEX). For the last few years,

petroleum hydrocarbons (PHC) have been detected in the vicinity of the former flare pit and east of the evaporation pond. Also, during the fall 2001 groundwater sampling event, elevated concentrations of sulfolane were detected in the same area.

In 2002, additional groundwater investigation programs were conducted in an attempt to delineate aerial extent of the groundwater with elevated concentrations of sulfolane. Subsequently, 11 groundwater monitoring wells were installed east of the former flare pit at the plant site and off the plant site on the agricultural land (Figure 1).

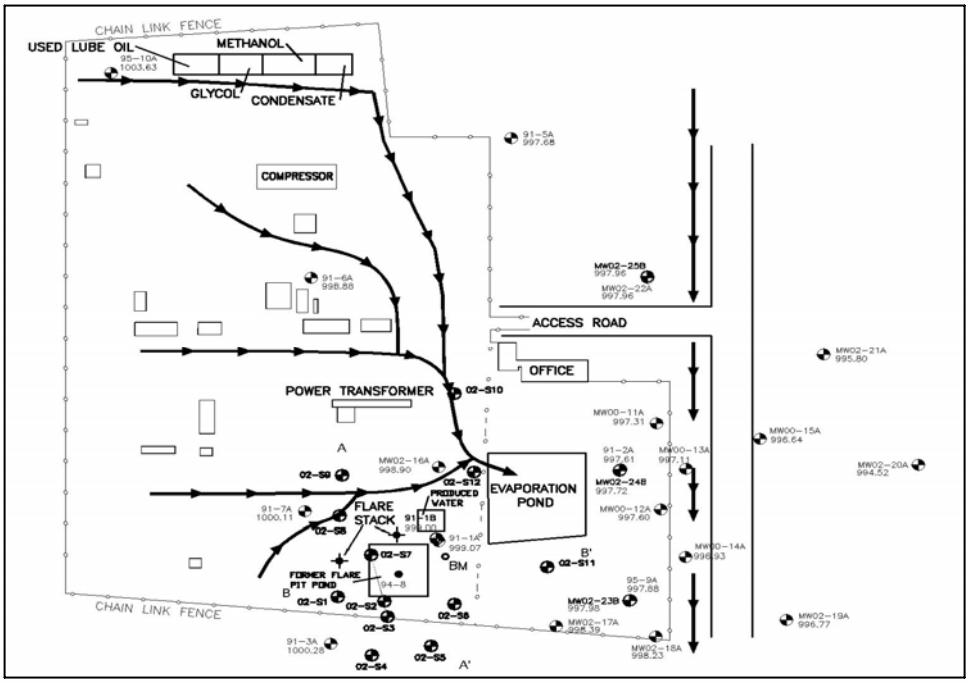

Figure 1 Plant Site Groundwater Monitoring Network

In addition to the groundwater investigation, in 2003, a detailed soil quality assessment program was conducted to determine the volume of soil with elevated concentrations of sulfolane and PHC, considered a secondary source of impact, in the vicinity of former flare pit area. A total of 54 soil samples were collected from 11 locations. It was estimated that approximately 9,600 m^3 of soil had concentrations of sulfolane greater than 500 mg/kg. The secondary source reduction was recommended.

In 2004, the groundwater quality investigation continued further east off the plant site. Additional 5 shallow and 3 deep wells were installed to delineate the aerial extent of the groundwater with concentrations of sulfolane greater than the background concentration, assumed to be 0.5 mg/L. Two of the 2004 monitoring wells returned concentrations of sulfolane greater than the assumed background concentration.

The plant site groundwater quality monitoring network is presented on Figure 1.

GEOLOGY AND HYDROGEOLOGY

The regional study area was defined as the area lying within a 5 km radius of the plant site. Information on regional bedrock and surficial geology and hydrogeology was compiled from various public sources. Information on regional groundwater use and quality was obtained from the Alberta Environment Water Well Drilling Report database.

Regional Geology

Upper Cretaceous continental deposits of the St. Mary River and Bearpaw Formations underlie the regional study area. These deposits comprise of sandstone, shale, siltstone, mudstone, ironstone beds, and thin coal beds.

Surficial geology in the regional study area includes Quaternary sand and gravel, and other unconsolidated sediments (clay, sand, silt).

Regional Hydrogeology

A total of 29 shallow domestic water supply wells are reportedly located within a 3 km radius of the plant site. These water wells meet industrial, domestic and livestock watering needs. The total depth of the domestic water wells range from 9 to 87 m, and their production rates range from 9 to 182 L/min. The static water levels appear to be below 30 m for the majority of the wells. Based on static water levels, these wells draw water from sources that are much deeper than the shallow water table at the plant site.

The closest shallow off-site domestic water well is located approximately 1.2 km east of the plant site.

The local groundwater quality, by potable standards, is poor with an average total dissolved solids content (TDS) of about 2,500 mg/L, ranging from <1,000 mg/L to 5,000 mg/L. The hydrochemical character is also quite variable with a significant sulphate component ranging from 131 mg/L to 1,449 mg/L and chloride concentrations ranging from 18 mg/L to 207 mg/L.

Topography and Drainage

The investigated area lies on the western edge of the Interior Plains. The highest elevation of the area is more than 1,600 m above sea level (m.a.s.l.) and is located in the southwest corner of the Porcupine Hills. The lowest point, where the Bow River leaves the area to the southeast, is 732 m above sea level (m.a.s.l.). The area has a variety of geomorphological structures, such as canyon-like river valleys, buried river valleys, smooth or pitted round moraine surfaces combined with eskers, gravel flats and level lacustrine plains. This area is a part of the South Saskatchewan River drainage basin.

There are a number of lakes in the area. Some among them (McGregor Lake, Travers Reservoir and Little Bow) are man-made. Most of the other lakes and sloughs in the area are of glacial origin.

Site Geology and Drainage

The maximum depth reached by boreholes drilled on the site was 11.0 m below ground surface (bgs). Geological sediments encountered beneath the site consist mainly of silty clay till with some sand lenses. The clay till is highly heterogeneous.

The plant site topography is gently sloped towards east (4%). The plans site surface runoff water is collected and stored at the plant site.

Plant Site Hydrogeology

The thickness of Quaternary deposits in the plant site area, as documented by Alberta Environment water well records, is estimated to be in the order of 30 m. The dominant surficial deposit consists of clay tills with silty sand lenses and layers. The clay till bulk hydraulic conductivity, based on slug test results, range from 1.02×10^{-5} to 1.41×10^{-7} cm/s.

The water table lies from 0.88 to 2.96 m (bgs) and exhibits seasonal fluctuations with elevations generally lower in the autumn.

GROUNDWATER QUALITY

The plant site groundwater quality has been monitored for the last fifteen years. The plant site groundwater quality was assessed by comparing the analytical results from the groundwater monitoring network to the assumed background concentrations and Canadian Council of ministers of Environment (CCME) 2003 Canadian Drinking Water Quality Guidelines (CDWQG).

The time series chat of Benzene and Sulfolane concentrations are presented on Figures 2 and 3, respectively.

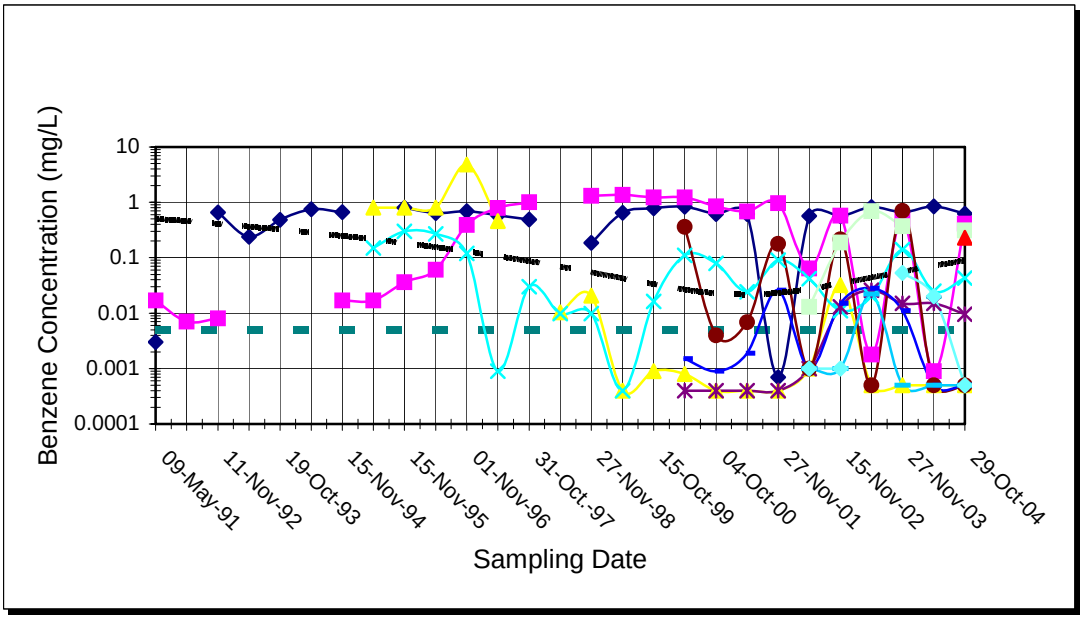

Figure 2. Time Series Plot of Benzene Concentration

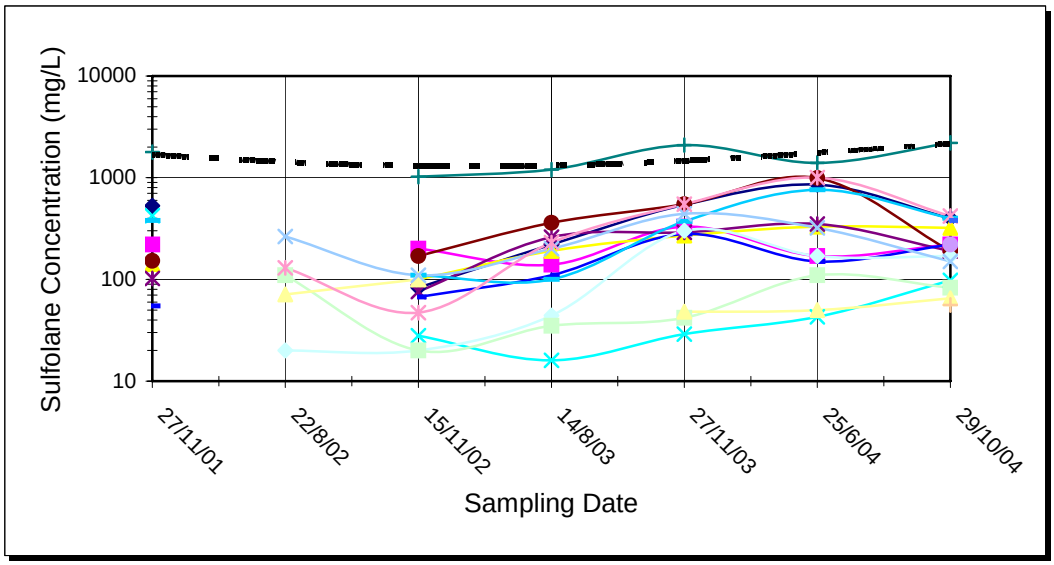

Figure 3. Time Series plot of Benzene Concentration

Figure 4 presents the sulfolane concentration distribution map for autumn of 2004.

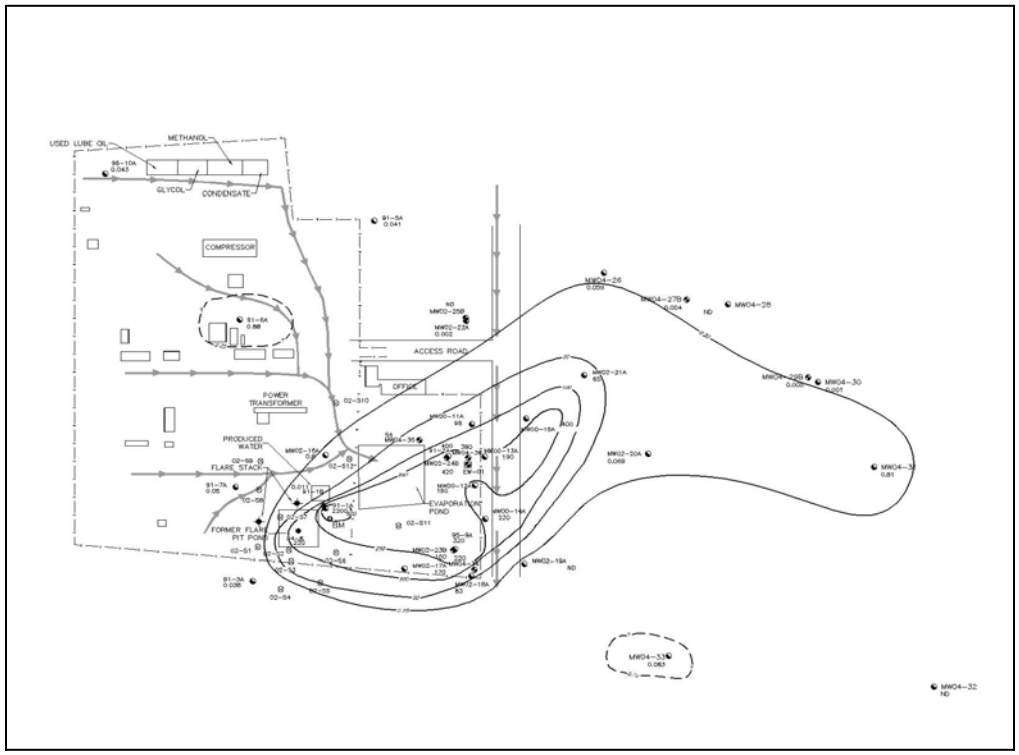

Figure 4 Sulfolane Concentration Distribution Map

Based on these result the sulfolane impacted soil and groundwater laboratory trials have been scheduled.

SULFOLANE DEGRADATION TRIAL

Sulfolane ($C_4H_8O_2S$) is common trade name for an organic chemical – tetrahydrothiophene 1,1-dioxide which is colourless, very polar, highly water soluble and extremely (chemically and thermally) stable compound. It was used in variety of industrial purposes, principally developed by Shell in early 1960's for extracting aromatics from hydrocarbon mixtures such as petroleum naphtha, pyrolisys gasoline or coke-oven light oil [1,2]. Its second major application is in the process of "sweetening" of natural gas streams such as, Sulfinol® and Sulfreen® processes, where it acts as the physical solvent for removal of sour components (acid gases) [3].

Sulfolane is known to have leached into groundwater through spills, landfills and unlined surface storage ponds. It was determined that Sulfolane mobility in soil is very high [4,5]. Thus, due to sulfolane high water solubility, stability and high mobility in soil and groundwater, poses a risk for an off-site impacts.

In 2005 CCME and AENV adopted CAPP guidelines for the maximum allowable concentration of sulfolane in soil and groundwater 2.3 mg/kg and 0.26 mg/L, respectively.

The sulfolane degradation trials for soil and groundwater were conducted utilizing chemical oxidation and aerobic bio-degradation.

SOIL TREATABILITY TRIAL

The soil treatability trial was conducted at Hydroqual Labs. The soil treatability trial investigated a potential for bio-cell or bioreactor application. Five samples of soil from suspected sulfolane impacted area of the former flare pit were submitted for the analytical analyses. The sulfolane concentrations in those samples varied from 450 mg/kg to 3400 mg/kg. The two samples with the highest concentrations of sulfolane (moist sandy clay) containing a heterogeneous mixture of black and brown colour soil and a strong hydrocarbon and sweet odour were homogenized and prepared for treatability trial.

The initial treatability trial design incorporated seven treatments to evaluate the effectiveness of two organic fertilize amendments on enhancing the biodegradation of sulfolane and available hydrocarbons. The seven treatments included: untreated control, sterile control, condensate contaminated soil, 83 mg/kg Nitrogen based fertilizer (35:0:0), 232 mg/kg Nitrogen based fertilizer (35:0:0), 83 mg/kg Nitrogen Phosphate based fertilizer (28:14:14), and 232 mg/kg Nitrogen Phosphate based fertilizer (28:14:14). In addition, media toxicity analyses were conducted. The tests were conducted in 4-L polycarbonate bioreactors fitted with air-tight lids and oxygen sensors.

During the tests the oxygen concentrations were maintained at >10%. The soils in bioreactors were mixed weekly to provide proper soil aeration. The soil samples from the bioreactors were collected at 0, 15, 30, 45, and 78 day of the treatment. The soil samples were analyzed for CCME BTEX and F1 +F2, Nutrients, TKN, Available Ammonia Nitrogen, and Sulfolane.

GROUNDWATER TREATABILITY TRIALS

The groundwater treatability trails were conducted at University of Calgary, Tomographic Imaging and Porous Media laboratory (TIPML) and at the Ecoterra Solutions Inc. facility.

The TIPML conducted three trials: sulfolane mineralization, UV irradiation and combination of both of the methods. Ecoterra conducted an aeration trial with fertilized amendment.

Sulfolane Mineralization

The first trial with stoichiometric amount of hydrogen peroxide required for sulfolane degradation, was intended for simulation of in-situ groundwater remediation. Mineralization of sulfolane by hydrogen peroxide is presented by the following reaction:

$$C_4H_8O_2S + 13\ H_2O_2 = 4\ CO_2 + H_2SO_2 + 16\ H_2O$$

Three groundwater samples with concentrations of sulfolane in range of 800 to 1,000 mg/L were used for this trial. In addition, the groundwater samples contained hydrocarbons that could use hydrogen peroxide for their own degradation. Since, the amount of hydrocarbons present in the samples varied significantly five times larger amount (that required by stoichiometry) of hydrogen peroxide was applied.

UV Irradiation

Before commencing UV irradiation experiments, spectrophotometer evaluation of light absorbance by sulfolane solution was performed to identify the possibility of photolysis. The result was that sulfolane solution did not show any absorption of the light in the visible region, only UV region seemed to be active indicating that direct photolysis of sulfolane was most probable under the UV irradiation.

Mineralization and UV Irradiation

In this trial combination of both of the previously conducted experiments were combined. However it is known that UV irradiation initiates significant production of hydroxyl radicals from hydrogen peroxide. Hydroxyl radicals act as a potent oxidant because if it's high oxidation potential and non-selective reactivity. As an example the oxidizing strength of common oxidizers in water such as OH^- , O_3, Cl_2, ClO^- are 2.8 V, 2.1 V, 1.4 V, and 0.9 V, respectively. Therefore, various water treatment technologies (ozonation, direct photolysis, H_2O_2) inherently produce some amount of hydroxyl.

In combined experiment the groundwater sample was treated with 50 ml/L of 30% H_2O_2 in a rotation setup under UV irradiation for a week. Irradiation was achieved using a 40W fluorescent bulb with emission centered at 350 nm.

Aeration Trial

The aeration trial was conducted utilizing micro bubbles technology® in conjunction with slurry mixing and two fertilizer amendments previously applied in the soil treatability trial. This trial was conducted at 15°C ambient temperature and constant mixing for 24 hours. The average dissolved oxygen concentration in the water sample was 7.7 mg/L.

SUMMARY OF RESULTS

Soil

The homogenized soil sample is toxic to Microtox® and remains toxic with no addition of fertilizer after 78 days of incubation. However, after 78 days of incubation with ammonia phosphate fertilizer the sample of soil becomes non-toxic to Microtox®.

The hydrocarbons presented in the soil sample were biodegraded before sulfolane in the treated samples. The sulfolane degrading bacteria required longer time to adapt than the hydrocarbon degrading bacteria.

Full sulfolane biodegradation occurred with ammonium phosphate addition of 83 mg/kg and 232 mg/kg. There was no obvious production of toxic by-products.

Groundwater

The following table summarizes the sulfolane degradation trial results.

Sample Description	Sulfolane (mg/L)	Removal Ratio (%)	Time (hours)
Blank	1200 (1800*)		
Mineralization	950	21	168
UV Irradiated sample	1000	17	168
Mineralization + UV	63	95	168
Aeration + Nutrients	490*	73	24

Chemo-physical Treatment

The combination of mineralization and UV irradiation revealed the highest ratio of sulfolane removal (95%) under the chemo-physical treatment after one week of treatment. Significant production of gases was observed during this experiment.

In order to estimate the time required for similar field application under the sunlight, the assessment of UV energy consumed in the lab trial was required. This value can be compared to the solar energy (W/cm^2) and the time of the field experiments is calculated based on the known lab trial time as follows:

Energy, P, consumed by the sample during the lab experiment was estimated using the following equation:

$$P = E_{photon} * I/S = 0.2 \ (m \ J/s \ cm^2)$$

Where
- E_{photon} is energy of a single photon
- I is intensity of the photon flux in the system, and
- S is surface of irradiated vessel.

Energy of single photon can be approximated as:

$$E_{photon} = h\upsilon = hc/\lambda = 5.67*10^{-19} \ (J/photon)$$

Where
- h is a Plank constant; $h= 6.62*10^{-34}$
- $c = 3*10^8$ m/s, and
- $\lambda = 350nm$

The intensity of the photon flux, I = 2.25*10^{16} (photons/s) was measured previously by ferrioxalate actinometry [6].

Therefore, solar energy required was calculated using the following formula;

$$E_{solar} = \mathbf{0.2\ m\ W/cm^2} \quad and\ E_{\lambda,400nm} = \mathbf{3.5\ mW/cm^2}$$

Thus, the week of UV irradiation on the lab will be equal to:

$$7\ days * (0.2\ m\ W/cm^2/3.5\ mW/cm^2) = \mathbf{10\ hrs}\ of\ sun\ exposure.$$

Biodegradation Treatment

The bioremediation treatment (aeration in conjunction with slurry mixing and ammonia phosphate amendments) and resulted in decrease of initial sulfolane concentrations of 1800 mg/L to 490 mg/L in 24 hours. Therefore, 73% of sulfolane was removed from the groundwater sample

CONCLUSIONS

The sulfolane treatability in soil samples was achieved utilizing aerobic conditions and ammonia phosphate fertilized amendments, after 78 days of treatment.

The groundwater impacted by sulfolane degradation occurred under the chemo-physical and biodegradation (aeration) processes.

The mineralization and UV irradiation treatment achieved 95% removal of sulfolane after one week of treatment. If field scale treatment utilizes sunlight, 10 hours of the daily light would be required. However, UV reactor should be considered as well.

The biodegradation treatment achieved 73% of sulfolane removal after 24 hours. The field scale treatment would require the water treatment and storage facility.

Based on these results, the field scale trials for soil and groundwater treatment should be scheduled. More aggressive methods should be considered in order to minimize the time required the successful treatment.

CREATING AND DELIVERING BETTER SOLUTIONS

Sulfolane Impacted Soil and Groundwater Treatability Study

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EBA ENGINEERING CONSULTANTS LTD.

Outline

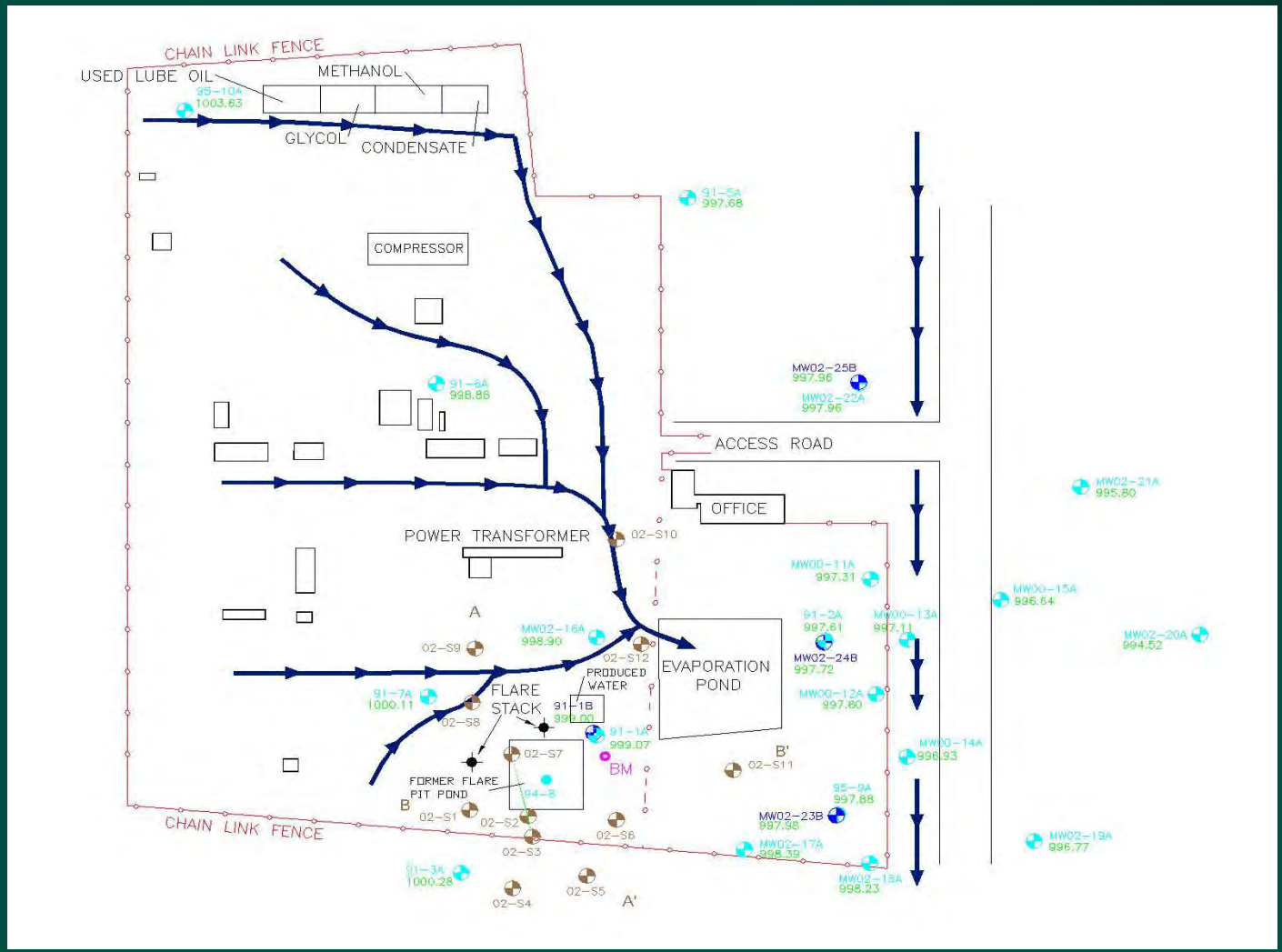
1. Introduction
2. Soil and Groundwater Quality Monitoring Results
3. Sulfolane – Sulfinol®
4. Laboratory Treatability Trial
5. Treatability Trial Results
6. Conclusions

Introduction

- Active Sour Gas Plants
- Gas Sweetening
- Gas Dehydration
- Treatment

Products : Condensate and Natural Gas

Site Plan


CHAIN LINK FENCE
USED LUBE OIL
METHANOL
95-10A
1003.63
GLYCOL
CONDENSATE
91-5A
997.68
COMPRESSOR
91-6A
998.88
MW02-25B
997.96
MW02-22A
997.96
ACCESS ROAD
MW02-21A
995.80
OFFICE
POWER TRANSFORMER
02-S10
MW00-11A
997.31
MW00-15A
996.64
A
MW02-16A
998.90
02-S9
02-S12
EVAPORATION
POND
91-2A
997.81
MW00-13A
997.11
MW02-20A
994.52
MW02-24B
997.72
PRODUCED
WATER
91-7A
1000.11
FLARE
STACK
02-S8
91-1B
996.00
MW00-12A
997.60
91-1A
999.07
02-S7
B'
02-S11
MW00-14A
996.93
BM
FORMER FLARE
PIT POND
94-8
95-9A
997.68
B
02-S1
02-S2
MW02-23B
997.36
MW02-17A
998.39
MW02-19A
996.77
CHAIN LINK FENCE
02-S3
02-S6
91-3A
1000.28
MW02-18A
998.23
02-S4
02-S5
A'

Physical Settings

Topography and Drainage:

- Porcupine Hills (1,600 masl).

Geology:

- Fill/gravel 0.5 m.
- Silty Clay Till – 2.5 m to 9.2 m, sand lenses.

Hydrogeology:

- Shallow water table at 1.7 m to 3.4 m.
- Groundwater flows towards east.
- Bulk hydraulic conductivity 1.02 E-5 cm/s to 1.41E-7 cm/s.

Soil and Groundwater Quality

Under the Alberta Environment Approval to Operate:

- Soil Management Program – Alberta Environment Soil Monitoring Directive (1996) – every five years.
- Groundwater Quality Monitoring Program initiated in 1991 – annually.

Soil

- Elevated concentrations of petroleum hydrocarbons (PHCs) detected – benzene, toluene, ethylbenzene, and xylenes (BTEX) and F_1, F_2, and F_3.
- Elevated chloride concentrations detected.

Groundwater

Historically elevated concentrations of:

- PHC – BTEX and F_1 and F_2.
- Dissolved Organic Carbon (DOC).
- Chlorides.
- Sulphate (naturally occurring).
- Nitrites and Nitrates.
- Total Dissolved Solids (TDS).

The DOC and PHC concentrations do not correlate.

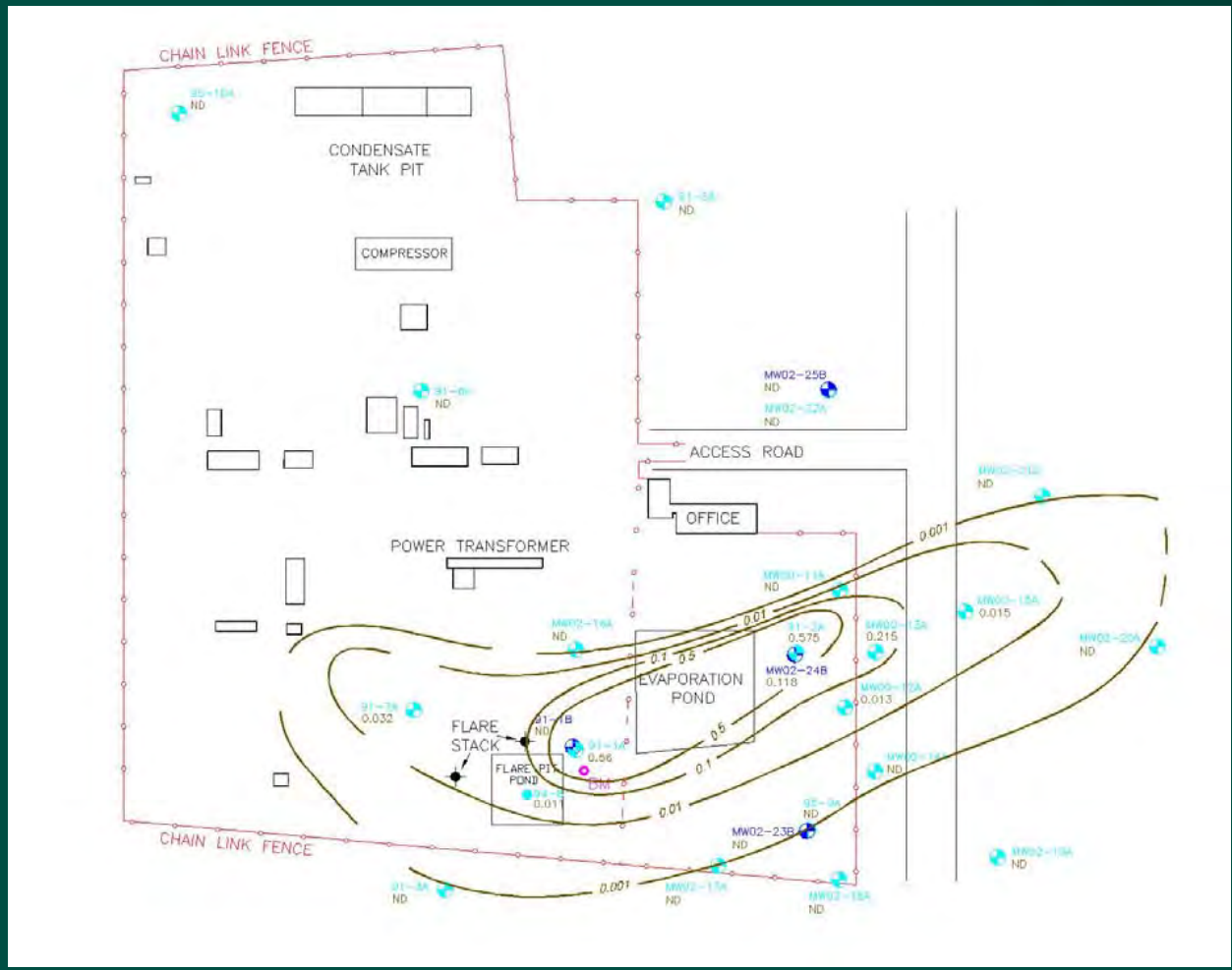
Assessment

- Resolution of elevated concentrations of DOC initiated the plant site product inventory review.
- Product review detected that, in 1992, existing amine process replaced Sulfinol process.
- Sulfinol process was mixture of Sulfinol® and DIPA.
- In 2000, Sulfolane analyses were added to the regular annual groundwater quality monitoring.

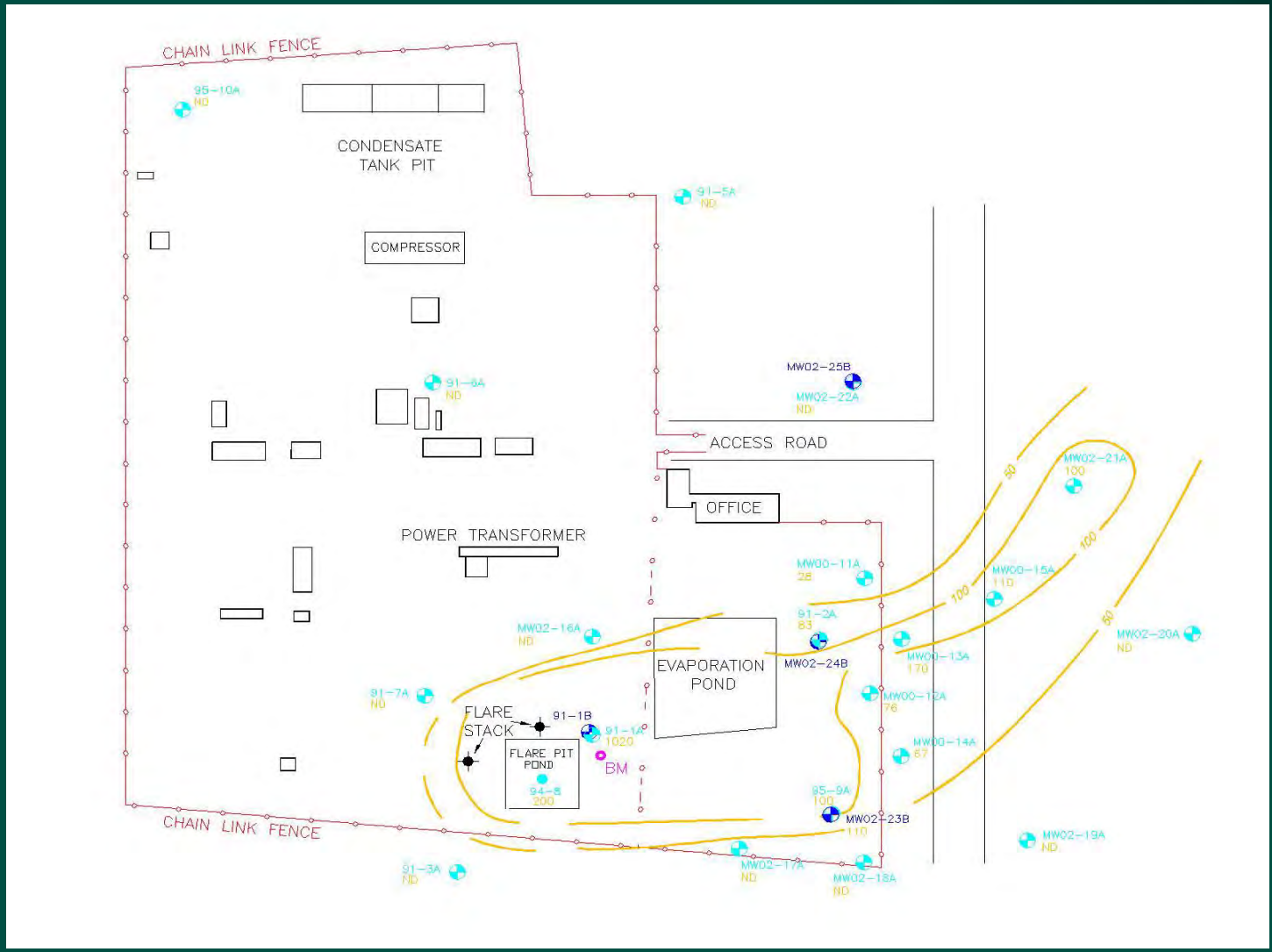
Assessment continued...

- Half the monitoring wells returned concentrations of sulfolane greater than background concentrations.
- In 2002, soil and groundwater with elevated concentrations of PHC and Sulfolane were partially delineated in the vicinity of the former flare pit and east of the Evaporation Pond.
- Sulfolane was detected in all collected soil samples in the vicinity of former flare pit.

Benzene Concentration Distribution Map 2002



Sulfolane Concentration Distribution Map 2002

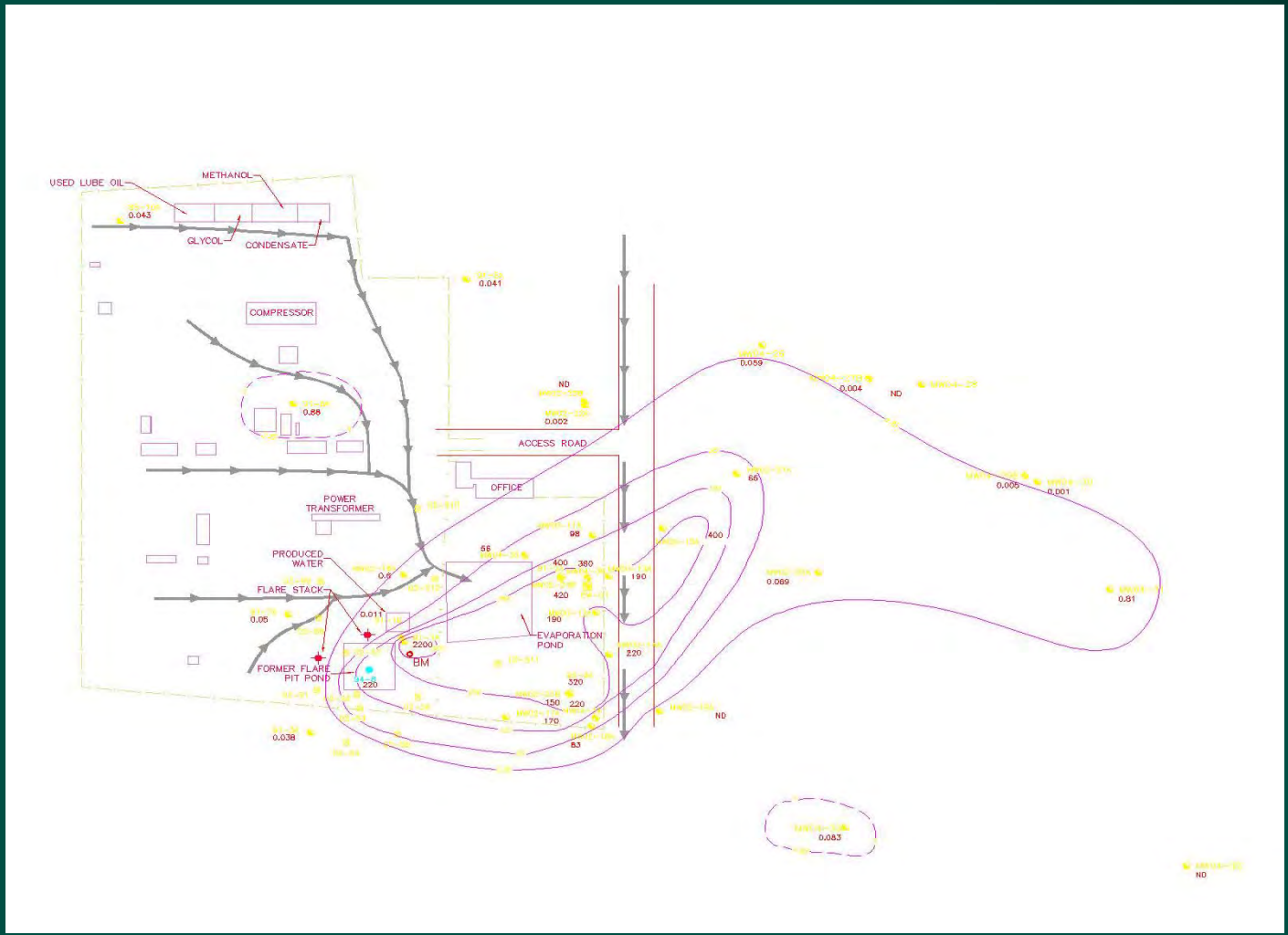


Assessment continued...

- In 2004, additional groundwater quality monitoring wells were installed to further delineate the groundwater with concentrations of sulfolane greater than background concentrations.

- One groundwater extraction well and one observation well were installed to determine hydrogeological properties of a shallow water-bearing zone.

Sulfolane Concentration Distribution Map 2004



Assessment continued…

- In 2005, the Canadian Council of Ministers of the Environment (CCME) and Alberta Environment adopted the Canadian Association of Petroleum Producers (CAPP) guidelines for sulfolane: in soil (2.3 mg/kg) and groundwater (0.26 mg/L).

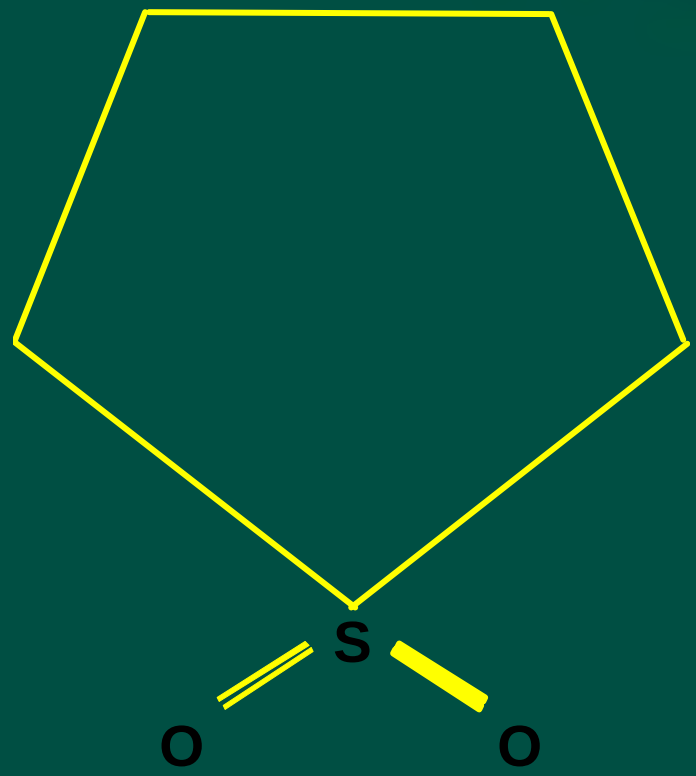
Sulfolane

- Sulfolane ($C_4H_8O_2S$) – common trade name for an organic chemical tetrahydrothioprene 1,1 -- dioxide, colourless, very polar, highly soluble in water, and extremely stable.

- Sulfinol® – solvent developed by Shell in early 1960s for extracting aromatics from hydrocarbons; second major application is in the process of 'sweetening' natural gas.

- Sulfinol® is slightly heavier than water (1,060 g/L).

Sulfolane



Laboratory Trials

Soil:

- Bio-treatability.

Groundwater:

- Bio-treatability.
- Chemical Oxidation (Mineralization).

Soil Trial

- Five soil samples collected.
- Sulfolane concentrations ranged from 350 mg/kg to 3,400 mg/kg.
- Two samples with highest concentrations of sulfolane were homogenized – 1,400 mg/kg.
- Samples for analytical analyses collected on days 0, 15, 30, 45, 63, and 78.

Soil Trial

7 Bio-reactors:

- Control – no additives.
- Sterile.
- Condensate impacted.
- Ammonia nitrogen (83 mg/kg).
- Ammonia nitrogen (232 mg/kg).
- Ammonia phosphate (83 mg/kg).
- Ammonia phosphate (232 mg/kg).

Oxygen concentrations maintained >10%.

Groundwater Trials

Bio-treatment:

- Aeration (GLR micro-bubbles®) and nutrient amendment.

Chemical Oxidation:

- H_2O_2.
- UV radiation.
- Combination of both of the methods.

Groundwater Trials

Aeration Trial:

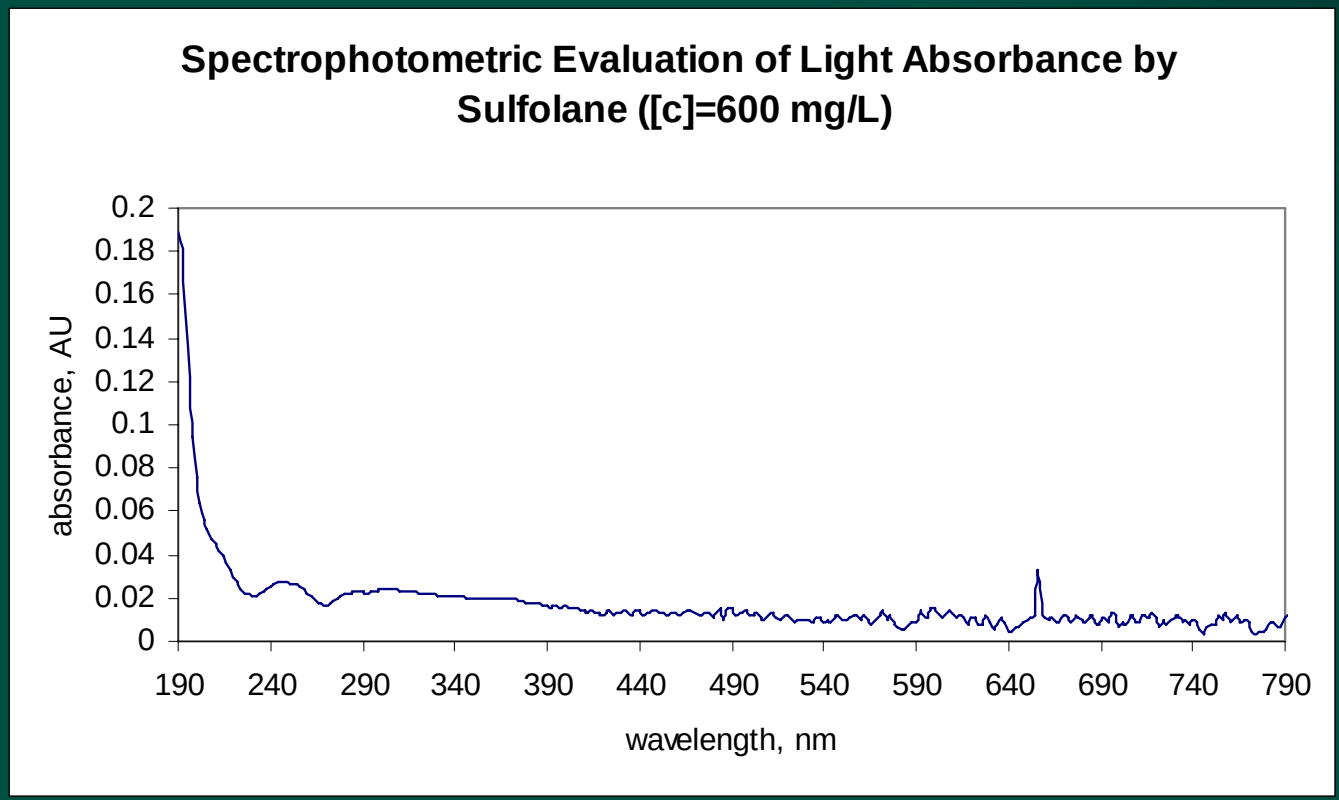
- 24–hour trial.
- Continuous aeration - O_2>7.7 mg/L.
- Nutrient - Ammonia phosphate.
- Samples collected at 0, 8, and 24 hours.

Groundwater Trials

Chemical Oxidation:

- 7-day trial.
- H_2O_2 concentration = 10 g/200 ml.
- UV radiation – 7 W UV bulb.
- $C_4H_8O_2S + 13H_2O_2 = 4CO_2 + H_2SO_2 + 16H_2O$.

Groundwater Trials



Results - Soil

Days	Control	Sterile	Ammonia 83 mg/kg	Nitrate 232 mg/kg	Ammonia 83 mg/kg	Phosphate 232 mg/kg
0	1,300	1,400	1,700	1,700	1,400	1,400
15	1,700	1,600	1,500	1,500	1,500	1,400
78	1,100	1,200	860	760	2.1	2.9

Results - Groundwater

Sample Description	Sulfolane (mg/L)	Removal Ratio (%)	Time (hours)
Blank	1,200 (1,800)		
Chemical oxidation	950	79	
UV Irradiated sample	1,000	83	
Chem. Oxidation + UV	13	99	168
Aeration + Nutrients	490	73	24

Results - Groundwater

Energy consumed by the samples was calculated using the following formula:

- $P = E_{photon} * I/S = 0.2$ m J/sec cm^2

Where:

- E_{photon} – energy of a single photon
- I – intensity of the photon flux in the system, and
- S – surface of irradiated vessel

Results - Groundwater

[Using the sun as source of UV radiation]

Based on commonly used potassium ferrioxalate system irradiation value, the estimated solar energy is:

$$E_{solar} = 3.5 \text{ mW/cm}^2$$

Therefore, a week of UV radiation in the lab will be equal to ***10 hours*** of sun exposure.

Conclusions

Soil:

- Sulfolane biodegradation is possible (bacteria require longer time to adjust to environment).
- After 78 days of incubation with ammonia phosphate fertilizer, the soil sample becomes non-toxic to Microtox®.
- Full sulfolane biodegradation occurred with an ammonium phosphate fertilizer.
- No obvious production of toxic by-products.

Conclusions

Groundwater:

- The sulfolane degradation occurred under the chemo-physical and biodegradation (aeration) processes.
- The chemical oxidation and UV irradiation trial achieved 95% removal of sulfolane after one week of treatment.
- The biodegradation treatment achieved 73% of sulfolane removal after 24 hours.

Conclusions

Chemical Oxidation:

- If field scale treatment utilizes sunlight, 10 hours of the daily light will be required.

Note: UV reactor should be considered as more effective method

Biodegradation:

- Field scale treatment would require a water treatment and storage facility.

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Sulfolane Attenuation by Surface and Subsurface Soil Matrices

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This study was undertaken to evaluate sulfolane (tetrahydrothiophene-1, 1-dioxide) attenuation by soil and subsurface materials collected from a sour gas plant site using batch equilibration systems. The analyzed sample materials used in this study showed a wide range in terms of their selected physical and chemical properties. The reaction of sulfolane with the sample materials was fast initially and followed by slower rates at longer times. There was not much increase in the amount of sulfolane sorbed after about 5 hours of equilibration time irrespective of the temperature of the system. The rate of sorption of sulfolane followed a first-order reaction at both 25 and 8°C temperature conditions and not affected by the temperatures range considered in this study. It appears that the sorption data of sulfolane on the various sorbents could be best described mathematically by the Freundlich equation. Kd values derived at 25°C ranged from 0.05 to 0.88 L/kg and from 0.30 to 1.23 L/kg at 8°C. Furthermore, increasing the ionic strength of the solution didn't affect sulfolane sorption by the various sorbents, which indicates that sulfolane sorption is not consistent with an ion-exchange mechanism but rather occurs through dipole-dipole interactions. Desorption of sulfolane was relative high in all systems. Multiple regression analysis shows a high level of correlation between Kd and several soil parameters. No sulfolane biodegradation was detected under anerobic conditions in any of the microcosms systems after 45 days of incubation at 25 and 8°C, respectively. Sulfolane biodegradation data could be all fitted to zero-order kinetics. Biodegradation rates of sulfolane in the microcosms was the highest in sample depth 0–0.20 m, decreased with sample depth but significantly increased with the addition of nitrogen, and markedly decreased with temperature. At 25°C and no supplement of N, biodegradation rate ranged from 4.26 to 12.70 mg/kg/day but with addition of N, the range was from 9.41 to 16.50 mg/kg/day.

Key Words: Sulfolane; Attenuation; Sorption; Biodegradation; Kinetic; Isotherms; Transport.

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INTRODUCTION

Tetrahydrothiophene-1,1-dioxide commonly known as sulfolane is used in combination with diisopropanolamine (DIPA) as a physical solvent in the Shell Sulfinol to remove toxic levels of sour gases such as hydrogen sulfide (i.e., H_2S) from raw natural gas condensate.[1] The Shell Sulfinol gas sweetening process is particularly effective at high H_2S concentrations,[2] therefore, it has been used in western Canada since the early 1960s.[3] Western Canadian natural gas supplies can contain up to 35% H_2S. The waste streams associated with the acid-gas removal process include spent Sulfinol, sludges, and industrial filters. These wastes have led to contamination of Sulfinol® plant sites through accidental spills as well as leakages from surface retention pits or landfills and therefore resulting in inadvertent contamination of the vadose zone, groundwater and wetland ecosystems at these sites. Understanding the mobility and persistence characteristics of particular contaminants helps in determining the likelihood that a contaminant of concern will reach a certain area.

Published data describes sulfolane (Fig. 1) as a colorless, weakly to moderately basic, globular molecule, highly polar water soluble with unusual solvent properties having a specific gravity of 1.26 g/cm^3. Because of its high hydrophilicity, sulfolane poses a potential risk for contamination of surface and groundwater, domestic wells around sour gas plants and off-site migration. The movement and attenuation of contaminants within soil or groundwater over time is affected by interactive mechanisms that cause transfer of contaminant mass between the liquid and solid phases or conversion of dissolved species from one form to another.

Sorption and desorption are probably the major factors controlling the movement and fate of contaminants in the terrestrial environment. Sorption is a process in which a solution component is concentrated at the solid-solution interface while desorption is the separation of the contaminant from the solid phase. As a result, the physical properties of the soil and ground water matrices (i.e., sorbent) such as porosity, bulk density, organic matter content, hydraulic conductivity, surface area, surface charge, mineralogy, homogeneity, and hydraulic gradient affect partitioning of organic contaminants. Contaminant (i.e., sorbate) properties also has a profound impact on its

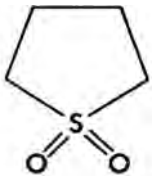

Figure 1: Chemical structure of sulfolane.

sorption behavior; these properties include water solubility, polar/ionic character, acid/base chemistry, oxidation/reduction chemistry.[4,5] Temperature as an environmental condition can also exert a profound impact on the mobility and attenuation of a contaminant.

Sorption mechanisms of organic contaminants onto soil constituents will affect the rate of volatilization, diffusion, leaching as well as the availability of these compounds to microbial or chemical degradation, or uptake plants or other organisms. Sorbate-sorbent interaction mechanisms may include hydrogen bonding, ion exchange, hydrophobic bonding, and specific and nonspecific sorption reactions.[6] Organic contaminants can also be attenuated by microbial degradation. Chou and Swatloski[7] reported sulfolane degradation in an activated sludge system. Greene et al.[8] also reported aerobic degradation of sulfolane by microbial communities obtained from uncontaminated and contaminated soils. Greene et al.[8,9], Fedorak and Coy[10] demonstrated the aerobic biodegradation of sulfolane in soil and groundwater samples from a sour gas processing plant but little or no degradation under anoxic conditions.

The objective this study was to evaluate sulfolane attenuation by soil and subsurface materials collected from a sour gas plant site using batch equilibration systems. Soil and subsurface samples were collected from a sour gas plant facility north of Calgary.

Because of the wide use of sulfolane and limited published literature data of its behavior and fate in terrestrial environment, this study will be useful in forecasting the potential risks associated with sulfolane as well as mitigative measures to manage cost-effectively potential impact on the environment.

MATERIALS AND METHODS

Sample Collection and Characterization

Soil and aquifer materials were collected from a sour gas plant site located north of Calgary. A truck-mounted drill equipped with a solid stem auger having the dimensions of 13.5 cm O.D. with section lengths of 1.50 m was used for the sampling program. A total of four boreholes were drilled. Samples were logged in the field and composited as a function of texture. Soil cores were obtained: 0–0.20-m; 0.20–0.91-m; 0.91–1.52-m; 1.52–1.83-m; 1.83–2.13-m; and groundwater sediments cores were taken from depths of 4.50 to 6 m. The cores were placed in clean, sterile plastic sleeves, labeled and transported to the laboratory. The sampled area covers approximately 0.50 ha.

The samples were dried at room temperature, homogenized and their coefficient of uniformity determined. Subsequently, the rest of the cores were ground to pass through a 2 mm sieve. Physical and chemical analyses were performed as shown in Tables 1 to 3.

Table 1: Field results of bulk density and permeability tests.

	Parameters			
Testing depth (cm)	**Bulk density (g/cc)**	**Rate of H_2O movement (cm/hr)**	**Viscosity correction* (cm/hr)**	**Moisture** (%)**
1.50	0.89	27.32 ± 14.67	24.31 ± 13.03	9.41
20	0.91	4.09 ± 0.001	4.30 ± 0.095	8.54
25	0.90	6.96 ± 0.250	7.90 ± 0.280	15.61
30	1.00	7.08 ± 0.755	7.08 ± 0.755	5.67
34	1.04	9.43 ± 0.931	11 ± 0.931	5.43

*Viscosity correction, n_t/n_{20}.
**% Moisture = ((Mass of water loss/Oven dry soil mass) 100) @ 105°C.

In-situ infiltration and percolation tests were performed on selected locations adjacent to the boreholes. Infiltration capacity was measured with a double ring infiltrometer. The metal cylinders, one smaller in diameter than the other, were pressed partially into the soil to a depth of 1.50-cm. Subsequently, percolation tests were carried out at depths of 20 cm; 25 cm; 30 cm; and 34 cm, respectively. The soil was saturated and then the decline in water infiltration and percolation was measured until five consecutive readings were recorded. Undisturbed soil samples were removed with a sharp bottom aluminum cylinder from each testing depth interval for bulk density determination. The rest of the testhole was bored with a 5.6 cm O.D. Dutch auger to the desired depth. The calculated volume from the length and diameter of the special sampler as well as weight of the undisturbed samples were recorded and the bulk density evaluated. Apparent bulk density was also

Table 2: Laboratory results of selected physical parameters for the samples.

	Parameters							
Sample depth (m)	**Sand (%)**	**Silt (%)**	**Clay (%)**	**P.D.[a] (g/cc)**	**B.D.[b] (g/cc)**	**C^*_μ**	**C^{**}_c**	**Moisture*** (%)**
0–0.20	37.37	28.87	33.76	2.06	1.18	13.70	1	16.49
0.20–0.91	34.02	27.01	38.97	2.61	1.20	8.97	1.60	13.50
0.91–1.52	28.07	32.97	38.96	2.29	1.40	14.55	1.60	10.33
1.52–1.83	28.12	39.29	32.59	2.46	1.40	16.67	1.36	8.67
1.83–2.14	27.26	36.19	36.55	2.28	1.41	13.04	1.17	9.15
4.60–6.10	64.93	8.36	26.71	2.64	1.64	12.50	1.01	40

[a] Particle density = Mass of dry soil/Volume of liquid displaced.
[b]Bulk density = Mass of dry soil/Bulk volume.
*Coefficient of uniformity = D_{60}/D_{10}.
**Coefficient of gradation = $(D_{30})^2/(D_{10}/D_{60})$.
***% Moisture = (Mass of water loss/Oven dry soil mass) 100 @ 105°C.

Table 3: Results of selected chemical analyses for the various samples.

	Sample depth (m)					
Parameters	**0–0.20**	**0.20–0.91**	**0.91–1.52**	**1.52–1.83**	**1.83–2.14**	**4.60–6.10**
pH	6.10	7.50	7.80	7.80	7.80	8.40
EC (DS/m)	2.60	1.32	0.62	0.30	0.32	0.11
TDS[a] (mg/L)	1850	930	400	250	250	100
CEC[b] (meq/100g)	19.40	11.40	12.60	6.39	5.89	1.50
NO_3-N (mg/kg)	6.50	4.00	5.50	5.00	ND[c]	ND
NO_2-N (mg/kg)	0.125	0.065	0.060	0.060	0.060	ND
NH_3-N (mg/kg)	1.14	0.30	0.10	0.18	0.14	0.25
P as P_2O_5 (mg/kg)	0.25	0.20	0.25	0.15	0.20	0.05
Chloride (mg/L)	1.67	12.49	12.48	4.99	4.99	2.91
SO_4^{2} (mg/kg)	8370	1948	562	305	320	50
Total Al (mg/kg)	2.00	3.13	18	1.20	1.35	1.20
Total Mn (mg/kg)	ND	ND	ND	0.50	ND	ND
Total Fe (mg/kg)	2.84	4.30	4.15	3.84	4.34	4.64
Ca (mg/kg)	485	68	22	18	18	13
Na (mg/kg)	11	130	87	35	38	11
Mg (mg/kg)	141	184	76	34	32	7
K (mg/kg)	39	5	3	8	8	5
%TOM[d]	8.81	1.36	0.85	0.85	0.87	0.66
%TOC[e]	5.11	1.79	0.49	0.49	0.50	0.38
SAR[f]	0.05	0.83	0.76	0.50	0.56	0.26

[a]TDS = Total dissolved solids.
[b]CEC = Cation exchange capacity.
[c]ND = Not detected.
[d]TOM = Total organic matter.
[e]TOC = Total organic carbon (i.e., TOM/1.724).
[f]SAR = Sodium adsorption ratio, $Na/((Ca \pm Mg)^{1/2}/2)$.

determined in the lab following drying of the soil core at 105°C. Soil saturation and percolation testing procedures were carried out as recommended by Soil Survey Staff.[11] Infiltration and percolation rates were corrected for viscosity of water at 20°C, n_r/n_{20}.

Chemical

Sulfolane was obtained from Aldrich (Milwaukee, WI) and was 99% pure. Aqueous solutions of sulfolane were prepared using deionized water as required.

Kinetic Study

A volume of 40 ml of 2000 mg/L of sulfolane aqueous solution was added to glass-stoppered centrifuge tubes containing 20 g of soil or groundwater materials. The suspension was gently mixed. Kinetic reactions were performed at room temperature and 8°C, respectively. The mixtures were sampled at predetermined times and analyzed for sulfolane concentration in the supernatant.

The suspensions were filtered through Whatman #40 filter paper. Similarly, 2000 ppm of aqueous concentration of sulfolane was passed through the filter paper and quantitatively analyzed. No retention of sulfolane onto the filter paper was observed. Experimental controls were prepared in the same way but in the absence of soil and groundwater materials.

Isotherm Study

Batch testing was utilized to obtain the equilibrium sorption capacity of a given sorbent for an individual sorbate, by developing equilibrium isotherms that describe the sorption capacity of a given sorbate exposed to various concentrations of aqueous solutions of sulfolane. Batching was conducted by gently mixing 20 g of soil or groundwater materials with 40 mL of fresh aqueous sulfolane solutions. Each sorbate/sorbent system was allowed to equilibrate overnight at either room temperature or 8°C, respectively. Concentrations of sulfolane for the isotherm study consisted of 0, 500, 1500 and 2000 mg/L. During equilibration, the systems were manually mixed end-over-end once after two hours of equilibration. The supernatant was analyzed for sulfolane concentration by directly sampling the supernatant for the 25 and 8°C equilibration isotherms, the supernatant was sampled at 2 mm above the sorbant/supernatant interface since sulfolane by virtue of its physical properties may transit from as an aprotic solute in the aqueous phase to form an immiscible dense nonaqueous phase gel (DNPG) under the experimental conditions at which the isotherm experiments were carried out. Based on the lab testing, this sampling approach was adopted and deemed more technical representative for evaluating mass distribution of sulfolane in the experimental systems and subsequent extrapolation of the findings to natural ecosystems in attempting to forecast potential fate and behavior of sulfolane.

The extent of sorption was estimated as the difference between initial and final sulfolane concentrations and corrected for sulfolane concentration detected in the initial soil and groundwater materials. Experimental controls were prepared in the same way but in the absence of soil and groundwater materials.

Desorption Study

The experimental design of the desorption experiment of sulfolane was performed on batch systems with a 1000 mg/L of sulfolane solution at room 25°C and 8°C, respectively. After equilibration, 20 mL of the supernatant was quantitatively removed from the system. The aliquot was quantitatively replaced with 20 mL of distilled water and the suspension was gently mixed intermittently for 3 hours which was followed by centrifugation at 3000 rpm

and filtration through Whatman #40 filter paper before analysis. The extent of sulfolane desorption was performed once.

The influence of freezing and thawing on desorption was also assessed on sorbate/sorbent systems similar to that of the above desorption experiment using only a 1000 mg/L concentration of sulfolane. The systems were frozen for 24 h, thawed, and sulfolane was extracted for analysis as in the former desorption experiment. The desorption experiment was carried out in triplicate.

Influence of Ionic Strength on Sorption

The influence on electrolyte concentration on sulfolane interaction with the soil and groundwater materials was assessed using only a 1000 ppm concentration of sulfolane. All other aspects of the experimental design were similar as described in the isotherm study section. In this experiment, sorption of sulfolane by the sorbents was determined at three different concentrations of $CaCl_2$ dihydrate: 0.03; 0.06 and 0.1 M. Calcium chloride, a major ion in soil and groundwater systems, was weighed and then added to the various sorbate/sorbent systems. The latter were equilibrated overnight at room temperature.

Biodegradation Study

Biodegradation of sulfolane was evaluated under aerobic and anaerobic conditions, in the presence of nitrogen, and at 25°C and 8°C, respectively. Aerobic degradation was conducted in 500-mL glass jar microcosms consisting of 100-g of the soil sample, 875 mg/kg of sulfolane and supplemented with 250 mg of NH_4NO_3 dissolved in the sulfolane solutions. Similar aerobic microcosms were prepared without NH_4NO_3 addition. In all cases, appropriate volume of sulfolane solution was quantitatively transferred to each system such as to achieve optimum soil moisture representative of field capacity and varied with the soil samples. Sterile control was prepared with autoclaved distilled water, soil, and groundwater materials without NH_4NO_3 dissolved in the sulfolane solutions. The bioreactors were covered with tin foil and parafilm to minimize water loss. Aerobic conditions were maintained through weekly manual mixing of the bioreactors. Subsamples of 60 g were removed from the systems at various times and quantify for sulfolane.

Biodegradation under anaerobic conditions was conducted in 50 mL glass centrifuge by mixing 20 g of soil or groundwater materials with 40 mL aqueous sulfolane solutions. The concentrations of sulfolane and NH_4NO_3 in the anaerobic systems were 500 and 100 mg/L, respectively. The microcosms and the controls were incubated at 25°C and 8°C, respectively, without shaking and sacrificed at various times. To determine the extent of sulfolane biodegradation, the soil suspensions were mixed, centrifuged at 4000 rpm,

and filtered through Whatman #40 filter paper and the filtrate analyzed for sulfolane.

Sulfolane Analysis

The concentration of sulfolane in the above experiments was determined by gas chromatography methods, using direct aqueous injections. The gas chromatograph used for this study was a Hewlett-Packard model 5890 Series II equipped with a flame ionization detector. A support-coated open tubular (SCOT) stainless-steel column OS-138 (25 ft $\times$ 0.020 in ID) Beta 45 was acquired from Supelco and used in a split less mode. The injector and detector temperatures were at 280°C, the oven temperature was operated isothermally at 260°C. Nitrogen was the carrier gas with a flow rate of 6 mL/sec and a column head pressure 3.0 psi. Sulfolane retention time was 2 minutes under the experimental conditions described. Using direct aqueous injection, the detection limit of sulfolane for the study was 6 mg/L. Additional QC included triplicate injections of each sample and the results reported as an average value.

RESULTS AND DISCUSSION

Sample Collection and Characterization

Results for selected physical and chemical parameters for the soil and aquifer samples are reported in Tables 1 to 3, respectively. Water, under most environmental soil contamination situations, is the primary transporting fluid. Leaching and runoff of sulfolane are apt to be favored by water movement. Upon contacting the soil, water movement is the entry of free water into the soil at the soil-atmosphere interface. Infiltration of water is a transitional phenomenon that takes place at the soil surface. Once the water has infiltrated the soil, the water moves downward into the soil profile by the process termed percolation and with it dissolved contaminants. The greatest leaching hazard of sulfolane will be promoted in permeable soils and with little potential for being attenuated. Soils with low infiltration rate are more apt to favor surface runoff losses of sulfolane. The potential rate of water entry into the soil for the tested area is relatively high with a value of 22.31 $\pm$ 13.03 cm/hr. Consequently, the high water-solubility of sulfolane favors leaching losses. Percolation rates generally tend to increase within a depth profile and the values ranged from 4.30 $\pm$ 0.095 to 24.31 $\pm$ 13.03 cm/hr. Field bulk density values increased as a function of depth and ranged from 0.89 g/cc for the soil surface to 1.04 g/cc for the 34 cm soil sample depth indicating an increase in the mineral content in the soil depth profile as evidenced by the particle size results (Table 3). The relative high infiltration capacity combined with the percolation rate values indicate a high potential for leaching and mobility of sulfolane into the site subsurface with potential for attenuation.

Deeper in the soil profile, bulk densities are generally higher, probably as a result of low organic matter contents, less aggregation, less roots and more compaction caused by the weight of the overlying layers. Field or in-place bulk density values (Table 1) increased with sample depth and ranged from 0.89 to 1.04 g/cc. Similarly, the bulk density values derived in the lab (Table 2) increased with depth.

Particle size distribution curves were plotted, grain size such as D_{10}, D_{30}, and D_{60} were obtained for the soil cores. The D refers to the size, or apparent diameter, of the soil particles and the subscript 10, 30, and 60 denotes the percent that is smaller. The D_{10} size is also called the effective size of a soil and can be expected to show marked physico-chemical colloidal properties in their interactions with contaminants introduced in the soil system. The smallest effective size which corresponds to 0.084 was recorded in sample depth 1.52–1.83 m. An indication of the spread (i.e., range) of particle sizes is given by the coefficient of uniformity, C_μ (Table 2). The latter indicates no appreciable difference between the D_{10} and D_{60} sizes in any of the sample depths. Likewise, the coefficients of gradation, C_c, (Table 2) were not greatly different from 1.0, indicating that particle sizes are not missing between D_{10} and D_{60} sizes.

The sample materials showed a wide range in terms of their chemical properties and are contained in Table 3. CEC, organic carbon and Ca content were several times higher in sample depth 0–0.20 m than that of the other samples.

Kinetic Study

The reaction of sulfolane with the sample materials was fast initially and followed by slower rates at longer times. There was not much increase in the amount of sulfolane sorbed after about 5 hours of equilibration time irrespective of the temperature of the system. The slower rates of sorption at longer times may be ascribed to slow diffusion of sulfolane from exterior sorption sites to the interior of the soil particles sorbing sites. Webber and Gould[12] reported that the rate-limiting step in the removal of a series of organic pesticides from dilute aqueous solutions by porous activated charcoal was one of intraparticle transport of the solute in the pores of the sorbent. Systems with this sorption mechanism show a linear relationship between the amounts of solute sorbed as a function of square root of time.

The fraction θ of the amount of sulfolane sorbed may be defined as:

$$\theta = N(t)/q(d)$$

where N(t) and q(d) are the amount of sorbed at time (t) and at equilibrium, respectively. It is shown that a large portion of the sorption sites in each system were occupied by sulfolane within 2 hours of reaction at both temperatures

studied. Although θ was always greater for sample depth of 0–0.20 m at 25°C than 8°C as well as than the rest of the sorbents used in the study, near-completion of sorption was attained in all cases within about 5 hours.

To determine if the reaction of sulfolane in each respective system follows a first-order rate law and to measure its rate constant, the latter can be determined by defining θ in terms of concentration sulfolane in each respective system:

$$\theta = [C_o - C_t]/[C_o - C_\infty]$$

where C_o, C_t and C_∞ are respectively, sulfolane concentration initially, at time (t) and at equilibrium, and by using the expression:

$$-\frac{d[\text{sulfolane}]}{dt} = K[\text{sulfolane}]$$

The integrated first-order rate law can be used to fit the sorption reaction of sulfolane:

$$\text{Ln}[\text{sulfolane}]_t = \ln[\text{sulfolane}]_0 - kt$$

As a first-order reaction, the plot of Ln $[\text{sulfolane}]_t$ against time should yield a straight line with a slope corresponding to the rate constant $-k$. The regression equations and the values for k are reported in Table 4. It can be noted that the highest rate constants k were derived for sample depth 0–0.25 m at both 25°C and 8°C and that the rate constant values were of the same magnitude for all the samples. These results tend to indicate that the rate of sulfolane sorption on these soil materials is directly proportional to the number of free sorption sites and not affected by the temperatures range considered in this study.

Table 4: Regression equations for rate constant determination of sulfolane sorption at 25 and 8°C on soil sample materials.

Sample depth (m)	Temperature (°C)	Regression equation	pH*	k (hour^{-1})	Fit (R)	Fit ($R^{2)}$
0–0.20	25	$y = 7.60 - 0.1530\ x$	6.10	1.53×10^{-1}	1.00	1.00
	8	$y = 7.59 - 0.1320\ x$	6.10	1.32×10^{-1}	0.91	0.83
0.20–0.91	25	$y = 7.57 - 0.0777\ x$	7.50	7.77×10^{-2}	0.97	0.94
	8	$y = 7.55 - 0.0592\ x$	7.50	5.92×10^{-2}	0.91	0.83
0.91–1.52	25	$y = 7.57 - 0.0594\ x$	8.00	5.94×10^{-2}	0.96	0.92
	8	$y = 7.58 - 0.5870\ x$	8.00	5.87×10^{-2}	0.98	0.96
1.52–1.83	25	$y = 7.56 - 0.0347\ x$	8.00	3.47×10^{-2}	0.83	0.69
	8	$y = 7.57 - 0.0258\ x$	8.00	2.58×10^{-2}	0.78	0.61
1.83–2.14	25	$y = 7.57 - 0.0403\ x$	8.00	4.03×10^{-2}	0.91	0.83
	8	$y = 7.56 - 0.0385\ x$	8.00	3.85×10^{-2}	0.87	0.76
4.60–6.10	25	$y = 7.59 - 0.0268\ x$	8.20	2.68×10^{-2}	0.97	0.94
	8	$y = 7.58 - 0.0128\ x$	8.20	1.28×10^{-2}	0.81	0.66

*pH is at background level and unadjusted.

Isotherm Study

Sorption isothems are normally obtained by measuring the amount of solute contaminant sorbed for a number of different concentrations of sorbate under specific conditions. They often can be described by the Freundlich or Langmuir equations.

The Freundlich isotherm, a commonly used curvilinear model has no upper limit to the amount of sorbate that could be sorbed by a system. The Freundlich equation can be written as:

$$X/M = KCeq^{1/n}$$

where X/M is the quantity of solute contaminant sorbed per unit mass of sorbent (mg/kg), Ceq is the equilibrium concentration of sorbate in solution (mg/L) and were K and n are the constants. The logarithmic form of the Freundlich equation to plot the data is:

$$\log[X/M] = [1/n]\log[Ceq] + \log[K]$$

The logarithm of the concentration of the solute in the sorbate state, X/M in mg/kg, is plotted as a function of the logarithm of the residual solute concentration, Ceq in mg/L. Linear regression of the data points yields a best-fit line with a slope of 1/n and intercept of log [K]. The slope, 1/n, is a measure of sorption intensity, and the K value, which must be determined by taking the antilog of the intercept, is the partition coefficient, Kd, an indicator of the sorptive capacity of the system. A strong correlation can be found between Kd and organic carbon content of the soil. When the sorption of the sorbent is expressed as a function of the organic carbon content of the soil, a constant K_{oc} is generated which is a unique property of the compound being sorbed:

$$K_{oc} = Kd\, f_{oc}$$

where K_{oc} is equal to the partition coefficient coefficient (Kd) multiplied by f_{oc}, the fractional mass of organic carbon content in the soil.[13]

A Langmuir plot models a system where there are a finite number sorption sites. The Langmuir equation may be expressed as follows:

$$X/M = abCeq/(1 + bCeq)$$

where X/M and Ceq are the same units as defined above, b is a constant related to the binding energy (L/kg), and a is the maximum amount of solute that can be sorbed by the sorbate, is the soil uptake quantity (mg/kg).

The Langmuir equation can be rewritten in the following linear form:

$$[Ceq]/[X/M] = 1/[ab] + [Ceq]/[a]$$

Ceq /X/M can be plotted as a function of Ceq. The linear regression of the data points yields a best-fit line with a slope of 1/a and 1/ab as the intercept. The maximum amount of sulfolane that can be sorbed onto the samples can be calculated from the Langmuir linear equation.

Sorption isotherms for each of the sample sobent/sulfolane systems were developed at two different temperatures without pH adjustment of the systems. Giles et al.[14] classified sorption isotherms into four types L, S, C, and H. In that regard, the C type isotherm was observed for sulfolane interactions with all sorbents at both temperatures. Since there was not a significant difference in sorption capacity of the sorbent/sulfolane systems at both temperatures, a weak interaction between sulfolane-soils as bonding mechanisms can be envisioned.

The experimental data points fitted to Freundlich and Langmuir linear isotherm equations. The isotherm models coefficients for the representative equilibrium studies are summarized in Table 5. The linear portion of the isotherms was considered where appropriate for better fitting the Langmuir isotherm. It appears that the sorption data of sulfolane on the soil sample materials could be best described mathematically by the Freundlich equation. For many contaminant modeling applications, it is useful to have a Kd value to evaluate mass or solute transport in the vadose or groundwater systems. The regression equations and the corresponding coefficient of determination (R^2), which were all significant at 5% level of significance for the Freundlich isotherm, are given in Table 5. The parameters Kd and 1/n of the regression lines in the Freundlich plots are thought to provide estimates of the sorbent capacity and intensity of sorption, respectively.[14–16] A comparison of the Freundlich parameters obtained at 25 and 8°C revealed that the values of the slope 1/n and Kd were not significantly affected indicating that the degree and mechanisms of interactions of sulfolane with the sorbents are not temperature dependent. Carbon-normalized partition coefficients distribution Koc provides a way of adjusting Kd values to account for differences in sorptive behavior among soils of differing content of native organic matter. The Koc values are depicted in Table 6 for the samples investigated. Kd values decreased with sample depth and was higher for sample depth 0–0.20 m while significantly lower for sample depth 4.60–6.10 m. One possible explanation for the higher Kd recorded for sample depth 0–0.20 m is the high degree of the soil organic matter humification. Research has shown that well humified soil organic matter will have substantial reactive functional groups such as ketone, carboxylic, quinone, phenolic, amide, imino, and ketonic.[17] The reactivity of such structural functional groups associated with soil organic matter is pH dependent and will have an influence of sulfolane sorption.

The soil-sulfolane systems investigated are exceedingly complex systems. Not only are they composed of a solid, liquid, and gaseous phases but each of these phases possesses organic and inorganic colloidal phase constituents as

Table 5: Freundlich and Langmuir linear regression model coefficients for sulfolane sorption.

Sample depth (m)	Temperature (°C)	Regression equation	Fit (R^2)	Value of constants
0–0.20		**Freundlich Isotherm:**		
	25	$\log X/M = -0.202 + 1.1782x$	0.98	Kd = 0.63; Koc = 12.33
	8	$\log X/M = 0.0909 + 1.0632x$	0.98	Kd = 1.23; Koc = 24.07
		Langmuir Isotherm:		
	25	$Ceq/X/M = 0.5657 - 5.930 \times 10^{-5}x$	1.00	$a = -1.69 \times 10^{4}$; $b = -1.05 \times 10^{-4}$
	8	$Ceq/X/M = 0.8446 - 3.244 \times 10^{-4}x$	1.00	$a = -3.08\ x10^{3}$; $b = -3.84 \times 10^{-4}$
0.20–0.91		**Freundlich Isotherm:**		
	25	$\log X/M = -0.1452 + 1.058x$	0.98	Kd = 0.72; Koc = 40.22
	8	$\log X/M = -0.2123 + 1.0961x$	0.83	Kd = 0.61; Koc = 34.08
		Langmuir Isotherm:		
	25	$Ceq/X/M = 1.1155 - 1.319 \times 10^{-4}\ x$	0.90	$a = -7.58 \times 10^{3}$; $b = -1.18 \times 10^{-4}$
	8	$Ceq/X/M = 1.3592 - 7.056 \times 10^{-4}\ x$	0.83	$a = -1.43 \times 10^{3}$; $b = -5.18 \times 10^{-4}$
0.91–1.52		**Freundlich Isotherm:**		
	25	$\log X/M = -0.359 + 1.11861x$	1.00	Kd = 0.44; Koc = 89.80
	8	$\log X/M = -0.2847 + 1.0989x$	1.00	Kd = 0.52; Koc = 106.12
		Langmuir Isotherm:		
	25	$Ceq/X/M = 1.1316 - 1.563 \times 10^{-4}x$	0.88	$a = -6.40 \times 10^{3}$; $b = -1.38 \times 10^{-4}$
	8	$Ceq/X/M = 1.1678 - 1.412 \times 10^{-4}x$	0.58	$a = -7.08 \times 10^{3}$; $b = -1.21 \times 10^{-4}$
1.52–1.83		**Freundlich Isotherm:**		
	25	$\log X/M = -0.0928 + 0.9259x$	0.98	Kd = 0.81; Koc = 165.31
	8	$\log X/M = -0.1065 + 0.8593x$	0.92	Kd = 0.78; Koc = 159.18
		Langmuir Isotherm:		
	25	$Ceq/X/M = 1.8306 + 2.198 \times 10^{-4}\ x$	0.59	$a = 4.57 \times 10^{3}$; $b = 1.20 \times 10^{-4}$
	8	$Ceq/X/M = 5.0549 - 0.0011x$	0.96	$a = -9.09 \times 10^{2}$; $b = -2.18 \times 10^{-4}$
1.83–2.14		**Freundlich Isotherm:**		
	25	$\log X/M = -0.0536 + 0.9120x$	0.98	Kd = 0.88; Koc = 176
	8	$\log X/M = -0.0928 + 0.9028x$	0.96	Kd = 0.81; Koc = 162
		Langmuir Isotherm:		
	25	$Ceq/X/M = 2.0069 - 5.136 \times 10^{-5}\ x$	0.44	$a = -1.95 \times 10^{4}$; $b = -2.56 \times 10^{-5}$
	8	$Ceq/X/M = 1.9575 + 3.218 \times 10^{-4}\ x$	0.77	$a = 3.11 \times 10^{3}$; $b = 1.64 \times 10^{-4}$
4.60–6.10		**Freundlich Isotherm:**		
	25	$\log X/M = -1.2932 + 1.2508x$	0.99	Kd = 0.05; Koc = 19.23
	8	$\log X/M = -0.5201 + 0.9543x$	1.00	Kd = 0.30; Koc = 115.38
		Langmuir Isotherm:		
	25	$Ceq/X/M = 5.2178 - 0.0019x$	0.92	$a = -5.26 \times 10^{2}$; $b = -3.64 \times 10^{-4}$
	8	$Ceq/X/M = 4.2527 + 2.598 \times 10^{-4}\ x$	0.49	$a = 3.85 \times 10^{3}$; $b = 6.11 \times 10^{-5}$

Table 6: Desorption of sulfolane from the sorbents.

Sample depth (m)	Treatment	% Desorbed	% CV[a]
0–0.20	25	90	10
	8	91	11
	F&T[b]	92	11
0.20–0.91	25	91	11
	8	90	12
	F&T	90	10
0.91–1.52	25	92	11
	8	90	13
	F&T	91	12
1.52–1.83	25	91	12
	8	89	11
	F&T	91	10
1.83–2.14	25	92	14
	8	91	11
	F&T	91	11
4.60–6.10	25	93	10
	8	91	11
	F&T	93	12

[a]CV = Coefficient of variation; [b]F&T = Freezing and thawing.

well as inert and active compounds. This heterogeneous character strongly influences the physical and chemical properties of soil, thereby having a direct effect on sulfolane sorption and transport in the vadose and saturated zone. Given the total complexity of the sulfolane-water-soil complex, one can envisage that more one sorption mechanism may involve in the sorption process of sulfolane. Sulfones are more complicated structurally than they appear to be at first. Sulfolane as molecule is not planar, but approximately tetrahedral, and the oxygen atoms form the dipoles. Sheila et al.[18] reported that the dominant mechanism for sorption of sulfolane may have been through dipole-dipole interaction between sulfolane and clay minerals. This form of sorption tends to be weaker and less specific than when sorption occurs through a true chemical reaction as in chemisorption.

The relationship between the Kds with several soil physical and chemical parameters was examined. The independent variables chosen for inclusion in developing the correlation with Kd as the response variable, were CEC, %TOC, %clay, D_{40}, and SAR and the process was based on a literature review. The statistical analysis involved correlation matrix, stepwise regression analysis and multiple linear regression analysis and was performed with Stat View 512^{+}. A plot of the residuals indicate that the statistical results are normally distributed with mean zero. Regression equation models were developed for Kd at 25 and 8°C as well as average Kd for both temperatures. The results of the multiple regression analysis are as follows.

For Kd at 25°C:

$$\text{Kd} = -1.736 - 0.068(\text{CEC}) + 0.15(\%\text{TOC}) + 0.568(\%\text{Clay}) - 0.454(\text{D40}) + 0.294(\text{SAR});$$
$$R^2 = 1.00$$

For Kd at 8°C:

$$\text{Kd} = 0.276 - 0.074(\text{CEC}) + 0.413(\%\text{TOC}) + 0.028(\%\text{clay}) - 5.102(\text{D40}) + 0.598(\text{SAR});$$
$$R^2 = 1.00$$

For average Kd:

$$\text{Kd} = 0.196 - 0.106(\text{CEC}) + 0.51(\%\text{TOC}) + 0.029(\%\text{clay}) - 6.381(\text{D40}) + 1.242(\text{SAR});$$
$$R^2 = 1.00$$

The regression equation models derived in this study has practical importance in assessing potential movement of sulfolane in the environment. Although, a very strong correlation was observed, however, the sample size (N = 6) used in this study was relatively small. In the current context of this study, the results leading to the creation of the regression equation model are promising and a starting point for future research.

Desorption Study

The reversibility of sulfolane sorption on the soil materials was evaluated only for batch systems with a 1000 mg/L of sulfolane solution. The extraction procedure was carried out once. Desorption of sulfolane on all the sorbent materials was greater than 90% at both temperatures, 25 and 8°C and following freezing and thawing under the background pH of the sorbate-sorbent system (Table 6). Therefore, there was not apparent hysteris effect of temperature as well as freezing and thawing on the desorption of sulfolane.

Influence of Ionic Strength on Sorption

The sorption behaviour of sulfolane under competitive conditions in this study was evaluated only for systems consisting of 1000 mg/L of sulfolane solution. The results are reported in Table 7 and indicate that increasing the ionic strength of the solution does not concurrently affect sulfolane sorption

Table 7: Effect of ionic strength on sulfolane sorption.

Sample depth (m)	Ionic strength (mole/L)	X/M (mg/kg)
0–0.20	0.03	287
	0.06	270
	0.10	260
	Background	910
0.20–0-91	0.03	79
	0.06	65
	0.10	66
	Background	740
0.91–1.52	0.03	79
	0.06	85
	0.10	85
	Background	615
1.52–1.83	0.03	53
	0.06	50
	0.10	56
	Background	495
1.83–2.14	0.03	30
	0.06	30
	0.10	36
	Background	395
4.60–6.10	0.03	ND[a]
	0.06	ND
	0.10	ND
	Background	250

[a]ND = Not detected.

by the various sorbents. The fact that sulfolane it was found that sulfolane sorption is reversible, these results obtained with the different concentrations of electrolyte support the conclusion that sulfolane sorption is not consistent with an ion-exchange mechanism but rather occurs through dipole-dipole interactions.

Biodegradation Study

The results of the bidegradation of sulfolane were investigated under both aerobic and anerobic conditions. The sterile control systems showed no loss of sulfolane during the monitoring period. CO_2 production was qualitatively monitored as an indicator for sulfolane toxicity to the indigenous soil microbial community. There was no apparent indication that the initial concentration of 875 sulfolane mg/kg was toxic to any of the microcosms. None of the aerobic and anaerobic microcosms were supplemented with phosphate as a nutrient. The soil chemical analyses indicated initial concentration of P as P_2O_5 ranging from 0.25 to 0.05 mg/kg.

No sulfolane biodegradation could be detected under anerobic conditions in any of the microcosms systems after 45 days of incubation at 25 and 8°C.

Table 8: Biodegradation of sulfolane in selected microcosms under aerobic conditions.

Sample depth (m)	NH_4NO_3	Temperature (°C)	Days	Sufolane concentration (mg/kg)
0–0.20	0	25	0	875
			12	729
			53	0
	Yes	25	0	875
			12	677
			52	0
	0	8	0	875
			36	650
			85	0
0.20–0.91	0	25	0	875
			54	559
			91	0
	Yes		0	875
			54	216
			76	0
0.91–1.52	0	25	0	875
			53	614
			76	551
	Yes		0	875
			53	488
			76	160
	No	8	0	875
			64	689
			91	590

As a result, this part of the experiment was not further extended. Loss of sulfolane under aerobic condition is reported in Table 8. The data were plotted and fitted for best-fit line to determine whether there were better described by first-order or zero-order kinetics or polynomial. The sulfolane biodegradation data can be all fitted to zero-order kinetics better than first order kinetics although for some data set, a better polynomial fit was determined. A zero-order reaction indicates that the biodegradation of sulfolane occurs at a constant rate, independent of concentration and time provided that the concentration of sulfolane is not at a toxic level. For comparative purposes, the zero-order degradation rate constant for the data are given in Table 9. Biodegradation rates of sulfolane in the microcosms was the highest in sample depth 0–0.20 m, decreased with sample depth but significantly increased with the addition of nitrogen, and markedly decreased with temperature. Greene et al.[8] reported marked increases in the rates of sulfolane and DIPA biodegradation after P supplementation. The current results clearly demonstrate that the biodegradation of sulfolane by microbial communities in the microcosms is affected by the supply of oxygen, nitrogen, and temperature. Since no sulfolane biodegradation was observed under anoxic conditions in any

Table 9: Biodegradation rates of sulfolane in selected microcosms under aerobic conditions.

Sample depth (m)	NH_4NO_3	Temperature (°C)	Biodegradation rate (mg/kg/day)
0–0.20	0	25	12.17
	yes	25	16.50
	0	8	6.25
0.20–0.91	0	25	5.85
	yes	25	12.20
0.91–1.52	0	25	4.26
	yes	25	9.46
	0	8	3.13

of the microcosms in the presence of the sample initial P, it can be inferred that oxygen is the most critical and an essential element for the biodegradation of sulfolane in the environment. The equation for complete oxidation of sulfolane is:

$$C_4H_8O_2S + 6.5\ O_2 \rightarrow 4\ CO_2 + 3\ H_2O\ +\ 2\ H^+ + SO_4^{-2}$$

Greene et al.[8] reported a drop of 1 to 1.5 pH units during the biodegradation of sulfolane and DIPA. However, during this study, the pHs of the microcosms were not monitored. The pH drop in the systems will be function of the buffering capacity of the sample materials as well as the presence of carbonates. When the dried soil materials were treated with 0.10 M HCl, effervescence was observed in the samples due to CO_2 from carbonates in the sample matrices except for sample depth 0–0.20 m.

Implications for Sulfolane Transport/Fate Processes

Interest in vadose zone transport processes have recently focused on source characterization for groundwater contamination problems. A conceptual model for predicting transport of sulfolane with a simple source is considered. Basically, infiltrating and percolating water at a constant velocity, $V\alpha$, is flowing through the vadose zone and carrying dissolved sulfolane at a specific concentration, $C\alpha$. This component can be sorbed by the soil or biodegraded by the microbial communities. The concentration of sulfolane will be a function of both depth and time. The advection-dispersion equation for this case is:

$$\partial C\alpha/\partial t = D\alpha(\partial^2 C\alpha/\partial X^2) - V\alpha(\partial C\alpha/\partial X) - p/\theta\ (\partial Cs/\partial t) - \mu_\alpha C\alpha - p/\theta\mu_s Cs$$

where: t = time; $D\alpha$ = dispersion coefficient; X = depth; p = bulk density of the soil; Cs = concentration of sulfolane in the soil phase as mg of sulfolane/kg of soil; μ_α = zero-order degradation constant in the aqueous phase; and μ_s = zero-order degradation constant in the soil phase.

The above equation assumes that sorption is essentially linear such that:

$$Cs = KdC\alpha$$

Therefore, the advection-dispersion equation can be rearranged as follows:

$$\partial C\alpha/\partial t = (D\alpha/R)(\partial^2 C\alpha/\partial X^2) - (V\alpha/R)(\partial C\alpha/\partial X) - \mu_\alpha C\alpha/R$$

where: R = retardation factor; μ = new degradation coefficient given by:

$$R = 1 + p(p/\theta)$$
$$\mu = \mu_\alpha + \mu_s p(Kd/\theta)$$

The concentration profiles in the vadose zone can be solved for a variety of different cases. A plug flow case with sulfolane degradation is a sound assumption since flow at the site will be advection dominated and that dispersion can be neglected. In this case, the advection-dispersion equation with zero-oder biodegradation and without dispersion reduces to:

$$R(\partial C\alpha/\partial t) = -V\alpha(\partial C\alpha/\partial X) - \mu_\alpha C\alpha$$

This equation can be solved for the case of step and pulse inputs, respectively.

In the case of the saturated zone, the main transport mechanism for sulfolane will likely to be by advection with no significant biodegradation and/or dispersion as attenuation mechanisms operating in the system. Therefore, a synthesized transport equation representing the seepage velocity of sulfolane assuming to be a conservative substance, in the saturated zone may be written as follows:

$$V = \frac{K(dh/dL)}{\Phi R}$$

where: V = velocity of sulfolane; K = groundwater hydraulic conductivity; dh/dL = groundwater hydraulic gradient; Φ = porosity; and R = retardation factor.

The retardation factor can be calculated:

$$R = 1 + \{[Pb/\Phi]Kd\}$$

CONCLUSIONS

The results of this study showed that sorption of sulfolane on the soil sample materials could be best described mathematically by the Freundlich equation. For many contaminant modeling applications, it is useful to have a Kd value to evaluate mass or solute transport in the vadose or groundwater systems. Kd values derived at 25°C ranged from 0.05 to 0.88 L/kg and from 0.30 to 1.23 L/kg

at 8°C. Sorption capacity of the sorbent/sulfolane systems was essentially not affected by temperature.

Multiple regression analysis indicated a high level of correlation between Kd and several soil parameters. The regression equation models derived in this study has practical importance in assessing potential movement of sulfolane in the environment.

In the current context of this study, the results leading to the creation of the regression equation models are promising and represent a practical starting point for future research.

Increasing the ionic strength of the solution did not affect sulfolane sorption by the various sorbents. The fact that it was found that sulfolane sorption was reversible in conjunction with the results obtained with the different concentrations of electrolyte, support the conclusion that sulfolane sorption is not consistent with an ion-exchange mechanism but rather occurs through dipole-dipole interactions.

No sulfolane biodegradation was detected under anerobic conditions in any of the microcosms systems after 45 days of incubation at 25 and 8°C. Sulfolane biodegradation data could be all fitted to zero-order kinetic better than first order kinetic although for some data set, a better polynomial fit was determined. Biodegradation rates of sulfolane in the microcosms was the highest in sample depth 0–0.20 m, decreased with sample depth but significantly increased with the addition of nitrogen, and markedly decreased with temperature. At 25°C and no supplement of N, biodegradation rate ranged from 4.26 to 12.70 mg/kg/day but with addition of N, the range was from 9.41 to 16.50 mg/kg/day. The current results demonstrate that the biodegradation of sulfolane by microbial communities in the microcosms was significantly affected by the supply of oxygen, nitrogen, and temperature.

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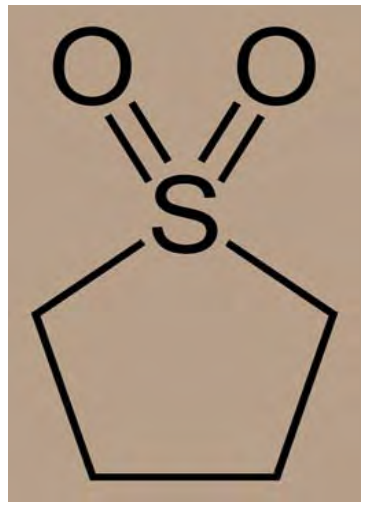
Remediation of Sulfolane Impacted Groundwater – Characterization, Treatment and Disposal

Stacy Gibb, Jamie Fairles

Outline

- History of Sulfolane
- History of Impacted Groundwater at Facility
- Piloting and Full Scale Treatment system
- Basis of System Design
- System Construction, Start up and Operation
- Future Actions

Sulfolane



- $C_4H_8O_2S$ (Sulfolane molecular formula)
- Developed by Shell Oil in 1944
- Fully soluble in water with low volatility and low Henrys Law Constant
- Used in Sulfinol process along with DIPA and is a highly recoverable solvent
- Used to purify natural gas by removing acid gases and aromatics from hydrocarbon mixtures
- Now used in a wide variety of applications including polymers and electrical applications

History of Sulfolane Remediation

- Originally studies completed on biodegradation of Sulfolane in industrial wastewaters
- Research studies were completed by University of Alberta in the mid 1990's focusing on soil/groundwater remediation
- Stoichiometry of Sulfolane oxidation under ideal conditions :

$$C_2H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO^{-4}$$

- Canadian Environmental Quality Guidelines for Sulfolane; Water and Soil (CCME 2006) provides the primary criteria for Sulfolane remediation

History of Impacted Groundwater at the Facility

- Sulfolane and DIPA were first detected in groundwater at the site in the 1980's
- In 1994 a detailed monitoring program was initiated
- In 1997 a five (5) year program was started to remove primary sources of Sulfolane and DIPA
- A regional Sulfolane monitoring program started in 1998 detected offsite Sulfolane
- Between 1990-2000, 56 monitoring wells were installed to determine baseline concentrations

History of Impacted Groundwater at the Facility

- Treatability of Sulfolane-impacted groundwater was investigated in 2001-2002 focusing on:
  - Groundwater recovery
  - Lab scale In-situ remediation
  - Lab scale biodegradability testing
- Eight (8) recovery wells were installed in 2001-2002 in the capture zones
- 2002-2003 a standalone pilot system was commissioned onsite
- Capture Zone Modelling was completed in 2003-2004 for the plume delineation of the three different groundwater zones (A, B, and C)

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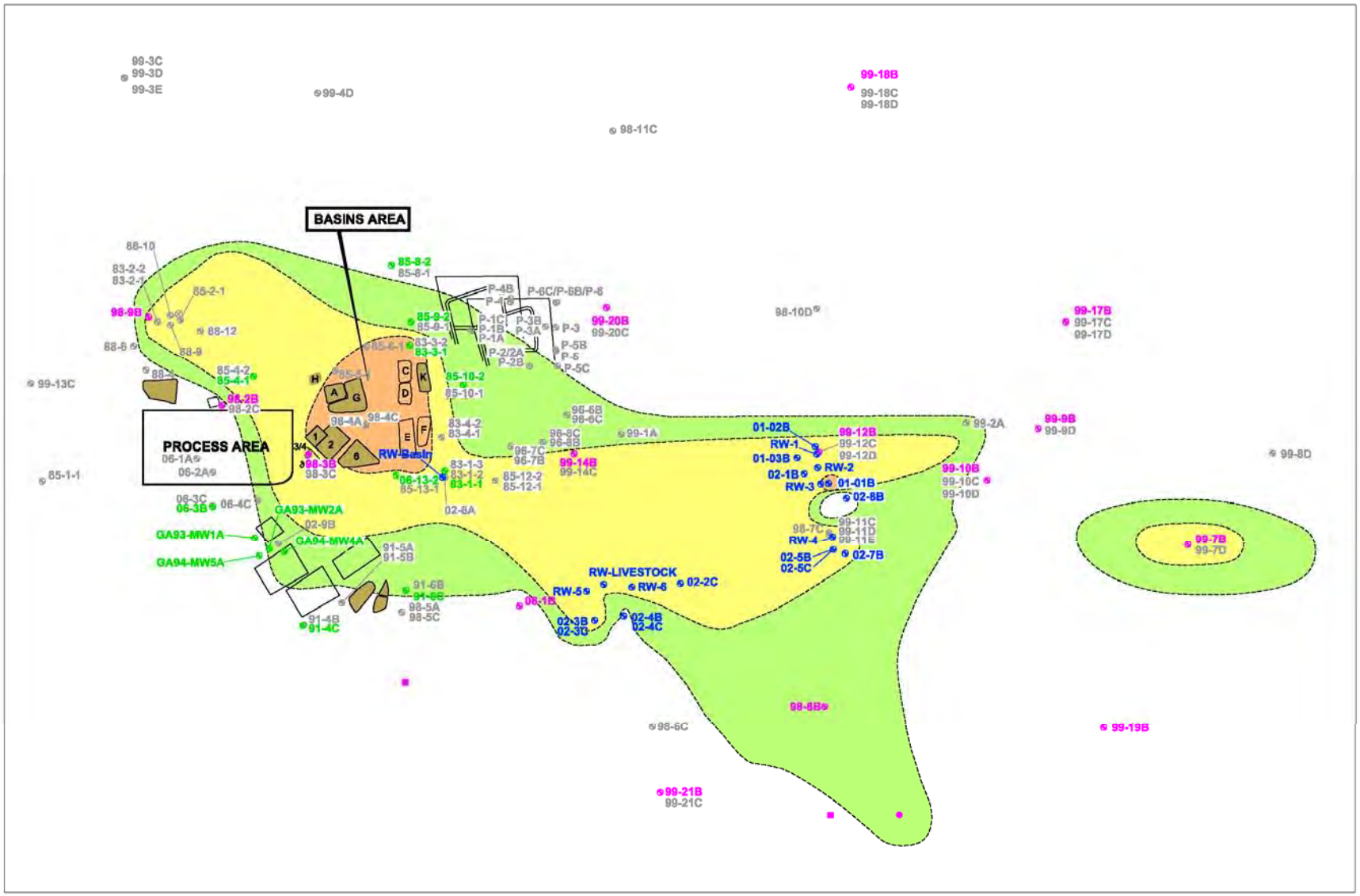
Zone B Plume Delineation



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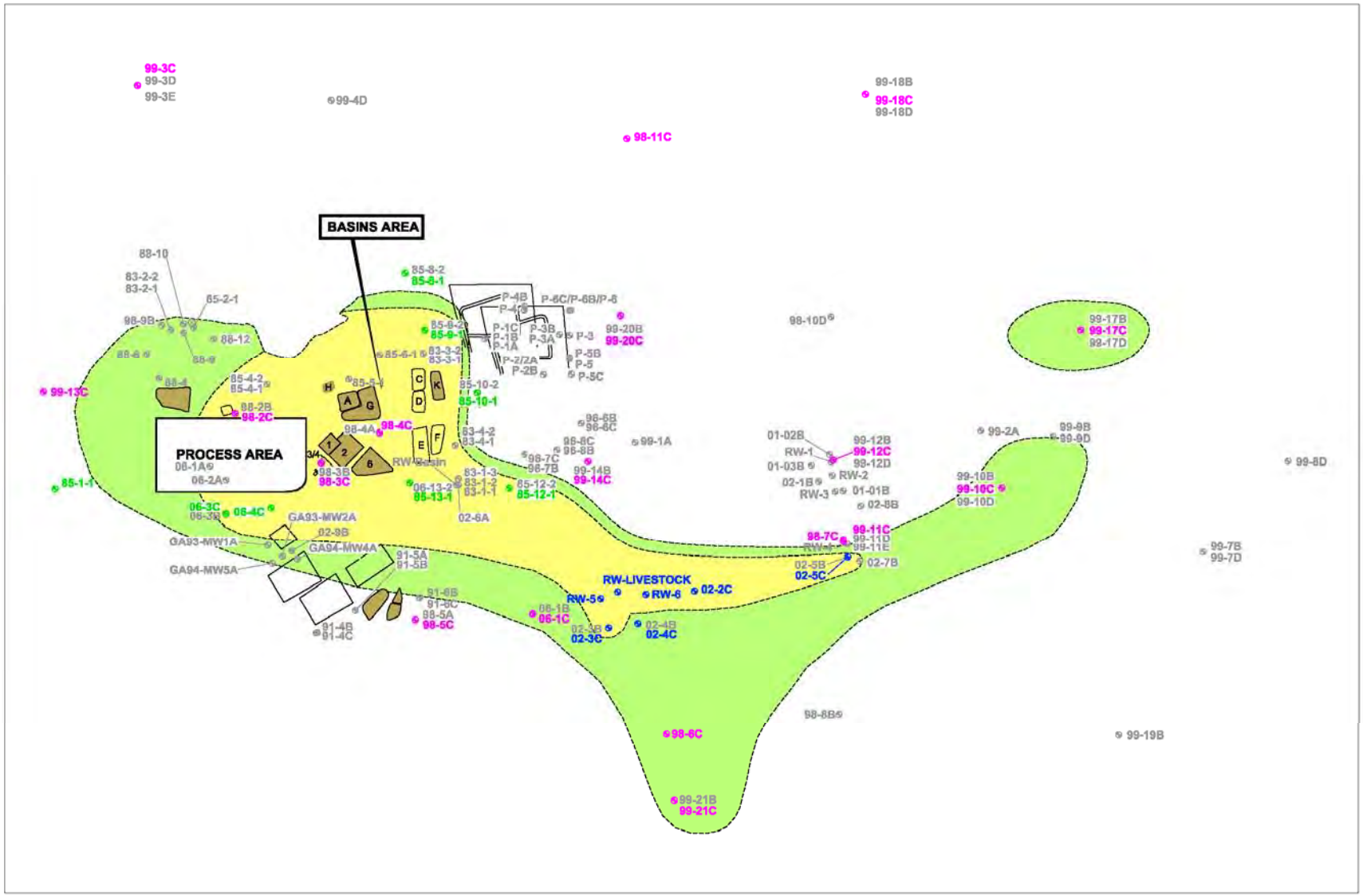
Zone C Plume Delineation



Piloting of Treatment System

- Pilot treatment system was aerobic biological system with activated sludge and clarifier
- Activated sludge from the plant process wastewater treatment system was used for pilot system inoculation
- Treatment effective to 0.001 mg/L
- Treatment capacity 150m^3/day
- Effluent was sent to plant wastewater treatment system
- Treatment system was susceptible to loss of suspended solids
- Pilot system was operated seasonally for 2 years

Piloting of Treatment System Results

Pumping Location	2003	2004
East Boundary		
Months of Operation	4	3
Volume Treated	3,700 m^3	2,400 m^3
Estimated Mass of Sulfolane Removed	≈ 28 Kg/month	≈ 15 Kg/month
South Boundary		
Months of Operation	5	5
Volume Treated	> 12,000 m^3	> 12,000 m^3
Estimated Mass of Sulfolane Removed	≈ 5 Kg/month	≈ 5 Kg/month

Expanding to Full Scale Treatment System

- Due to promising results in pilot stage, full scale and year-round treatment was feasible
- Design for full scale treatment system initiated in 2005
- Existing water treatment infrastructure at the site was available to be retrofitted for the process
- Recovery wells required upgrading to accommodate pumping all year round

Full Scale Treatment System Design Criteria

- Design for maximum flow rate of 400 m^3/d
- Designed to reduce Sulfolane by 99.99% (objective of below detectable levels in effluent)
- Clarifier Hydraulic Retention Time (HRT) is the size limiting constraint on system
- pH adjustment included based on groundwater chemistry
- Chemical addition to aid in solids removal as required
- Effluent to be commingled with plant's wastewater effluent

Design Parameter	Influent Value	Target Effluent Value	Units
Flow Rate	400	400	m^3/d
pH	8	7-7.5	-
Temperature	8	8-14	°C
BOD_5	15	5	mg/L
COD	25	10	mg/L
Ammonia (NH_3-N)	<0.1	0.5	mg/L
Phosphorous	<0.1	0.5	mg/L
Total Suspended Solids	---	25	mg/L
Sulfolane	8	Non-detect	mg/L

System Design

- Network of five (5) groundwater wells are tied into system (communication via radio link)
- Aerated biological system with clarifier and filter for final polishing
- System is fully automated, requires little operator input with alarms tied to plant control system
- System is set up with spare pumps and blowers that alternate duty cycle
- Computer for human machine interface (HMI) and local control

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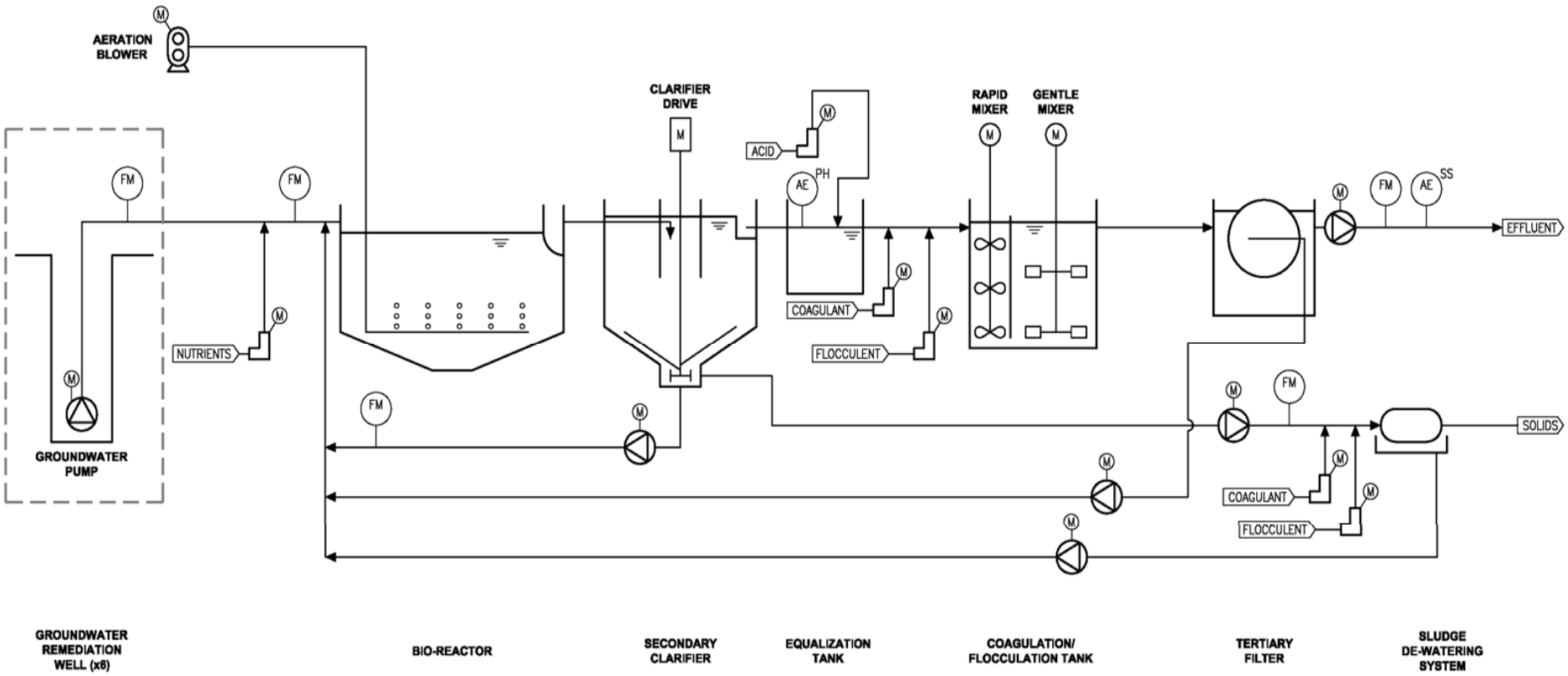
Full Scale Treatment Process



System Construction

- Space constraints and existing equipment limited equipment/pipe locations
- Existing concrete tanks required upgrading to meet engineering standards
- Construction was scheduled to have minimal impact on plant operations
- Pipeline construction connecting wells required significant safety measures to avoid existing infrastructure
- System construction was completed with excellent safety record

System Start up and Operation

- System was inoculated with seed bacteria from the plant's wastewater system
- During commissioning, AENV required the system be shown to be operating properly prior to creek discharge through lab analysis for aquatic toxicity

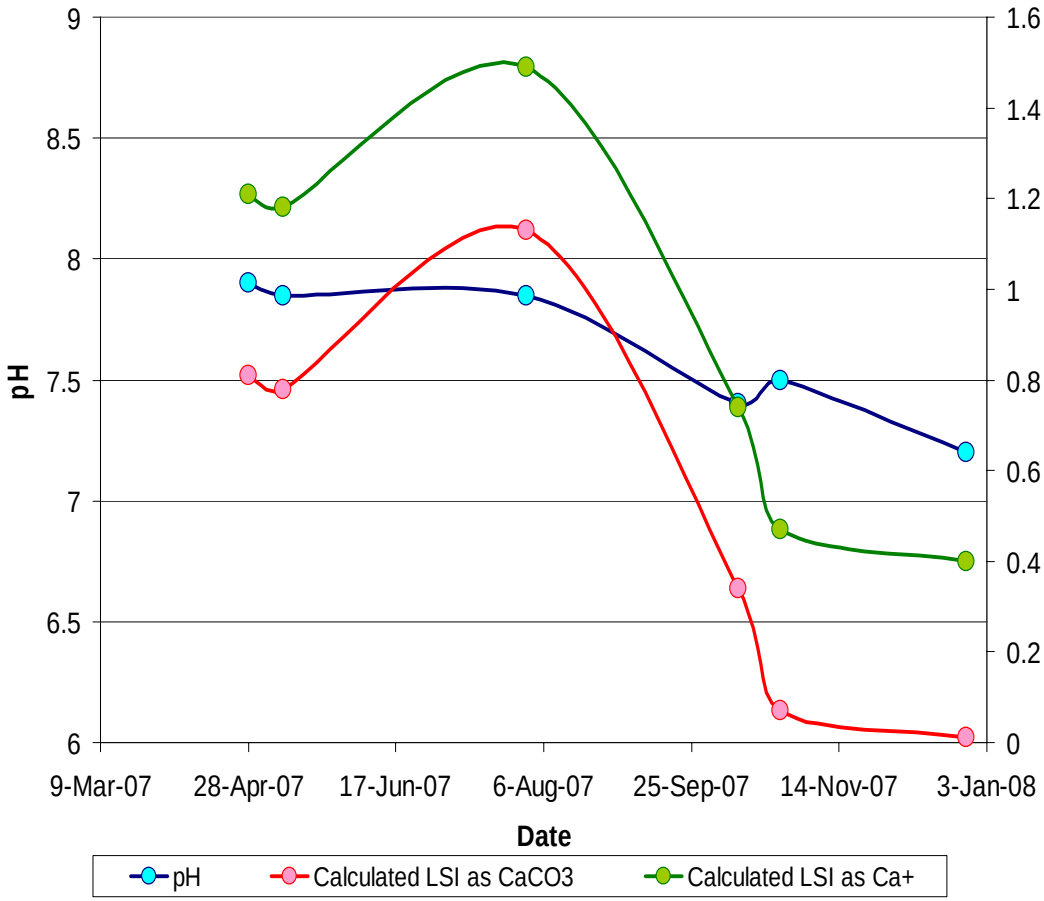
System Start up and Operation

- Lab samples are taken bi-weekly to test for sulfolane removal and to confirm system meets discharge criteria
- Facility lab takes bi-weekly samples to monitor health of the system
- Maintenance performed by plant personnel as part of regular plant maintenance
- System is automated and requires routine visits 2-3 times per week for visual inspection by plant personnel

System Start up and Operation

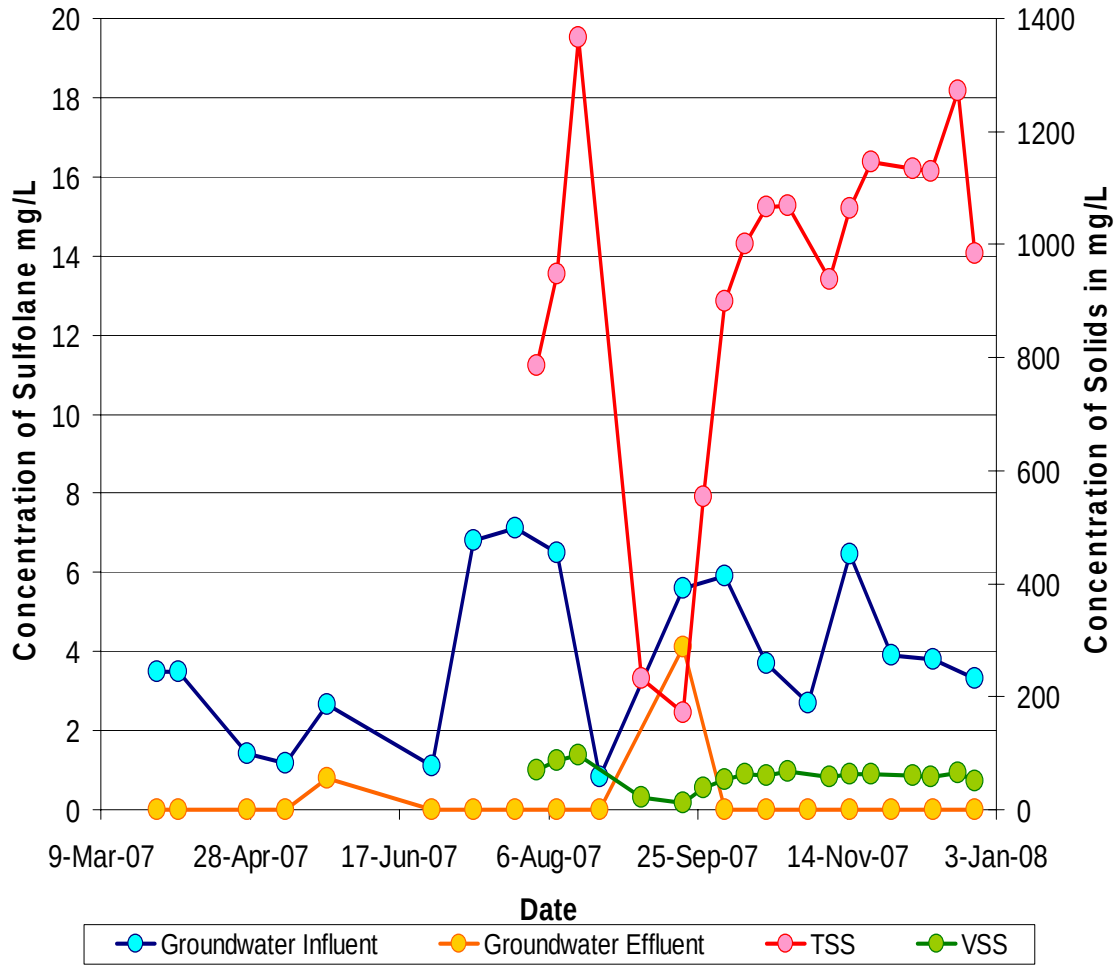
Acid Addition

- Acid addition is important to the system to decrease the Langelier Saturation Index (LSI)
- Negative LSI will dissolve $CaCO_3$
- Positive LSI Scale can form and $CaCO_3$ precipitation may occur
- LSI greater than +1.0 there is a higher potential scale will occur
- Water with a LSI of 1.0 is one pH unit above saturation
- Reduction of pH from 7.8 – 7.2 in the systems final effluent greatly reduced the potential for the water to scale
- Prior to acid addition after each pumping step there was subsequent increase in pH



System Start up and Operation – Health of Biomass

- Direct correlation between Volatile Suspended Solids (VSS) concentration in bioreactor and sulfolane removal in effluent
- Loss of VSS in bioreactor resulted reduction of sulfolane removal
- 5 -10% of the Total Suspended Solids (TSS) in the bioreactor are Volatile
- System maintenance accounted for loss of solids in September which resulted in increased sulfolane in the effluent



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System Start up and Operation – 2007
Sulfolane Removal

- Removal rates vary between months due to recovery well combinations (higher vs lower concentrations in wells)
- Commissioning in March to April resulted in inconsistent removal due to system instrumentation and communication issues
- In June the system was shutdown for evaluation of acid addition to reduce scaling potential
- July to December the system operated as designed at a reduced flow for biomass health

Month	Total Flow (m^3)	Removal (kg)
March	808.8	2.8
April	1715.2	4.2
May	3800.5	5.8
June	106.0	0.1
July	3773.1	26.2
August	3166.9	11.6
September	2106.5	24.4
October	4056.1	19.5
November	3860.5	16.9
December	3865.0	13.7
FLOW TOTAL	**27258.6**	**125.2**

Future Actions

- Additional monitoring and recovery wells to be installed
- Target higher concentrated groundwater around plant site will increase and stabilize biomass population
- Continue pumping from plume boundary
- Pilot system has been relocated to another facility to apply technology elsewhere

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- Roy Hunt – WorleyParsons
- Sean Kelly – WorleyParsons
- Norris Graham – WorleyParsons

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Strategies for Sour Gas Field Developments

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Increasing energy costs and growing demand for natural gas have driven the development of sour gas fields around the world. About forty percent or 2600 Tcf of the world's natural gas reserves are in the form of sour gas where H_2S and CO_2 compositions exceed 10% volumetric of the raw produced acid gas. In some cases the acid gas composition in these reserves is very high and economics of producing pipe line quality gas are marginal. Natural gas almost always contains contaminates or other unacceptable components, including heavy hydrocarbons, mercaptans, mercury, water and the acid gases H_2S and CO_2.

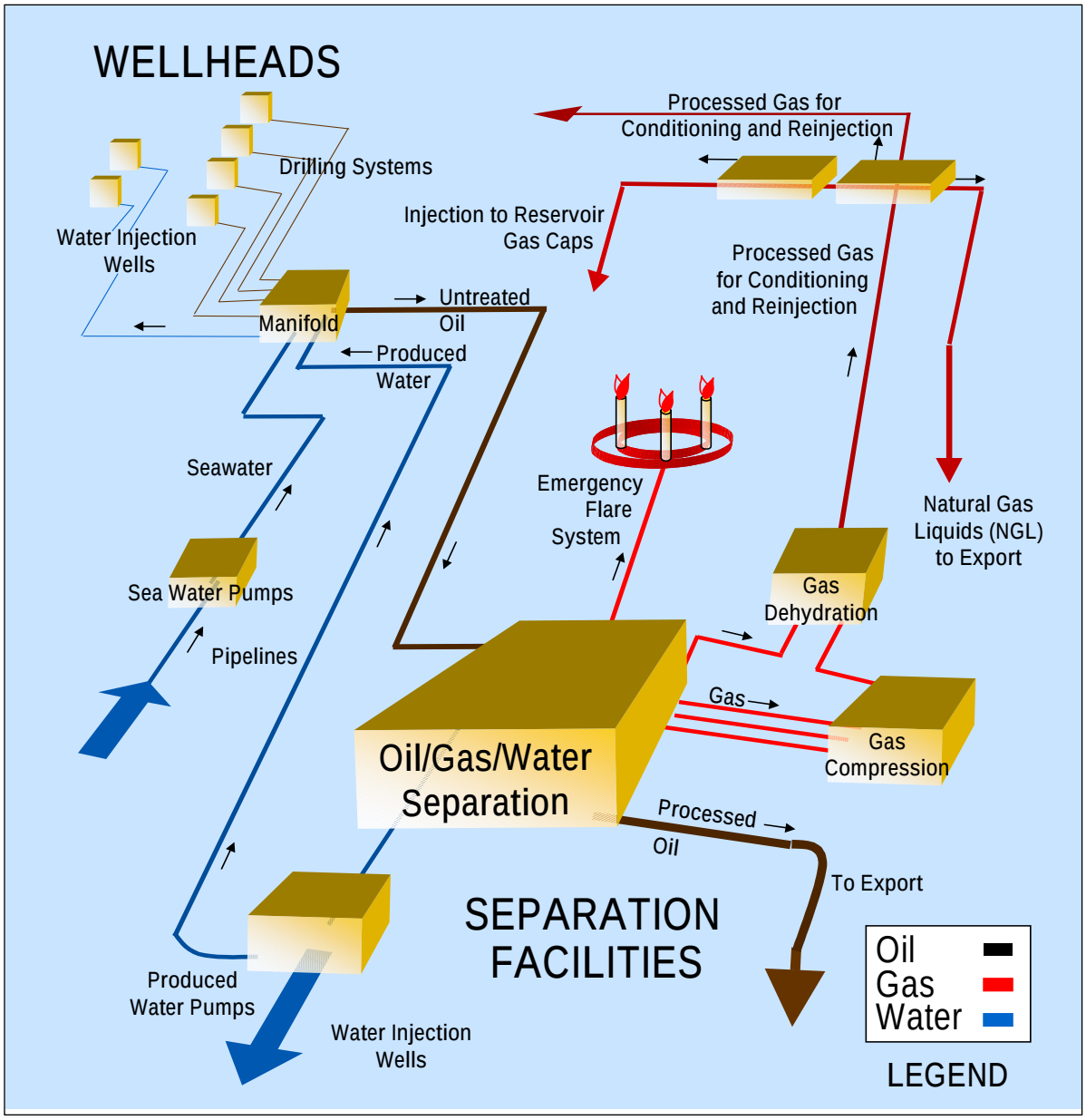
Conditioning natural gas for pipeline LNG or GTL requires the removal of these undesirable contaminants.

Emission regulations are getting tighter and there is increasing demand to achieve higher sulfur removal and recovery.

Middle East counties such as Qatar, Saudi Aramco, and Canada, China, Venezuela, Brazil and many other countries have a high demand to treat sour gas fields.

WorleyParsons has designed over 34 LNG feed gas treating units, over 110 gas processing and gas treating units, over 510 sulfur plants and over 100 tail gas treating units.

The following diagram represents the general scheme for an oil and gas production facility.



In general acid gases could be treated using generic solvents such as DGA, DEA, MEA, or MDEA or using proprietary solvents such as aMDEA, Sulfinol, Selexol, Ucarsol, Flexsorb, or other processes from Ryan Homes, BASF, IFP, ADIP, membranes, or molecular sieves options depending on the acid gas compositions and the product specifications considering optimization for affordable capital and operating costs.

For Dew Point Control, water has to be removed to meet the pipe line specifications, by using Glycols, Membranes, or molecular sieves according to the project specification, application, and cost.

The primary differences in process by using generic amines are in solution concentrations. MEA is ordinarily used in a 10 to 20 percent by weight in the aqueous solution. DEA is also used in the 10 to 30 percent by weight in the aqueous solution. DIPA, DGA, and MDEA are used in higher concentrations. Typical concentration ranges for DIPA and MDEA are 30 to 50 percent by weight in the aqueous solution. DGA concentrations range from approximately 40 to 50 percent by weight.

As the results of the new revolutions in challenging the various solvents and different process configurations, gas processing in gas industries and refineries has become more complex. In response to this trend and to comply with the product specifications, more equipment and more processing upstream or downstream of gas processing should be implemented.

The selection criteria for gas processing is not limited to the selection of gas treating configurations by itself; it is expanded to the selection criteria of more side process / downstream configurations, to complete the gas processing in order to meet the product specification and to satisfy environmental regulatory agency requirements.

Acid gas removal is the removal of H_2S and CO_2 from gas streams by using absorption technology and chemical solvents. Sour gas contains H_2S, CO_2, H_2O, hydrocarbons, COS/CS_2, solids, mercaptans, NH_3, BTEX, and all other unusual impurities that require additional steps for their removal.

There are many treating processes available. However, no single process is ideal for all applications. The initial selection of a particular process may be based on feed parameters such as composition, pressure, temperature, and the nature of the impurities, as well as product specifications. The second selection of a particular process may be based on acid/sour gas percent in the feed, whether all CO_2, all H_2S, or mixed and in what proportion, if CO_2 is significant, whether selective process is preferred for the SRU/TGU feed, and reduction of amine unit regeneration duty. The final selection could be based on content of C_3^+ in the feed gas and the size of the unit (small unit reduces advantage of special solvent and may favor conventional amine).

Final selection is ultimately based on process economics, reliability, versatility, and environmental constraints. Clearly, the selection procedure is not a trivial matter and any tool that provides a reliable mechanism for process design is highly desirable.

The variety of the acid gas sources that have different gas compositions, pressure, temperature, and nature of impurities and might require different means of gas processing to meet the product specification, are presented in table I.

Selection of the right tools is very crucial. Establishing and conducting all the elements together at the same time, would generate such a beautiful art in gas treating.

Natural Gas Processing

Natural gas is one of the common sources of gas treating, with a wide range in CO_2/H_2S ratios and high pressure treating. If natural gas is not an LNG application, it could be treated with selective H_2S removal if significant CO_2 is present. If C_3^+ is present, the desirability of using physical or mixed solvents is reduced. If organic sulfur is present, the desirability of using physical or mixed solvents is increased.

It is favored to use proprietary solvents if natural gas has significant CO_2 and /or H_2S for large units/ and to use conventional solvents for small units particularly with modest acid /sour gas levels.

Petroleum Refining

Petroleum refining is another source of gas treating with low CO_2 content, unless the refinery has catalyst cracking unit, in which case the gas may contain COS, organic sulfur, cyanides, ammonia, and organic acids. The acid gas from hydrotreating and hydrocracking essentially contains H_2S and ammonia. The gas treating pressures and H_2S specifications vary for individual applications, and MEA/DEA/MDEA/DGA or formulated amines are the typical solvents. The refinery typically has multiple absorbers and a common regenerator as listed below:

- Fuel gas treating
- Hydrotreater product/fuel gas
- Hydrotreater recycle gas
- Hydrocracker product/fuel gas
- Hydrocracker recycle gas
- LPG liq-liq contactor
- Thermal/catalyst cracker gases
- Services independent or combined as practical

Synthesis Gas Treatment

Synthesis gas treatment is characterized by high CO_2 and low (or no) H_2S. If the amount of CO_2 is limited, it is preferred to use selective H_2S treating via formulated/hindered amine, mixed solvent or physical solvent. If H_2S is not present and there is modest or essentially complete CO_2 removal, it is preferred to use activated MDEA, hot potassium, mixed amine, and physical solvent.

Table I represents the most common process being used in gas plant industries.

Table I- Data Base Outline

HP Gas Treating System, Bulk CO_2 Removal from Natural Gas, and Selective H_2S Removal Physical Solvent Process (SELEXOL, Murphreesorb, IFPEXOL) Other Solvent Process (DEA, MDEA, DGA, aMDEA, Sulfinol M/D, Flexsorb, Gas/SPEC *SS, Membrane + amine, UCARSOL, Chevron-IPN, Benfield, K_2CO_3)		
Tail Gas Treating (H_2S Recycle & Selective Cat. Oxidation Process Typical Solvent (MDEA, HS-101/103, Gas/Spec *SS, Sulfinol, Flexsorb)		
BSR /Amine Process	Shell SCOT/ ARCO	Parsons BOC Recycle
Resulf	Dual-Solve	BSR / Wet Oxidation
MCRC	CBA	Sulfreen
BSR /Selectox	BSR/Hi-Activity	Super Claus
Incinerator Tail Gas		
Wellman-Lord	Clintox	Elsorb
Claus Master	Cansolv	Bio-Claus
Clausorb		
Acid Gas Enrichment Typical Solvent (MDEA, Sulfinol M/D, FLEXSORB, UCARSOL, Gas/SPEC *SS)		
Ammonia Plants Physical Solvents, aMDEA, Hot Potassium, Dow 800 series, etc.		
Cryogenic Systems **Chemical Solvents**		
Enhanced Oil Recovery (EOR) **Chemical & physical Solvents**		
EOR CO_2 Recovery Plants Similar to Bulk CO_2 Removal		
Ethylene Plants Similar to Bulk CO_2 Removal		
Flash Regeneration CO_2 Removal Similar to Bulk CO_2 Removal		
Hydrogen Plants **Chemicals Solvents**		
LPG Treating **Chemical Solvents**		
Oil Refinery Systems **Chemical & Physical Solvents**		
Dehydration systems EG, DEG, TEG, Solvents, Methanol, Molecular Sieve Process, etc.		

Table II represents the solvent capabilities.

Table III- Solvent Capabilities

Solvent	Meets ppmv, H_2S	Removes Mercap. COS, Sulfur	Selective H_2S Removal	Solution Degraded by
MEA	Yes	Partial	No	Yes (COS,CO_2, CS_2)
DEA	Yes	Partial	No	Some (COS, CO_2, CS_2)
DGA	Yes	Partial	No	Yes (COS,CO_2, CS_2)
MDEA	Yes	Partial	Yes (1)	No
Sulfinol	Yes	Yes	Yes (1)	Some (CO_2,CS_2)
Selexol	Yes	Yes	Yes (1)	No
Hot Potassium Benfield	Yes (2)	No (3)	No	No
Iron Sponge	Yes	Partial	Yes	
Mol Sieve	Yes	Yes	Yes (1)	
Strefford	Yes	No	Yes	Yes (CO_2 at high Conc.)
Lo-cat	Yes	No	Yes	Yes (CO_2 at high Conc.)

1. These processes exhibit some selectivity.
2. Hi-Pure version.
3. Hydrolysis COS only.

Selective H_2S Removal

The absorption of H_2S and the selectivity of H_2S over CO_2 are enhanced at a lower operating temperature; consequently, it is desirable to minimize the lean amine temperature.

To achieve low H_2S slippage in the absorber operating at high pressure, it is necessary to strip the amine to a very-low H_2S loading (typical loading is < 0.01 mole-acid gas/mole amine). Steam stripping occurs in the regenerator at high temperature and reverses the reactions given above. The steam reduces the partial pressure of H_2S and CO_2 over the amine, thus reducing the equilibrium concentration (or loading) of these components in the amine.

For highly selective H_2S removal, solvents by The DOW Chemical Co. (Gas Spec), Union Carbide (Ucarsol), BASF (aMDEA), EXXON (Flexsorb), and others have been developed that exhibit greater selectivity and H_2S removal to lower treated gas specifications. However, these solvents are MDEA-

based solvents. These solvents have other applications; such as H_2S removal from CO_2 enhanced oil recovery (ROR) enrichment processes.

Solvents for H_2S selectivity are used for refinery systems with high CO_2 slip, tail gas treating, natural gas treating, H_2S removal from liquid hydrocarbon streams, natural gas scrubbing, and refinery systems with LPG streams containing olefins.

Bulk CO_2 Removal

Solvents for CO_2 removal are used for natural gas treaters, landfill gas facilities with high CO_2 feed, ammonia and hydrogen plants, and natural gas or LNG facilities with downstream cryogenic facilities. MDEA solvent and mixtures of amines can be used for bulk CO_2 removal. However, this performance is very sensitive to one or more of the operating parameters, such as liquid residence time on the trays, circulation rate, and lean amine temperature.

MDEA has a number of properties, which make it desirable for applications such as:

- High solution concentration up to 50 to 55 wt %
- High-acid gas loading
- Low corrosion
- Slow degradation
- Lower heats of reaction
- Low- vapor pressure and solution losses

Amine solvents and physical solvents are used over a wide variety of process conditions, ranging from atmosphere pressure for refinery off-gas and Claus tail gas treating, to high pressure for natural gas sweetening.

Amine solution in water is very effective at absorbing and holding H_2S and CO_2 from weak acids, when dissolved in water. The weak acids react with the amine base to help hold them in the solution. Therefore, a chemical solvent (such as amine) is used for these components.

The Hot Potassium Carbonate Process has been utilized successfully for bulk CO_2 removal from a number of gas mixtures. It has been used for sweetening natural gases containing both CO_2 and H_2S. If the gas mixture contains little or no CO_2, potassium bisulfide is very difficult to regenerate, and it the Hot Potassium Carbonate Process is not suitable.

The usage of the DGA solvent has been increased recently for the following reasons.

- DGA has a higher molecular weight compare to MDEA and higher stability
- Capability of absorption of CO_2 and H_2S

- Operate at higher concentration, which allows to increase the capacity in existing units and improve the emissions
- DGA could be reclaimed thermally as required during normal operation
- DGA absorbs H_2S and CO_2 which means the treated gas meet pipeline specifications, for a better sulfur removal and recovery
- Lower capital cost due to capability at higher concentration
- DGA has lower heat stable salts rate
- DGA has lower degradation product rate

Contaminates Removal

As mentioned above, contaminants such as mercury, mercaptans, heavy hydrocarbons, and H_2S and CO_2 concentrations have to be evaluated carefully in order to select the appropriate solvent to meet the desired product specifications. The contaminants could be removed in front of the gas treating if it is possible or could be done where the product stream leaves the absorber and before the dehydration unit.

Mercaptans are commonly present in natural gas and if the bulk of the mercaptans permitted into the amine plant, due to the mercaptanes solubility in the amine solvent, the lean amine absorbs the mercaptans in the absorber and rich amine leaving the absorber contains some mercaptanes. In the stripper column, a portion of the mercaptans are present in the stripper overhead entering the sulfur plant and it is required to be destructed in the reaction furnace.

Therefore, the selection of the amine solvent in regard to their mercaptans solubility is essential. If the combustion temperature of the reaction furnace is not adequate to destruct heavy hydrocarbons and mercaptans, then several options could be considered as follows.

1. Using Oxygen enrichment to boost the reaction furnace temperature
2. if the H_2S concentration of gas to the sulfur recovery unit is low, the acid gas enrichment unit is recommended. Acid gas from the gas-treating unit flows through the acid gas enrichment unit where the H_2S has substantially separated from the CO_2 and N_2. The stream that is enriched in H_2S is fed to the sulfur recovery unit while the desulfurized CO_2 and N_2 stream is sent to the thermal incinerator.
3. Use regenerable activated Carbon Beds downstream of the reaction furnace and upstream of Claus reactors to prevent catalyst deactivation.

4. Acid Gas Injection is another option instead of sulfur recovery unit that could be evaluated with a different criteria and the acid gas behavior at high pressure using high pressure compressors.

If COS presents in the treated gas, membranes could be used.

Mercury is another substance commonly present in natural gas, and particularly in LNG facilities it must be removed to meet the product specification. Activated carbon in a non regenerable adsorbent bed is commonly used for mercury removal.

Recent WorleyParsons Experience

WorleyParsons recently evaluated different schemes and solvent for bulk acid gas removal versus selective solvent. Sour Gas Field Developments normally includes amine unit or sulfur removal unit, Dehydration, SRU, TGU and incineration. A typical flow diagram and the process flow diagram for the Case 2 are provided on the following pages.

Two schemes will be described.

Case 1 – our evaluation for new Upgraders and Oil Sands mostly in Canada dealing with a lot of high content H2S and CO2 in sour gas indicates that using DGA solvent in the amine unit will meet the product specification. There will be more CO_2 and H_2S to the sulfur recovery unit since DGA absorbs most of the H_2S and CO_2. The Claus unit is then followed by the BSR/TGU-amine tail gas treatment unit. MDEA solvent is selected in the tail gas unit and the evaluation of potential benefits of using selective solvent such as Flexsorb or similar is in progress.

Case 2 - Our evaluation indicates that using common regeneration unit for the amine unit and the tail gas unit is very cost effective in reducing capital and operating cost. The amine unit is designed with a special features of split flow configuration and using turbine to save the electricity where the pressure from the absorber bottom will let down to a lower pressure. TEG is selected for the dehydration unit.

- Common Regeneration unit lower operating and capital cost
- Absorber with split flow configuration
- Smaller reboiler duty
- Recover the majority of horse power required by recovering the energy from absorber bottom
- One solvent, less operating cost
- Easier to operate

A brief description of our schemes is described below. The sulfur recovery and BSR-TGU is not included since it is typical WorleyParsons design features.

(Sulfur Removal) Amine Process Description

The amine unit is an integrated split flow configuration and a common regeneration with the tail gas unit. MDEA flows into the Amine absorber where H_2S is preferentially absorbed by the MDEA solution. The MDEA solution reduces the H_2S content in the absorber overhead stream to less than 4 ppmv. A 50 wt% MDEA solution is used to treat the acid gas.

The absorber is split into two sections, the absorption section and the water wash section. The absorption section of the tower is trayed with lean solution feed to top of each bed. The absorption section serves as the main contacting section between the gas feed stream and the lean MDEA solution. The water wash section is contained one section and is provided above the lean solution feed point to minimize solvent losses in the treated product stream. A de-entrainment device is also provided above the water wash section of the absorber to minimize the entrainment of liquid out of the top of the absorber in the treated gas. The amine absorber water wash section is integrated in the column shell and provides separation of entrained MDEA and wash water from the overhead gas. Wash water is drawn from the chimney tray top section of the amine absorber, pumped and injected into the absorber top through a flow control valve. Fresh makeup cold condensate is added to the circulating wash water loop and a small purge stream is continuously withdrawn to keep the concentration of MDEA in the wash water relatively low. This minimizes MDEA losses. Treated gas from the Amine absorber overhead gas flows to the dehydration unit.

Rich MDEA leaving the bottom of the absorber operates at high pressure the energy could be recovered as a electricity by providing a turbine to recover the energy. The energy being recovered by the turbine will provide abut 70 to 80% of the required horse power in the sulfur block.

Rich MDEA is sent to the flash drum to remove any hydrocarbon in the solution, by providing a flash section at the top of the drum, then is preheated in the lean/rich MDEA exchanger before entering the regenerator below the wash trays through a flow control valve, which is designed for flashing service.

The amine absorber will have two MDEA streams, one from the Tail Gas Treating Unit absorber as a semi-lean and another from the amine regeneration as a lean solution. This process is integrated split flow configuration that the amine absorber will be provided with the semi-lean and super lean MDEA with a common regeneration that serves TGU absorber and the amine absorber. The circulation rate is reduced and the size of the regeneration is smaller due to less circulation rate. Therefore, the Reboiler and associated equipment will be smaller.

The CO_2 and H_2S are stripped from the rich MDEA solution in the 24-stripping tray MDEA regenerator by cascading the rich solution, counter-current to steam produced by the Reboiler. The top section of the regenerator tower contains a rectifying (reflux) section consisting of 4 trays for washing of the stripped acid gas. Stripping steam is formed in the Regenerator Reflux Reboiler, and reboiler heat is supplied from the LP steam system. The stripped CO_2 and H_2S then flow to the sulfur recovery unit. The lean MDEA solution is collected on a chimney tray, which distributes the solution to the reboiler. As the lean solution passes through the reboiler, stripping steam is generated and flows up the

column, while the lean solution is returned to the sump section in the base of the column. This stripping steam provides agitation and the heat to release the absorbed H_2S and CO_2 from the rich MDEA solution, as it rises up through the column, counter-current to the rich MDEA solution. The reboiler is equipped with the Reboiler condensate pot.

The regenerator column consists of a lower stripping section and an upper condensing section. The stripping heat is provided by saturated low-pressure steam through a kettle-type regenerator Reboiler. In the condensing section, the rising vapor is cooled by contact with sub-cooled quench water. The quench water is recycled and cooled. The cooling load is adjusted to control the overhead gas temperature. Overhead gas from the regenerator is recycled to the front of the Claus sulfur recovery unit. A de-entrainment device is provided above the top tray of the tower to minimize the entrainment of liquid out of the top of the regenerator tower into the acid gas stream.

Lean MDEA is pumped through Hot Lean pump then pre-cooled in the lean/rich MDEA exchanger. The MDEA is further cooled in the lean MDEA air cooler and lean MDEA trim cooler. The MDEA storage tank has capacity to hold the total MDEA inventory and is used to take system surges during operation. The tank also serves as a convenient location for MDEA make-up. The MDEA make up from truck connection and cold condensate is provided to the surge tank. Nitrogen blanketing prevents degradation of the MDEA by preventing oxygen to the tank. The cooled lean MDEA is pumped through Lean MDEA circulation pump.

A slip stream of the MDEA is circulated through lean Filter where solid impurities such as iron oxide, iron sulfide, pipe scale, dirt, and degradation products are removed from the solution.

In the Future, after full MDEA filtration, a slipstream may be routed to the Carbon Filter, where soluble MDEA degradation products, more commonly referred to as Heat Stable Salts (HSS), would be removed through adsorption into the carbon active sites. The operation of the Carbon Bed is important to controlling foaming and corrosion in the MDEA unit. Samples of the MDEA solution upstream and downstream of the Carbon Bed should be taken periodically, and the content of Heat Stable Salts should be determined and compared to previous samples. When the capacity of the carbon reaches saturation, inlet and outlet analyses will be indistinguishable. Before this occurs, the carbon should be replaced with fresh charge of activated carbon. The activated carbon in the Carbon Filter will become prematurely saturated with anti-foam constituents instead of the Heat Stable Salt constituents.

Downstream of the rich, lean filtration and on the quench water line to the regenerator, provisions for anti-foam injection are included and should be used only if required. Excess use of anti-foam should be avoided.

The cool, lean, and filtered MDEA solution is returned to the Lean MDEA line and the lean MDEA is routed to the Absorber on flow control valve. The lean MDEA will be routed to two different nozzle locations at the normal operation. A third nozzle connection and a new bed will be considered for future expansion.

The collected drain will be routed to the sump, which is a concrete sump under ground. The sump pump is designed to transfer the liquid from the sump to the bottom of the MDEA absorber (or to the Surge Tank). The Filter is located downstream of the pump-out pump. Nitrogen blanketing prevents degradation of the MDEA by preventing oxygen to the sump.

Amine Tail Gas Treating Process Description

Tail gas from the contact condenser flows into the amine absorber where H_2S is preferentially absorbed by the amine solution. The amine solution reduces the H_2S content in the absorber overhead stream to less than 150 ppmv. The amine solution is a 50-wt% solution of MDEA in water. A packed column is used to minimize the pressure drop through the absorber.

The amine absorber overhead K.O. drum, integral with the absorber column, provides separation of entrained amine and wash water from the overhead gas. Wash water circulated by the wash water pump is injected into the absorber overhead line upstream of the K.O. drum. Fresh makeup condensate is added to the circulating wash water loop and a small purge stream is continuously withdrawn to keep the concentration of amine in the wash water relatively low to minimize amine losses. Tail gas absorber overhead gas flows to the thermal oxidizer for oxidation and release to the atmosphere.

Rich amine is pumped from the bottom of the amine absorber to the amine absorber as a semi-lean solution to the amine absorber. Lean amine is provided from the common regenerator in the amine unit to the TGU absorber.

Incinerator

The gases exiting the amine Absorbers are routed to the Incinerator. Fuel gas is burned with excess air to a sufficient temperature to heat the tail gas from the tail gas unit.

The current design represents a natural draft Incinerator.

The Thermal Oxidizer is designed to oxidize the residual amount of Hydrogen Sulfide (H_2S) and other sulfur compounds in the tail gas to Sulfur Dioxide (SO_2), and raise the temperature of the waste gas stream from the TGTU to about 1200°F (648 °C). Higher temperature has to be achieved if CO destruction required. Fuel gas and air are combusted in the Thermal Oxidizer and then the waste gas stream (primarily CO_2 and N_2) is added so that any sulfur compounds are completely oxidized and mixed. The temperature is normally sufficient to oxidize the residual H_2S and other sulfur components to SO_2, while minimizing SO_3 formation. The hot combustion gas exits the facility through the Stack.

The Stack is equipped with an Oxygen/CO/SO_2 analyzer, to monitor the excess Oxygen in the Stack gas along with an analyzer, to monitor the Sulfur Dioxide (SO_2) content to the Stack gas. In addition to the analyzers, the Stack is equipped with a thermocouple, to monitor the Stack temperature.

2. TEG Dehydration Process Description

The Sales gas from the Amine Unit is sent to the Dehydration Unit, for which we have slected TEG as the drying solvent. There are other dehydration processes that could be selected.

The Sales Gas from the each amine Absorber in the acid gas removal is routed to the Dehydration units. The Dehydration TEG Contactor is an absorption column with structure packing. The wet gas is fed to the bottom of the column and the lean TEG is fed to the top of the column. The TEG absorbs water from the wet gas as the two streams are contacted counter-currently in the column. The rich TEG flows to the bottom and is sent to the sales gas dehydration feed/OVHD exchanger to heat the solution prior to entering the Sales gas dehydration TEG flash drum. The rich TEG solution from the flash drum is filtered in the Sales Gas dehydration rich filter.

The rich TEG solution is routed to the TEG Regeneration Unit, which is a package unit through the dehydration lean / rich exchanger. The dried gas exits the top of the column and is sent to the Sales gas dehydration/dry gas/lean solution exchanger, to cool the stripper OVHD gas and heat the dry gas, before it is sent to the sales gas compression.

The basic components in the TEG Regeneration Package are as follows:

Sales Gas Dehydration Regeneration Column is where the water in the rich TEG is stripped off. The Regenerator includes a tray section in part A and a packed column in part B.

Sales gas Dehydration Regeneration Reboiler is a bath type Reboiler. It supplies the heat for stripping via Glycol. It is located directly under the Regenerator Column.

Sales Gas Dehydration TEG Surge Drum directly receives the lean TEG from the Reboiler.

The Sales Gas dehydration regeneration is operated with the dry fuel gas as a strip gas. The fuel gas is introduced to the reboiler through the fuel gas filter. The overhead vapor from the Regenerator Column is cooled by heating the Rich TEG solution with the Sales Gas dehydration TEG Feed/OVHD Exchanger and then is routed to the Sales Gas dehydration Regeneration OVHD KO. Drum to separate the condensate water. The separated gas then is sent to the Sales Gas Dehydration TEG Vent compressor. Condensate water separated from the KO drum is pumped to the sales Gas TEG regeneration. The compressed gas is cooled in the Sales gas Dehydration TEG OVHD Cooler. The condensed water is separated in the Sales Gas Dehydration KO drum and the gas is routed to the CO_2 compression unit.

The lean TEG from the sales gas Dehydration regeneration section is sent to the Sales Gas dehydration Lean/rich Exchanger to exchange the heat to the rich solution. The lean TEG solution is further cooled in the Sales Gas dehydration Dry gas/Lean solution exchanger.

The lean TEG solution is filtered in the Sales Gas Dehydration Particulate filter. A slipstream from the lean TEG is sent to the Dehydration Charcoal filter and the guard filter respectively. The lean TEG solution is then pumped to the sales Gas Dehydration TEG contactor.

The TEG make-up will be pumped through Sales Gas dehydration TEG make-up pump and the Sales Gas Dehydration TEG sump filter to the Rich TEG solution prior entering the TEG rich flash drum.

A common TEG sump will serve both the Sales Gas dehydration and the CO_2 dehydration units to collect the TEG drainage. The solution from the TEG sump is pumped by the Sales Gas Dehydration TEG sump pump, and will be routed to the TEG rich flash drum joining the TEG make-up.

For Case 2 application, the following are the typical feed gas compositions and the product specification for natural gas application in the gas plant.

Component	Composition (% mol)
He	0.01
H_2	0.02
N_2	0.552
CO_2	8.63(2)
H_2S	14.14(1)
CH_4	76.52
C_2H_6	0.12
C_3H_8	0.008
Organic S	<150 mg/Nm^3
Total	100
Critical Temperature, K	227.65
Critical Pressure, Mpa (a)	5.496
Temperature, °C	25~30
Pressure, Mpa (a)	8.3

It was Assume: H_2S content: 13-18%, CO_2 content: 8-11%, and Sour feed gas also contains organic sulfur compounds: content of organic sulfur compounds <150mg/m3. Sour feed natural gas is saturated with water and also contains some solid particles (maximum average of 0.2 mg / m3). The treated natural gas will contain less than 6mg/Nm^3(20C, 1.013×10^{5}Pa) of H2S, less than 3vol % of CO2 and less than 200mg/Nm^3(20℃, 1.013×10^{5}Pa) of sulfide.

The typical specification of the water dew point of treated natural gas will be -10°C. The Sulfur Recovery Unit shall recover essentially minimum 99.9 wt. percent of the sulfur contained in the feedstock. The vent gas leaving the absorber of the Tail gas treating section shall contains no more than 150 ppmv of sulfide. The liquid sulfur shall contain no more than 10 ppmv of H_2S.

Refer to Block Flow diagram and the process flow diagram for case 2 study.

Case -3 – WorleyParsons experience on LNG application indicates using activated MDEA is a very cost effective solvent to meet pipeline specifications and followed by dehydration unit to meet the water specifications. A typical LNG feed composition is provided below.

LNG Typical Feed Gas Composition

Component		Composition (mol %)
CO2		12.76
N2		0.59
CH4		78.86
C2H6		5.50
C3H8		1.92
n-C4		0.18
i-C4		0.12
C5		0.04
C6		0.01
C7		0.00
C8		0.00
C9		0.00
H2S		0.01
Total		100
PROPERTIES		
Temperature	C	60
Pressure	Bara	50

References:

Rameshni, M. “State of the Art in Gas Treating”, presented at British Suphur, 2000, San Francisco, CA, USA.

BP Boqueron is an Enhanced Oil Recovery (EOR) project at an existing field located in eastern Venezuela.

WorleyParsons was awarded the project management and construction management services contract by the Saudi Arabian Oil Company (Saudi Aramco) for the Hawiyah Gas Development Project.

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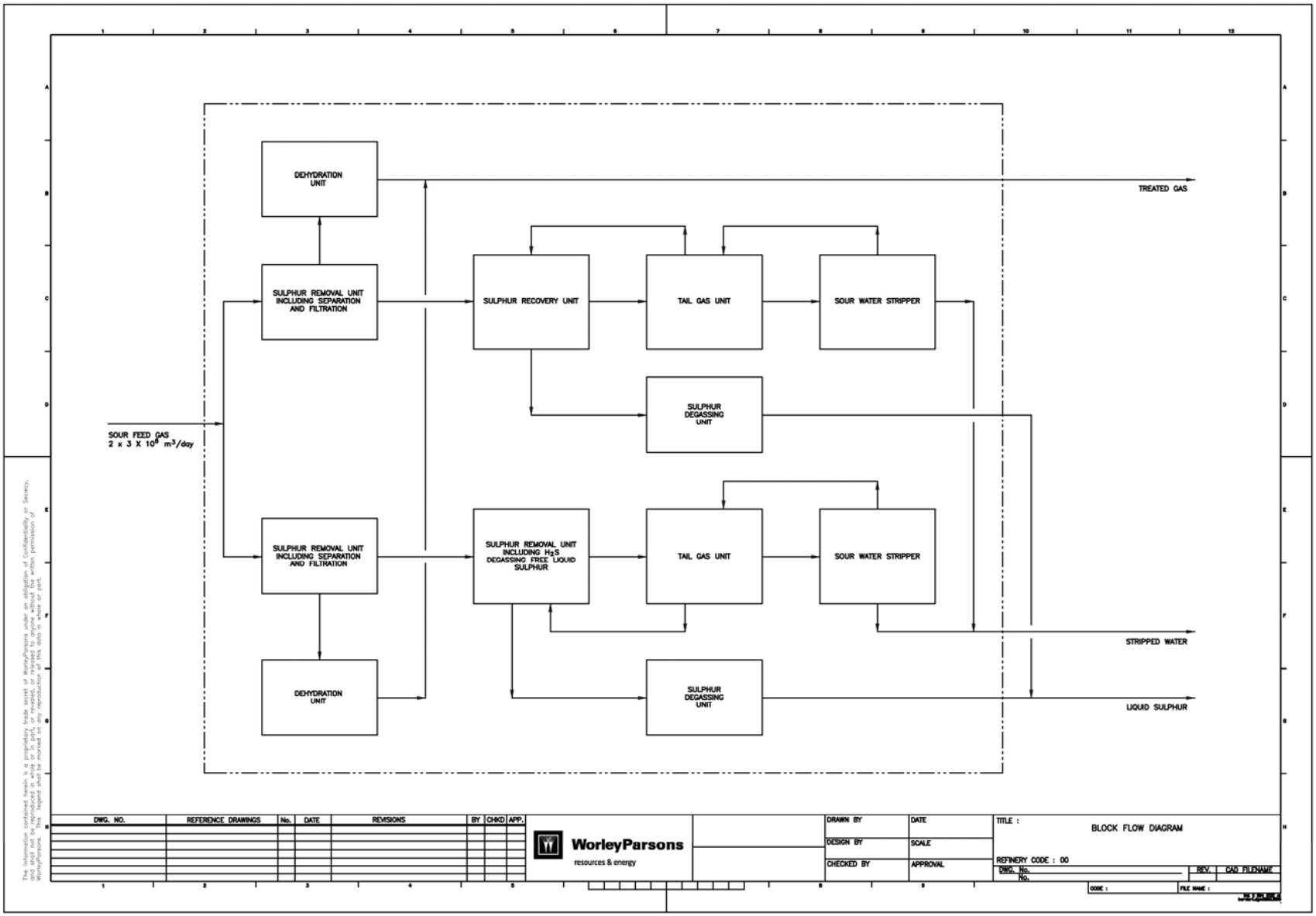

WorleyParsons

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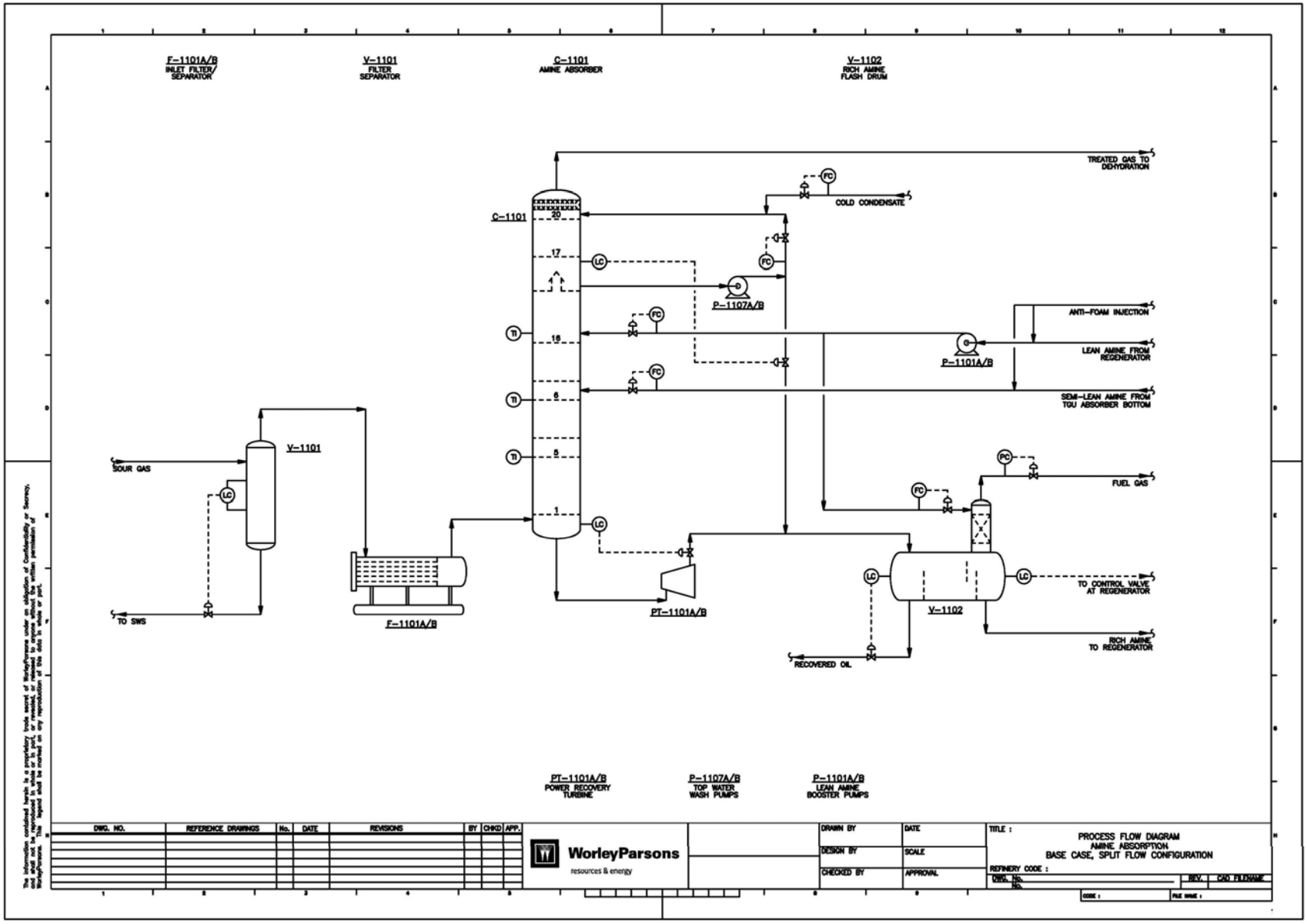

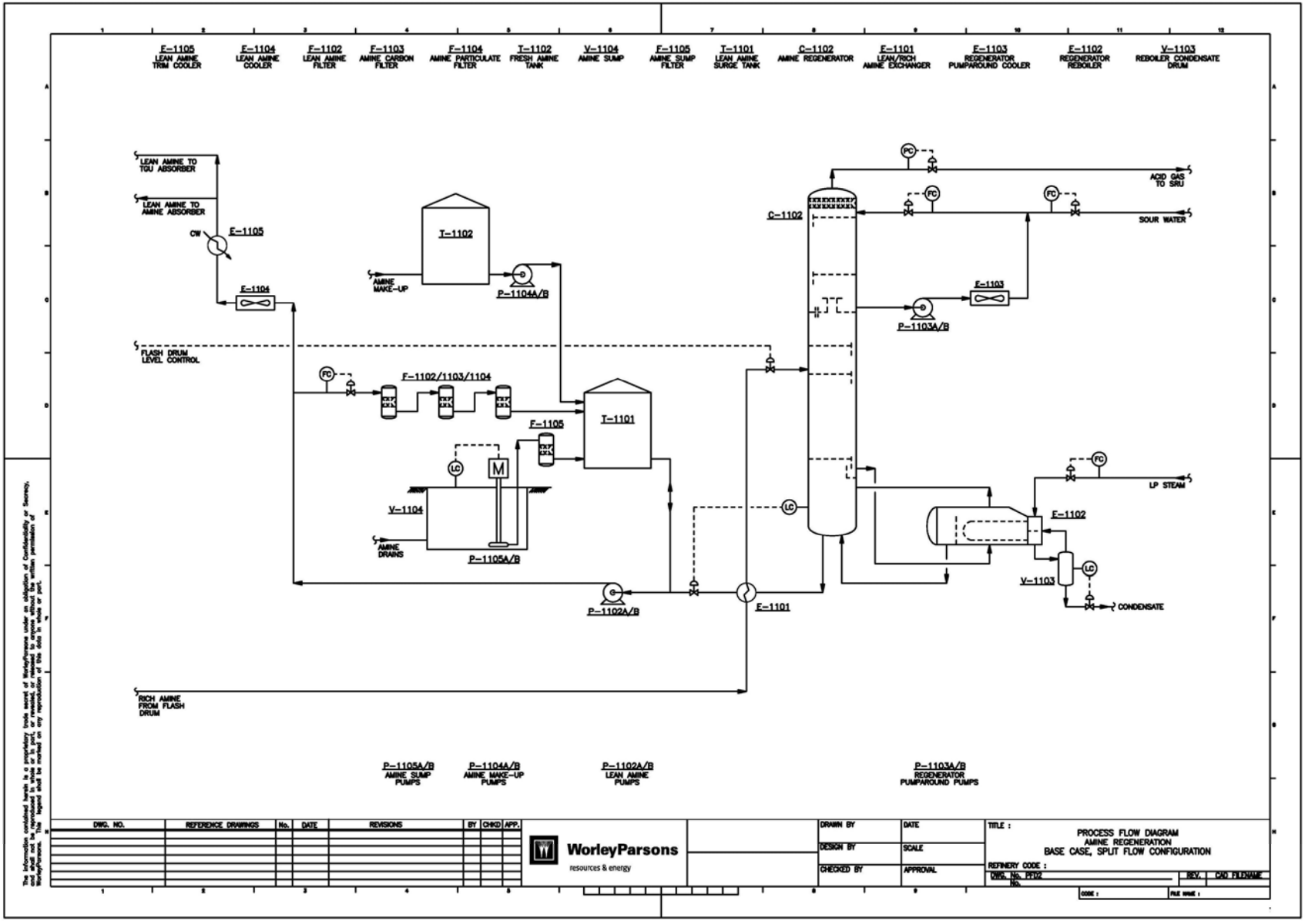
E-1105 LEAN AMINE TRIM COOLER
E-1104 LEAN AMINE COOLER
E-1102 LEAN AMINE FILTER
E-1103 AMINE CARBON FILTER
E-1104 AMINE PARTICULATE FILTER
T-1102 FRESH AMINE TANK
V-1104 AMINE SUMP
E-1105 AMINE SUMP FILTER
T-1101 LEAN AMINE SURGE TANK
C-1102 AMINE REGENERATOR
E-1101 LEAN/RICH AMINE EXCHANGER
E-1103 REGENERATOR PUMPAROUND COOLER
E-1102 REGENERATOR REBOILER
V-1103 REBOILER CONDENSATE DRUM
LEAN AMINE TO TGU ABSORBER
LEAN AMINE TO AMINE ABSORBER
CW
E-1105
E-1104
T-1102
AMINE MAKE-UP
P-1104A/B
FLASH DRUM LEVEL CONTROL
F-1102/1103/1104
F-1105
T-1101
V-1104
AMINE DRAINS
P-1105A/B
P-1102A/B
E-1101
C-1102
ACID GAS TO SRU
SOUR WATER
E-1103
P-1103A/B
LP STEAM
E-1102
V-1103
CONDENSATE
RICH AMINE FROM FLASH DRUM
P-1105A/B AMINE SUMP PUMPS
P-1104A/B AMINE MAKE-UP PUMPS
P-1102A/B LEAN AMINE PUMPS
P-1103A/B REGENERATOR PUMPAROUND PUMPS
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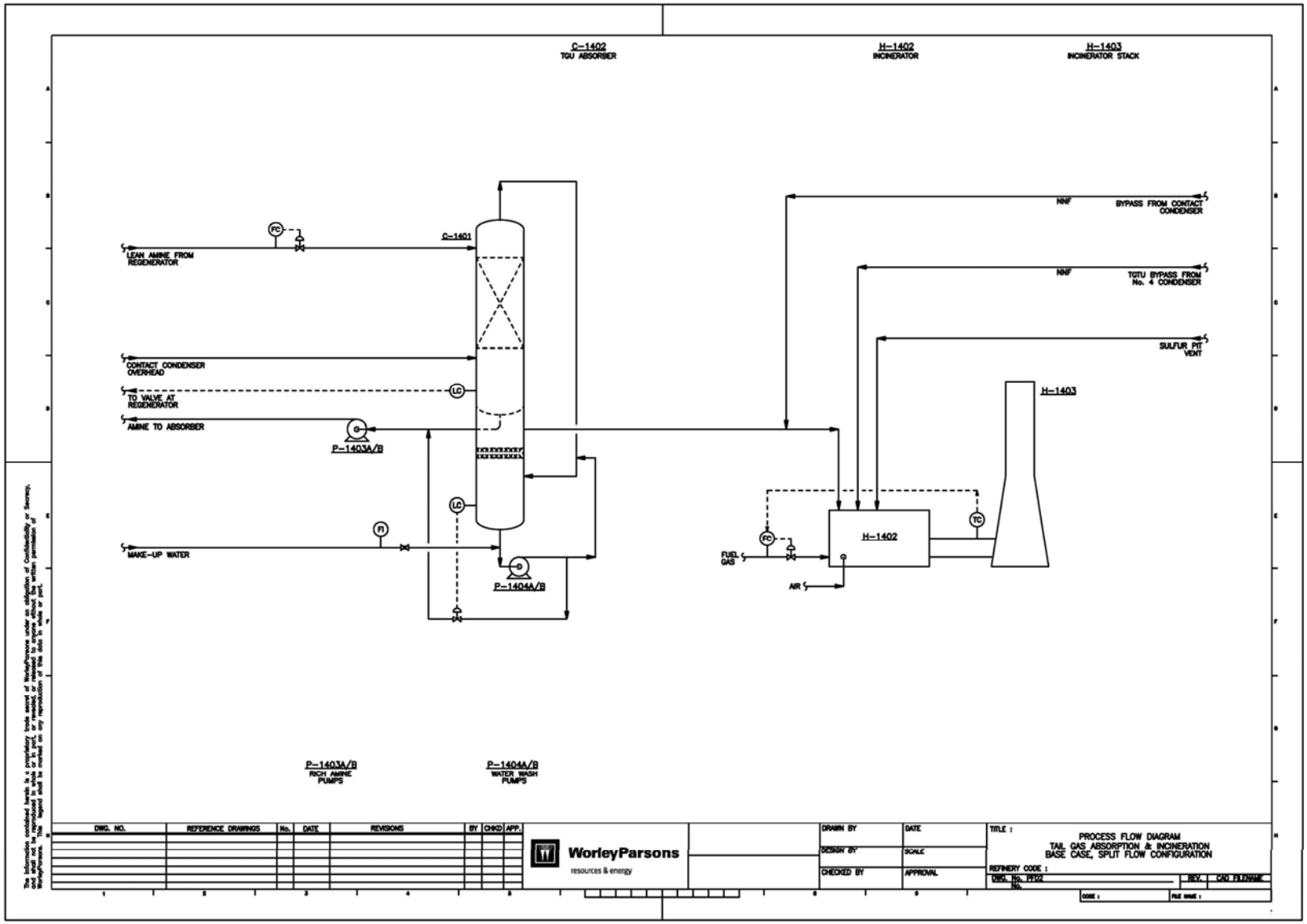

SANTA BARBARA COUNTY FIRE DEPARTMENT

Public Information Office

News Release

Date: January 23, 2008 2:30 PM
To: All News Media, FOR IMMEDIATE RELEASE
Subject: Popco Onshore Gas Plant Spill
Contact: Captain Eli Iskow, 805 689-0599

INCIDENT UPDATE:

According to plant officials, at approximately 11:45 PM Tuesday evening, January 22, a worker noticed a leak coming from a flange on a gas processing exchanger unit and immediately initiated the plant shut-down procedure. They state that this initial action probably helped to minimize the gallons of product spilled. At the same time, other workers closed a weir gate in Corral Creek to try to contain the contaminated water. That containment procedure was overwhelmed by the amount of creek runoff plus the water soluble nature of the product, Sulfolane W, causing some amount and concentration to travel down creek into the ocean. A plant worker notified the County Dispatch Center at 12:12 AM, approximately 27 minutes after the incident began. Workers instituted their safety plan and containment measures in an effort to mitigate danger and possible damage prior to making the initial notification. Plant officials have downgraded the estimated number of gallons spilled from 420 to 100.

Investigation is underway by the Santa Barbara County Fire Department Hazardous Materials Unit, County Office of Emergency Services, SB County Energy Division, California Fish and Game, State Division of Oil and Gas, and the US Coast Guard. There are no current or projected threats to the public or plant employees. There were no injuries to firefighters or civilians. General Plant operations have restarted after isolating the process that experienced the flange gasket failure causing the leak.

LIFE SAFETY MESSAGE: *REPORT SUSPICIOUS MATERIALS TO 911

CONTACT: PIO
NEWSLINE: 681-5546
PAGER: 692-7660
CELL: 689-0599

# # #

Date: January 23, 2008 2:30 AM
To: All News Media, FOR IMMEDIATE RELEASE
Subject: Popco Onshore Gas Plant Spill
Contact: Captain Eli Iskow, 805 689-0599

There has been a leak of a liquid material called Sulfolane into Las Flores Creek (near El Capitan Canyon) at the Popco Oil and Gas facility. According to facility safety personnel there is no current threat to employees or the public. The Popco plant is owned by Exxon. Santa Barbara County Fire Engine Company 18 is on-scene and our on-call Hazardous Materials Specialist is enroute. Other appropriate County, State and Federal agencies,

including County Petroleum Division, California Department of Fish and Game, US Coast Guard, State Division of Oil and Gas, etc., have been or are currently being notified. Apparently there was a mechanical failure of a gasket on an extractor unit causing the leak of an estimated 10 barrels (420 gallons) of the material into the creek. Las Flores Creek is currently running because of the rain. It merges with Corral Creek and heads south to the ocean. The leak has been stopped and the situation at the facility is static. It has not been determined yet whether the material has traveled off the site itself into the ocean. Popco techs are sampling the creek south of the facility to determine levels in the water down-canyon.

Initial notification was made to County Dispatch by a Popco employee at 12:12am. The suspect material has a low health toxicity level as well as a low flammability level. It is used in the process of stripping Hydrogen Sulfide gas (H2S) from other gasses. There have been no H2S alarm activations at the site and no levels detected. I will update this information for you after our HMU (Hazardous Materials Unit) Specialist has made a determination or if anything significant develops in the interim.

LIFE SAFETY MESSAGE: *REPORT SUSPICIOUS MATERIALS TO 911

CONTACT: PIO
NEWSLINE: 681-5546
CELL: 689-0599

# # #

Santa Barbara County Fire Department Photos

Weir gates on Corral Creek that attempted to contain contaminated water

Gas processing exchanger units

Location of failed flange gasket that caused leak

Reprinted from

JOURNAL OF

Contaminant Hydrology

Journal of Contaminant Hydrology 32 (1998) 159–176

Sorption of sulfolane and diisopropanolamine by soils, clays and aquifer materials

Sheila M. Luther [a,1], Marvin J. Dudas [a,*], Phillip M. Fedorak [b,2]

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Contaminant Hydrology

Scope of the journal

The primary purpose of this international journal is to publish scientific articles pertaining to the contamination of groundwater. Emphasis is placed on investigations of the physical, chemical and biological processes that influence the behaviour of organic and inorganic contaminants in both the unsaturated (vadose) and the saturated zones. Articles on contamination of surface water are not included in this journal unless they specifically deal with the linkage between surface water and groundwater. This journal will strive to provide a common forum for publication of articles from a diverse group of scientists involved in investigations of groundwater contamination.

The scope of this journal will cover diverse topics including: experimental investigations of contaminant sorption, diffusion, transformations, volatilization and transport in the unsaturated and the saturated zones; characterization of soil and aquifer properties, but only as they influence contaminant behaviour; development and testing of mathematical models of contaminant behaviour; innovative techniques for restoration of contaminated sites; and development of new tools or techniques for monitoring the extent of soil and groundwater contamination.

ELSEVIER

Journal of Contaminant Hydrology 32 (1998) 159–176

JOURNAL OF
Contaminant
Hydrology

Sorption of sulfolane and diisopropanolamine by soils, clays and aquifer materials

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Received 6 May 1997; revised 3 November 1997; accepted 1 December 1997

Abstract

The natural gas sweetening chemicals, sulfolane and diisopropanolamine (DIPA), are highly water soluble and have leached into the ground water from landfills and spills at some sour gas processing plant sites in western Canada. This paper reports on the results of batch equilibration studies designed to evaluate sulfolane and DIPA sorption parameters, which are of relevance to modeling fate and behavior of these compounds in the saturated zone. The sorbents included aquifer materials from three plant sites, reference montmorillonite and kaolinite, and six soils of various clay and organic matter contents. The DIPA sorption isotherms were curvilinear, the slope decreasing with increasing concentration. DIPA adsorption by montmorillonite decreased as the solution concentration of K_2SO_4 increased, consistent with a cation-exchange reaction. A decrease in pH from 8.3 to 6.8 produced a slight increase in DIPA adsorption by montmorillonite. X-ray analysis of DIPA-saturated montmorillonite showed that DIPA enters the interlayer space of the mineral. The sulfolane sorption isotherms were linear and sulfolane sorption by the aquifer materials was very low ($K_d < 1$ l/kg), whereas DIPA uptake was somewhat higher ($K_d < 4$ l/kg). Both compounds were sorbed more by clay minerals than by organic matter and cation exchange capacity was a reasonable predictor of the sorption of sulfolane and DIPA by soils and aquifer materials with low contents of organic C (< 1 g/100 g). DIPA desorption from montmorillonite was low relative to adsorption, and some hysteresis was found for some aquifer

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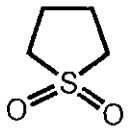
materials in the desorption of DIPA. Based on estimates of retardation, sulfolane was predicted to move farther than DIPA under the conditions at plant sites.

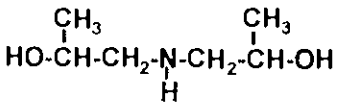
Keywords: Desorption; Diisopropanolamine; Ground water; Soils; Sorption; Sulfolane

1. Introduction

Some western Canadian natural gas supplies contain up to 35% hydrogen sulfide. A mixture of sulfolane and the alkanolamine diisopropanolamine (DIPA) is used in the Shell Sulfinol™ process to remove hydrogen sulfide from the gaseous hydrocarbons (Goar, 1971; Taylor et al., 1991). Landfills, evaporation ponds and spills at sour gas plants have introduced sulfolane and DIPA into soils, and because of their high water solubility, these two compounds are now ground water contaminants. However, no information on the sorption and desorption properties of sulfolane and DIPA in soils is available in the literature. Thus this study was done to provide information required to predict the transport of these compounds in the subsurface.



Sulfolane



DIPA = Diisopropanolamine

Attenuation of organic compounds through sorption by soil components exerts a major control on the transport and fate of substances released into the terrestrial environment. Sorption mechanisms may include partitioning, ion exchange, and specific and nonspecific adsorption reactions (Chiou, 1989). Partition uptake by native soil organic matter usually describes the interaction of nonionic organic chemicals with soil. The distribution coefficient (K_d) derived from linear isotherms has been applied to describe this sorption behavior. Determining a carbon-normalized partition coefficient (K_{oc}) ($K_{oc} = K_d/f_{oc}$, the fraction of soil organic C) provides a way of adjusting the distribution coefficient to account for differences in sorptive behavior among soils of differing content of native soil organic matter.

Unlike hydrophobic nonionic organic chemicals, the high water solubility and polar nature of DIPA and sulfolane indicated that sorption reactions were likely to include not only partitioning into soil organic matter but other mechanisms involving hydrogen bonding and ionic interactions with charged soil colloids (clay minerals and oxyhydroxides of Fe, Mn, and Al). Some researchers have related sorption parameters of polar and N-containing compounds to clay content or specifically montmorillonite content in addition to organic matter content (Means et al., 1982; Rebhun et al., 1992). The inclusion of total surface area in formulations has been recommended for predicting sorption in cases where organic C contents are so low that sorption to inorganic surfaces is significant in comparison to sorption by organic material (American Society for

Testing Materials, 1995). Cation exchange capacity (CEC) of clay minerals is known to be a factor governing the sorptive capacity for the cationic, N-containing herbicides, diquat and paraquat, which adsorb to a maximum equal to the CEC (Weber and Weed, 1968). Pennington and Patrick (1990) found that the K_d for sorption of 2,4,6-trinitrotoluene was most highly correlated with extractable Fe, CEC, and clay content. DIPA is a weak base with a pK_a of 8.88 (Kim et al., 1987). Thus at the neutral pH of ground water at plant sites, most of the DIPA is protonated, yielding a positively charged molecule. Therefore, DIPA was considered to enter into exchange reactions with metal cations on the surface of clays, a process that is well documented for other protonated amines (Mortland, 1986).

In cases where the subsoil content of native organic matter is low, as would be the case for the gas-plant sites of interest, adsorption by clays may be a significant mechanism controlling the fate of sulfolane and DIPA. To test this hypothesis, we studied sulfolane and DIPA sorption by aquifer materials from three gas-processing plant sites, soils with various clay and organic C contents, and reference clays. We also tested the hypothesis that the sorption of the compounds by soils, clays, and geological materials with low organic matter content would be proportional to the CEC of the sorbent.

To elucidate the interaction of DIPA with clay, adsorption by reference montmorillonite was studied at different concentrations of background electrolyte and at different pH values. A study using X-ray diffraction was also performed to determine whether DIPA penetrates the interlayer space of montmorillonite.

Desorption of DIPA from montmorillonite and from aquifer materials was also examined, because complete sorption reversibility is often assumed in transport modeling (Freeze and Cherry, 1979). In addition, some preliminary estimates of the potential for DIPA and sulfolane transport in the subsurface were made using the sorption parameters determined for the aquifer materials.

2. Materials and methods

2.1. Sample collection and characterization

A sample of aquifer material from each of three sour gas plant sites was included in this study. The samples were from areas outside or near the edge of contaminant plumes, and they contained no aqueous extractable sulfolane or DIPA. Site 1 material, a weathered sandstone from a 2- to 3-m depth, and site 2 material, a glacial till from a 3- to 4-m depth, were from south western Alberta. Site 3 material, a weathered shale/sandstone from a 9-m depth, was from east central British Columbia.

The reference montmorillonite and kaolinite, included in the study, are clay minerals commonly found in soils in Alberta (Dudas and Pawluk, 1982). The montmorillonite was supplied by the Clay Minerals Society and is designated as STx-1, a white, Ca-saturated montmorillonite from Gonzales County, TX. The kaolinite was supplied by Ward's Natural Science Establishment and is designated as Kaolinite No. 4, from Oneal

Pit, Macon, GA. These two minerals represent a highly reactive clay with a large surface area and high CEC (montmorillonite) and one that has a low surface area and CEC (kaolinite).

Sorption studies were also conducted with six surface soils collected near Edmonton, Alberta. Five of the six soils were selected to have a wide range of clay content and low levels of organic C. They were included in the study to provide the data base for the formulation of relationships between soil CEC and sorption properties. The sixth soil is a black surface soil, designated as the humus-rich soil. It was included in the study to determine if organic matter contributes to the sorption of sulfolane and/or DIPA.

Prior to starting experimental work with the soils and aquifer materials, they were air-dried and sieved to less than 2-mm diameter (10 mesh). Each of the samples was fully homogenized and then a subsample was ground to pass through a 0.1-mm sieve (140 mesh) for the sorption studies. All results were expressed on an oven-dry weight basis (105°C, 24 h).

The aquifer materials and the humus-rich soil were characterized for clay content by sedimentation (Carter, 1993); inorganic C by titration (Bundy and Bremner, 1972); total C by Leco CR12 induction furnace (Tabatai and Bremner, 1970); and organic C by subtraction of inorganic from total C. The CEC of all sorbents was determined at pH 7.0 using ammonium as the index ion (McKeague, 1978). At least three replicates were included in these analyses.

After the completion of particle-size analysis, the remainder of the clay fraction was separated by sedimentation, to be used for clay mineralogical analyses. Clay mineralogy of one of the replicates of the humus-rich soil and the aquifer materials was determined using a set of seven clay slide pretreatments and X-ray diffraction (XRD) conditions (Dudas and Pawluk, 1982).

2.2. Chemicals

The DIPA used in these studies was the highest purity that was commercially available. It was purchased from TCI America (Portland, OR) and the supplier determined its purity to be 99.7% by titration. DIPA, which is also called bis(2-hydroxypropyl)amine, has two chiral carbons and a plane of symmetry. Thus, there are three stereoisomers; two of them are enantiomers and one is a meso compound. The supplier stated that the preparation also contained a contaminant 2-hydroxypropyl-2′-hydroxy-1′-methylethylamine, which is an isomer of DIPA. Gas chromatographic analysis by TCI showed that two resolved stereoisomer peaks of DIPA comprised 43.9 and 43.4% of the mixture, and two peaks corresponding to the contaminant isomers comprised 3.3 and 3.0% of the mixture. The sulfolane was of 99% purity from Aldrich (Milwaukee, WI).

2.3. DIPA and sulfolane analysis

Gas chromatography (GC) methods, using direct aqueous injections (2 μL) without pH adjustment, were used for DIPA and sulfolane analysis. A Varian 3600 GC, equipped with a 15-m nonpolar, megabore, thick-filmed capillary column which had

been base-deactivated (Rtx-5 Amine from Restek; bonded and cross-linked 5% diphenyl–95% polysiloxane phase; 15 m, 0.53 mm internal diameter, 3 μm film thickness) connected to an N-selective detector, was used for DIPA analysis. A packed sleeve, containing base-deactivated glass wool (Restek) and 10% OV-1 on Chromosorb W-HP, was installed into the injection port. Helium was the carrier gas and the split flow was set to 5:1 with a column flow rate of 5 ml/min. The injector temperature was 220°C, the detector temperature was 300°C, and the temperature program was 120°C for 2 min, increasing by 12°C/min to 168°C, then held for 2 min. Under these conditions the detection limit was approximately 5 mg/l DIPA. Others have used similar direct aqueous injection GC methods, without pH adjustment, for the analyses of alkanolamines (Kennard and Meisen, 1983; Dawodu and Meisen, 1993; Shahi et al., 1994).

For sulfolane analysis we used a Hewlett-Packard 5700A gas chromatograph with a flame ionization detector. The instrument was fitted with a 6 ft $\times$ 1/8 in. (1.8 m $\times$ 0.32 cm) stainless-steel column packed with Tenax GC coated with 5% polyphenyl ether (6-ring). The injector and detector temperatures were at 250°C, the oven temperature was at 200°C, and N_2 was the carrier gas with a flow rate of 30 ml/min. The detection limit was 5 mg/l sulfolane.

2.4. Sorption isotherms

Sorption was studied using batch equilibration as outlined by the American Society for Testing Materials (1995). Solid-to-solution ratios were selected to obtain 20–80% of the material sorbed and varied from 1:0.9 to 1:18 (weight:volume). The glass vials with Teflon-lined lids were of various sizes from 4–17 ml. Sorption was studied by combining the sorbent with an aqueous solution containing a known concentration of the target compound and allowing for a 24-h equilibration. The air-dry sorbents were moistened overnight prior to exposure to the compound and glass beads were added to each vial to facilitate mixing. During the equilibration, the samples were mixed end-over-end at 16 rpm and 22°C. Sampling involved centrifuging the vials at 800 $\times$ g for 30 min, then the supernatant was transferred into plastic 1.5-ml centrifugable tubes and these samples were stored frozen at -20°C. In a few experiments, the centrifuge speed for the initial sampling was lowered to 460 $\times$ g and the time was increased to I h. Prior to GC analysis, the samples were thawed and centrifuged at 16,000 $\times$ g for 14 min. The amount of compound taken up by the sorbent was determined from the difference between the equilibrium solution concentration of samples and controls that contained no sorbent.

Sorption experiments were conducted using a background electrolyte, 0.01 M K_2SO_4, to standardize the ionic strength at 0.03 M (Xing et al., 1994) and 200 mg $HgCl_2$/l was used to eliminate microbial activity (Wolf et al., 1989). The pH was buffered near 8.0 by carbonate indigenous to the soils and aquifer materials or through the addition of $CaCO_3$ (4 mg) to those samples lacking indigenous carbonates. DIPA stock solutions were adjusted to pH 8.0 with H_2SO_4. Experiments included two to four replicates of each concentration for both samples and controls. The pH (combination electrode, Cole Palmer) and electrical conductivity (EC) (conductivity bridge, YSI) of the supernatant solution were monitored after each experiment.

We did not attempt to determine the maximum amount of DIPA or sulfolane that could be sorbed but rather our measurements apply to the contaminant concentration ranges and levels of background electrolyte expected in ground water. The uptake of DIPA and sulfolane in the sorption isotherm experiments was less than 15% of the CEC and so no predictions about maximum sorption were made. For the sulfolane–kaolinite experiment and for other sulfolane sorption experiments with K_d values of less than 0.1 l/kg, sorption was studied at only one starting concentration of contaminant (500 mg/l) because of the low sorption observed. The K_d values below 0.1 l/kg were of limited accuracy but they were retained for the purpose of estimating the relationship between K_d and CEC.

2.5. DIPA adsorption by montmorillonite at two pH levels

Adsorption of DIPA by montmorillonite at two different pH levels was studied to cover the pH values typically observed in ground waters at plant sites. Four milligrams of $CaCO_3$ was used to buffer the pH near 8.0 and H_2SO_4 was added to the second treatment to lower the pH below 7.0. Experimental controls were prepared in the same way but in the absence of soil.

2.6. DIPA adsorption by montmorillonite at three concentrations of background electrolyte

Isotherms for DIPA adsorption by montmorillonite were determined with three different concentrations of K_2SO_4: 0.001, 0.01 and 0.1 M. All other aspects of the experimental design were the same as that described for other isotherms (Section 2.4). We selected K_2SO_4 as a background electrolyte because both K^+ and SO_4^{2-} are major ions in ground waters in western Canada. Calcium chloride, a commonly used background electrolyte (Xing et al., 1994), interfered with DIPA analysis and $CaSO_4$ could not be used because of the limited solubility of gypsum ($CaSO_4 \cdot 2H_2O$).

2.7. X-ray diffraction analysis of DIPA-saturated montmorillonite

Two slurry samples of montmorillonite (1 g) and distilled deionized water (5 ml) were mixed overnight in 50 ml Nalgene centrifuge tubes. Twenty millilitres of distilled deionized water was then added to the control tube (Ca^{2+}-saturated) and the other was spiked with a DIPA stock solution brought to pH 8 by the addition of H_2SO_4 (DIPA-saturated). The DIPA added was 15 times greater than the moles of negatively charged exchange sites present in the vial (0.012 M). The slurries were mixed end-over-end at 16 rpm for 24 h and then centrifuged at $27{,}000 \times g$ for 20 min. The supernatant was discarded and moist clay slides were prepared of each sample. These were analyzed by XRD immediately at 54% relative humidity (RH), and then they were oven-dried for 24 h at 105°C and analyzed again by XRD at 0% RH. This entire experiment was performed a second time to verify the results.

2.8. DIPA desorption from montmorillonite and from aquifer materials

The experimental design of the desorption experiment was similar to that for other sorption isotherms. However, exactly 10 ml of the total 16.25-ml solution volume were removed during supernatant sampling. The aliquot was replaced with 10 ml of solution containing 0.01 M K_2SO_4 and 200 mg $HgCl_2$/l and brought to pH 7.0 by adding a small amount of 2 M KOH; this step was required to maintain a pH near neutral in the batch equilibrations. The pellet was resuspended using a vortex and the tubes were mixed end-over-end for another 24 h, which was followed by centrifugation and supernatant sampling. This desorption procedure was repeated a total of three times. Similar desorption experiments were conducted for the aquifer materials, using only one starting concentration of DIPA, 500 mg/l.

2.9. Data analysis and interpretation

All regressions and comparisons were performed using the SAS statistical software for personal computers. The fit of the Freundlich and the Langmuir models to the DIPA sorption data was investigated by testing the significance of the decrease in residual sum of squares (RSS) by each model. Significance was determined by calculating the F statistic, obtained by dividing the difference of the RSS of the two models by the residual mean square (RMS) of the model with the lowest RMS (Robinson, 1985). The significance of the difference between different isotherms was tested by calculating an F statistic as outlined by Janzen et al. (1996). For comparisons between sorption and desorption, the processes were described by a linear model with a Y intercept which were compared using the GLM SAS procedure.

3. Results and discussion

3.1. Characteristics of aquifer materials and soils

The aquifer materials had a wide range of clay contents and CECs and they contained low levels of organic C (Table 1). The organic C content of the humus-rich soil was

Table 1
Clay and organic C content, and CEC of samples from the three sour gas plant sites, a humus-rich soil and reference montmorillonite

Sorbent	Clay (g/100 g)	Organic C (g/100 g)	CEC (cmol(+)/kg)
Site 1	8.3 (0.4)	0.2 (0.01)	3.7 (0.08)
Site 2	27 (0.7)	0.4 (0.01)	14 (0.2)
Site 3	8.0 (0.4)	0.9 (0.03)	4.3 (0.02)
Humus-rich soil	16 (0.7)	3.6 (0.01)	25 (0.5)
Kaolinite	100	< 0.01	10 (0.3)
Montmorillonite	100	< 0.01	81 (0.9)

Mean of three or more replicates, standard deviation provided in brackets.

several times higher than that of the other samples. Our measured CEC of 81 cmol(+)/kg for STx-1 montmorillonite was comparable to the levels determined by other laboratories for this reference clay (mean: 84.4; range: 80–88 cmol(+)/kg) (Van Olphen and Fripiat, 1979). No inorganic C was detected in the humus-rich soil and no C was detected in the reference clays. The soils numbered 4 through 8 had a wide range of CECs, covering the range typically found in soils and surficial materials of aquifers in western Canada (Table 2). All but Soil 6 contained carbonates based on the presence of effervescence following the addition of a few drops of dilute HCl.

The site 2 and the humus-rich samples had a clay mineralogy typical of Alberta soils (Dudas and Pawluk, 1982), with montmorillonite being the dominant clay mineral followed by mica and kaolinite. A similar clay mineral assemblage is likely to occur in the soils 4 through 8. Based on the XRD analysis, the site 1 clay separate was made up of kaolinite, montmorillonite and mica. The CEC of the site 1 sample indicated that

Table 2
Results of experiments of DIPA and sulfolane sorption by montmorillonite, kaolinite, aquifer materials, and surface soils

Test compound	Sorbent	Treatment	CEC (cmol (+)/kg)	Mean pH	Mean EC (dS/m)	K_d (l/kg)	R^2
DIPA	Montmorillonite[a]	–	81 (0.9)	8.0 (0.05)	2.4 (0.2)	32	0.985
	Montmorillonite[b]	0.001 M	81 (0.9)	8.0 (0.2)	0.90 (0.2)	43	0.963
	Montmorillonite[a,b]	0.01 M	81 (0.9)	8.1 (0.1)	2.4 (0.2)	32	0.938
	Montmorillonite[b]	0.1 M	81 (0.9)	8.1 (0.05)	13 (0.4)	16	0.990
	Montmorillonite[c]	pH = 6.8	81 (0.9)	6.8 (0.2)	2.6 (0.2)	42	0.897
	Montmorillonite[a,c]	pH = 8.3	81 (0.9)	8.3 (0.2)	2.6 (0.2)	36	0.936
	Kaolinite	–	10 (0.3)	8.1 (0.2)	2.4 (0.1)	3.5	0.980
	Humus-rich soil	–	25 (0.5)	7.0 (0.2)	2.4 (0.2)	2.0	0.982
	Site 1	–	3.7 (0.08)	7.9 (0.1)	2.2 (0.2)	0.54	0.967
	Site 2	–	14 (0.2)	7.7 (0.08)	2.3 (0.1)	3.2	0.877
	Site 3	–	4.3 (0.02)	8.3 (0.3)	2.1 (0.3)	1.1	0.992
	Soil 4	–	8.9 (0.5)	8.2 (0.1)	2.1 (0.2)	0.95	0.959
	Soil 5	–	20 (1)	8.2 (0.1)	2.4 (0.1)	4.0	0.986
	Soil 6	–	5.3 (0.3)	8.2 (0.2)	2.3 (0.2)	0.73	0.966
	Soil 7	–	24 (1.4)	8.0 (0.09)	2.2 (0.1)	3.7	0.946
	Soil 8	–	14 (0.2)	8.2 (0.07)	2.7 (0.1)	3.8	0.953
lfolane	Montmorillonite	–	81 (0.9)	7.6 (0.3)	2.3 (0.5)	0.94	0.988
	Kaolinite	–	10 (0.3)	7.8 (0.3)	2.1 (0.01)	0.18	ID
	Humus-rich soil	–	25 (0.5)	6.9 (0.09)	2.3 (0.01)	0.099	ID
	Site 1	–	3.7 (0.08)	7.9 (0.02)	2.1 (0.02)	0.008	ID
	Site 2	–	14 (0.2)	7.9 (0.2)	1.7 (0.01)	0.14	0.937
	Site 3	–	4.3 (0.02)	7.9 (0.03)	2.4 (0.04)	0.079	ID

tandard deviation provided in brackets.
ıll three experiments conducted under similar conditions, not statistically different using linear model ≤ 0.05), first data set from sorption experiment prior to desorption study (Fig. 4).
ıı three treatments significantly different from each other using linear model ($P \leq 0.005$) (Fig. 1).
wo treatments not significantly different using linear model ($P \leq 0.05$).
Standard treatment as described in Section 2.4.
, insufficient data.

montmorillonite made up approximately 40% of the clay mineral fraction (Table 1). The clay mineral assemblage of the site 3 sample, dominated by hydrous mica followed by chlorite and kaolinite, is typical of clays from several areas of British Columbia.

3.2. DIPA and sulfolane adsorption by montmorillonite

The results of the study of DIPA adsorption by montmorillonite in the presence of three different concentrations of background electrolyte are shown in Fig. 1 and the distribution of points over the entire concentration range studied is shown in Fig. 1a. For each of the three curves, this distribution was curvilinear and so the data were fit to a Langmuir model. A Langmuir plot models a system where there are a finite number of adsorption sites as is known to occur with clay mineral adsorption of positively charged species:

$$C_s = K_L b C_e / (1 + K_L C_e) \quad (1)$$

where K_L is a constant related to the binding energy, b is the maximum amount of solute that can be sorbed by the solid, C_s is the soil uptake quantity (mg/kg), and C_e is the equilibrium solution concentration (mg/l). Langmuir-type isotherms have previously been used to describe the uptake of alkylammonium ions by montmorillonite (Vansant and Uytterhoeven, 1972). The Freundlich isotherm, a commonly used curvilinear model, has less applicability to this system on a theoretical basis because it has no upper limit to the amount of solute that could be sorbed:

$$C_s = K_F C_e^{1/n} \quad (2)$$

where K_F and n are constants. For DIPA adsorption by montmorillonite in the presence 0.01 and 0.001 M K_2SO_4, the Langmuir and Freundlich models fit the data equally well

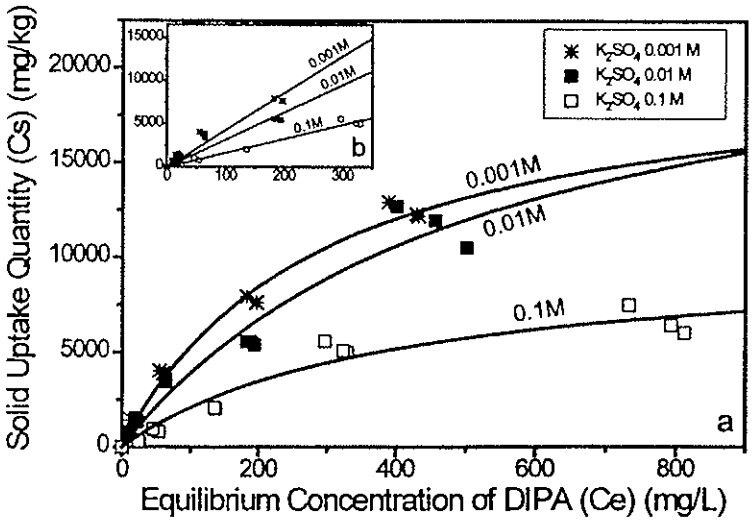


Fig. 1. DIPA sorption by montmorillonite in the presence of three different concentrations of K_2SO_4. Isotherms fitted to Langmuir model (a). Equilibrium concentrations less than 350 mg/l fitted to linear model (b). Each treatment is significantly different from the others ($P \leq 0.005$) for both the Langmuir and linear models.

($P \leq 0.05$) (Table 3). In the presence of 0.1 M K_2SO_4, the Langmuir model fit the data better than the Freundlich model ($P \leq 0.005$) because the adsorption of DIPA appeared to reach a plateau in the presence of high concentrations of K^+ (Fig. 1a, Table 3). This likely occurred because of increased competition for the exchange sites as the concentration of K^+ increased.

Fig. 1b shows a portion of the data from Fig. 1a fitted to linear isotherms. For many ground water modeling applications, it is useful to have a K_d value to quantify sorption. Although the DIPA isotherms are curvilinear, it is possible to approximate a K_d value particularly at the low concentration range where the curve approaches linearity. The concentration of DIPA currently found in the ground waters at plant sites is below 350 mg/l and so equilibrium solution concentrations of less than this level were used to approximate an equation for a linear isotherm and thus a K_d (Fig. 1b, Table 2). The regression was done with a Y intercept value of zero because this is assumed in the application of the K_d value in ground water modeling.

The adsorption of DIPA decreased as the concentration of background electrolyte increased (statistically significant for both the Langmuir and linear models at $P \leq 0.005$)

Table 3
Comparison of Freundlich and Langmuir models for DIPA sorption by montmorillonite, kaolinite, aquifer materials, and surface soils

Sorbent	Treatment	Freundlich			Langmuir			F ratio[a]
		K_F	$1/n$	R^2	bK_L	K_L	R^2	
Montmorillonite[b]	–	170	0.69	0.998	50	0.0022	0.999	5.23**
Montmorillonite[c]	0.001 M	260	0.64	0.995	71	0.0034	0.995	−0.06 NS
Montmorillonite[b,c]	0.01 M	170	0.69	0.981	46	0.0019	0.977	−2.12 NS
Montmorillonite[c]	0.1 M	120	0.61	0.962	26	0.0025	0.980	11.8****
Montmorillonite[d]	pH = 6.8	140	0.77	0.977	57	0.0017	0.978	0.240 NS
Montmorillonite[b,d]	pH = 8.3	160	0.69	0.998	50	0.0023	0.986	0.540 NS
Kaolinite	–	25	0.63	0.984	5.6	0.0023	0.992	10.4***
Humus-rich soil	–	20	0.54	0.976	3.8	0.0045	0.983	6.80**
Site 1	–	6.2	0.55	0.977	1.0	0.0034	0.985	9.67***
Site 2	–	23	0.63	0.979	4.9	0.0021	0.975	−4.16 NS
Site 3	–	12	0.52	0.961	1.9	0.0043	0.979	15.4****
Soil 4	–	7.0	0.65	0.987	1.6	0.0019	0.988	1.43 NS
Soil 5	–	12	0.80	0.980	5.0	0.00085	0.981	0.677 NS
Soil 6	–	3.5	0.71	0.992	0.95	0.0013	0.988	−5.42*
Soil 7	–	35	0.60	0.989	6.7	0.0027	0.992	3.38 NS
Soil 8	–	32	0.61	0.994	6.4	0.0025	0.993	−0.27 NS

[a]Where F ratio is positive, the data fit best to the Langmuir model; where F ratio is negative, the data fit best to the Freundlich model.
[b]All three experiments conducted under similar conditions, not statistically different from each other using Langmuir model ($P \leq 0.05$), first data set is from sorption experiment prior to desorption study (Fig. 4).
[c]All three treatments significantly different from each other using Langmuir model ($P \leq 0.005$) (Fig. 1).
[d]Two treatments significantly different from each other using Langmuir model ($P \leq 0.005$).
(–) Standard treatment as described in Section 2.4.
NS, not significantly different ($P \leq 0.05$).
*Significantly different at $P \leq 0.05$; **significantly different at $P \leq 0.025$; ***significantly different at $P \leq 0.01$; ****significantly different at $P \leq 0.005$.

consistent with an ion-exchange mechanism for the uptake of DIPA (Fig. 1, Tables 2 and 3). The ground water at plant sites would have an EC in the low range, likely less than 2.4 dS/m. Thus, the high concentration of 0.1 M K_2SO_4 would only be applicable in zones with high salt concentrations as may occur at or near the base of a waste repository. In these experiments Hg^{2+} and Ca^{2+} were each present at approximately 0.7 mM concentration and so these cations would have also been competing a with DIPA for exchange sites.

Solution pH was also studied as an important variable controlling DIPA sorption. There was an increase in DIPA uptake by montmorillonite at the pH of 6.8 compared with the pH of 8.3 (statistically significant for the Langmuir model ($P \leq 0.005$)) (Table 3). There was not a significant difference in K_d values between the two treatments ($P \leq 0.05$) indicating that fluctuations in pH in the neutral range will not produce a major change in DIPA sorption (Table 2). However, the increase in K_d from pH 8.3 to 6.8 was 17% which corresponds closely to the expected increase in protonation of DIPA of from 80% to 99% cationic. Sorption of some N-heterocyclic compounds by montmorillonite was observed to decrease as the pH increased above pH = pK_a (Zachara et al., 1990). Thus, if the pH of the ground water were to rise above the pK_a of 8.88 through anthropogenic influence, a large drop in DIPA sorption would likely occur.

The mechanism of DIPA adsorption by montmorillonite was further studied by analyzing DIPA-saturated montmorillonite by XRD (Table 4). The Δd values refer to the interlayer spacings after subtraction of the width of the silicate sheet (assuming 0.95 nm as the minimum width of the silicate sheet) (Weber et al., 1965). The Ca^{2+}-saturated montmorillonite behaved as established for this material (MacEwan and Wilson, 1980); the d spacing expanded to near 2 nm when moist and decreased to near 1 nm when dry. The moist DIPA-saturated montmorillonite had a d spacing (approx. 1.37 nm) that was distinct from the Ca^{2+}-saturated material and it did not decrease with drying. The d spacing observed for DIPA-saturated montmorillonite corresponds to those reported by Theng et al. (1967) for montmorillonite saturated with alkylammonium ions of from 1.3 to 1.6 nm depending on the size of the amine. Our results confirm that DIPA enters the interlayer space of montmorillonite.

The K_d values for sulfolane sorption are from linear isotherms (Fig. 2, Table 2). The Y intercept for sulfolane sorption was not significantly different from zero ($P \leq 0.05$) and so isotherms were drawn with a Y intercept equal to zero. Adsorption of sulfolane

Table 4
Basal spacings of moist and oven-dry montmorillonite saturated with DIPA or Ca^{2+}

Species	Trial	Interplanar spacings (nm)			
		Moist		Dry	
		d_{001}	Δd_1	d_{001}	Δd_2
Ca^{2+}	1	1.97	1.02	1.00	0.05
	2	2.01	1.06	1.00	0.05
DIPA	1	1.37	0.42	1.37	0.42
	2	1.38	0.43	1.36	0.41

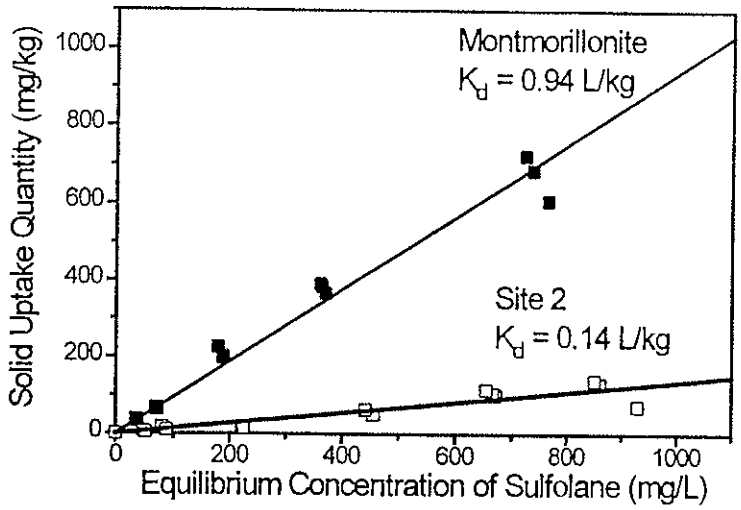


Fig. 2. Sulfolane sorption by montmorillonite and site 2 aquifer material.

by montmorillonite was over an order of magnitude less than that of DIPA (Table 2). Sulfolane remains nonprotonated at neutral pH, is highly water soluble, and does not interact with sorbents very readily. The isotherm was linear, as in partitioning, although the sorption of organic compounds to a mineral phase is considered a surface phenomenon. The linearity in this case may be a result of very low surface coverage (Rebhun et al., 1992) and/or a failure to reach the plateau in the concentration range studied.

3.3. DIPA and sulfolane adsorption by kaolinite

DIPA and sulfolane adsorption by reference kaolinite was performed to document adsorption by low surface area clays. The adsorption of these two compounds by kaolinite was much lower than by montmorillonite (Table 2). In addition, the CEC of kaolinite is lower than that of montmorillonite (Table 2) suggesting that the K_d for DIPA or sulfolane sorption is related to CEC or some other variable that is proportional to CEC such as surface area.

3.4. DIPA and sulfolane sorption by humus-rich soil

The nonlinear isotherm for DIPA sorption by humus-rich soil is not consistent with simple partitioning (Table 3). Using montmorillonite as a standard, sulfolane and DIPA K_d values for the humus-rich soil corresponded closely to the montmorillonite content (assuming montmorillonite comprises 50% of the clay fraction based on estimates from XRD analysis and previous studies of soils from Alberta (Dudas and Pawluk, 1982)) and were overestimated based on CEC (Tables 1 and 2). These results support the conclusion that organic matter contributes less to the uptake of DIPA or sulfolane than mineral material for the sorbents studied. Therefore, soils with high levels of organic C (> 1

g/100 g) should not be considered in any relationships developed between CEC and K_d.

The pH of sorption experiments using the humus-rich soil was lower than observed with the clay standards because the humus-rich soil had an acidifying effect on the system and the carbonate was insufficient to counteract this effect (Table 2). Sulfolane is nonreactive and remains uncharged at all pH values while DIPA is mostly protonated below pH 8.0. The cation exchange capacity was measured at the same pH as the experiments with the humus-rich soil (pH 7.0). The other experiments, with solids low in organic matter content, were not expected to show a large change in CEC between pH 7.0 and near 8.0 because for 2:1 clay minerals, the CEC is not pH dependent and for kaolinite, the CEC would fluctuate by less than 10 percent within this pH range (Helling et al., 1964). Thus the lower pH in the experiments with the humus-rich soil was appropriate and the results can be compared with the other experiments conducted near pH 8.0.

3.5. Sorption of DIPA and sulfolane by aquifer materials

Isotherms for DIPA sorption by the aquifer material from plant sites all showed a tendency for the slope to decrease as the concentration increased. The isotherm for Site 2 is provided as an example in Fig. 3. For sites 1 and 3, the Langmuir model fit best to the data ($P \leq 0.010$), whereas for site 2 the Langmuir and the Freundlich models fit the data equally well ($P \leq 0.05$) (Table 3). The isotherm for sulfolane sorption by site 2 is shown in Fig. 2. The sulfolane and DIPA K_d values observed for these materials were generally lower than expected based on CEC, compared with the K_d and CEC of kaolinite and montmorillonite. Rebhun et al. (1992) found that clays in natural soils had lower compound uptake than pure clay minerals which they attributed to blockage of the clay mineral by organic material in soils. In the present study, these differences could also be caused by differences in the mineralogy of natural and reference clays.

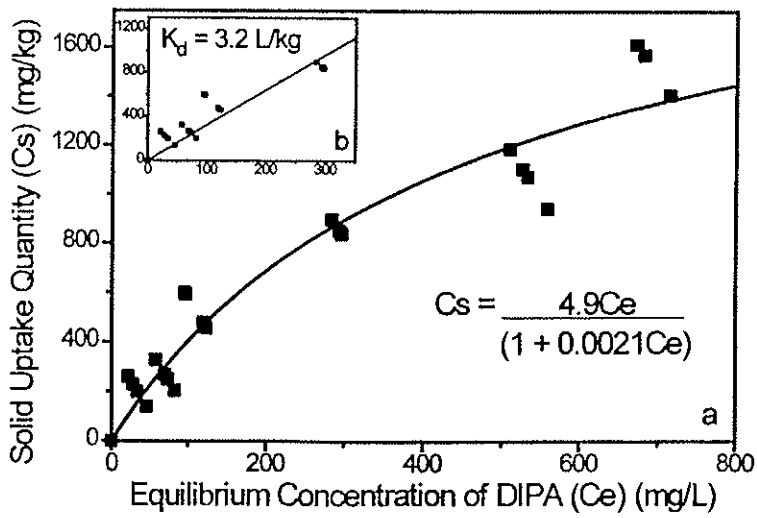


Fig. 3. DIPA sorption by site 2 aquifer material. Isotherm fitted to Langmuir model (a). Equilibrium concentrations less than 350 mg/l fitted to linear model.

3.6. Sorption of DIPA by surface soils

In most cases for DIPA sorption by the surface soils, other than the humus-rich soil, both the Freundlich and Langmuir isotherms fit the data equally well ($P \leq 0.05$) (Table 3). However, for soil 6, the Freundlich model fit best to the data ($P \leq 0.05$). The pH and EC were quite similar for all of the soils, except the solution from soil 8 which had a higher EC than that of the other soils (Table 2). The relationship between CEC and K_d is discussed in detail in Section 3.8.

3.7. Desorption of DIPA from montmorillonite and from aquifer materials

Desorption of DIPA from montmorillonite occurred to a limited extent with 0.01 M K_2SO_4 as the replacing solution, and thus there was apparent hysteresis (Fig. 4). Only 7–30% of the adsorbed DIPA was desorbed by the three desorption steps (Table 5). The failure of K^+ to replace all of the DIPA on the surface of montmorillonite was consistent with other research documenting the adsorption of N-containing compounds by montmorillonite (Zhang et al., 1993). Generally the slope of the desorption isotherm decreased and its Y intercept increased with increasing starting concentration (Table 5). Thus, the slope of both the adsorption and desorption isotherms for montmorillonite were higher at lower starting concentrations. The pH was maintained at 8.2 (± 0.1) and the EC at 2.4 (± 0.1) dS/m throughout this experiment.

The apparent desorption hysteresis observed with montmorillonite did not occur with the site 2 sample. Using a linear model, desorption of DIPA from this sample was not significantly different from the sorption ($P \leq 0.05$). Most of the DIPA sorbed by the site 2 material was desorbed by three desorption steps (Table 5). However, desorption from the samples from sites 1 and 3 was significantly less than sorption ($P \leq 0.005$). Approximately 30% of the DIPA sorbed by material from sites 1 and 3 was desorbed by

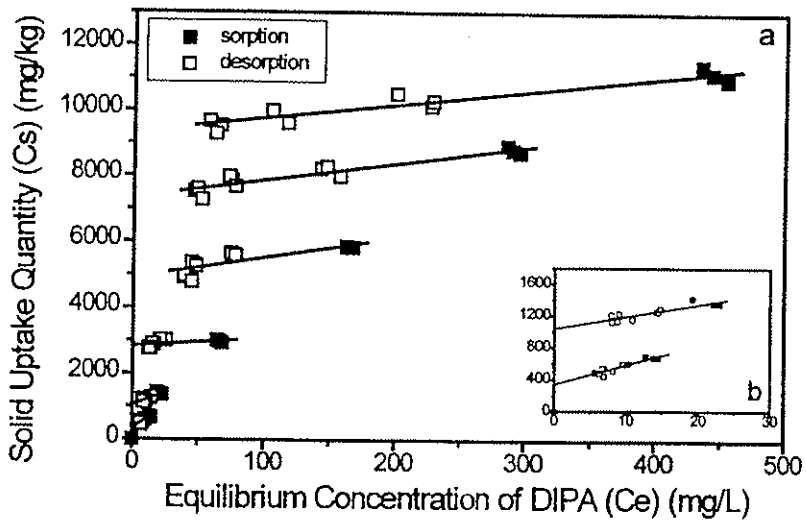


Fig. 4. DIPA sorption and desorption by montmorillonite. For the three replicates of each of the six starting concentrations (50, 100, 250, 500, 750, and 1000 mg/l), sorption was performed once followed by desorption three times: entire plot (a), lower two starting concentrations only (b).

Table 5
Equations for DIPA desorption from montmorillonite and from aquifer materials

Sorbent	Starting concentration of DIPA (mg/l)	Linear equation for desorption isotherm	R^2	% Desorbed of total sorbed after three desorption steps
Montmorillonite	50	$Y = 340 + 25X$	0.848	30 (3.4)
Montmorillonite	100	$Y = 1000 + 16X$	0.767	18 (0.33)
Montmorillonite	250	$Y = 2800 + 2.3X$	0.280	7.0 (0.19)
Montmorillonite	500	$Y = 4900 + 5.9X$	0.683	16 (1.7)
Montmorillonite	750	$Y = 7300 + 5.2X$	0.899	15 (2.0)
Montmorillonite	1000	$Y = 9300 + 4.1X$	0.897	15 (2.0)
Site 1	500	$Y = 110 + 0.20X$	0.561	29 (5.1)
Site 2	500	$Y = 140 + 2.5X$	0.871	62 (3.3)
Site 3	500	$Y = 130 + 0.51X$	0.712	31 (2.7)

Standard deviation provided in brackets.

three desorption steps which corresponds closely to the behavior observed for montmorillonite for the 50 mg/l starting concentration of DIPA (Table 5).

One possible explanation for the difference in desorption behavior between reference montmorillonite and the site 2 material, which contains montmorillonite, is that the crystallinity and surface charge density of the montmorillonite in each material is different. Soil clays typically display poorer crystallinity, blockage of exchange sites by amorphous weathering products, and some surface charge reduction due to mineral alteration under thermodynamic conditions that are unstable for montmorillonite (Brindley, 1980). Research has shown that different soil minerals desorb organic cations differently. For example most of the adsorbed paraquat and diquat could be desorbed from kaolinite (Weber and Weed, 1968) and vermiculite (Weed and Weber, 1969) while very little desorbed from montmorillonite.

3.8. Correlation of K_d and CEC

The relationship between the K_d of DIPA and the CEC of soils and aquifer materials with low organic C (< 1 g/100 g) was examined using the data from Table 2, excluding the humus-rich soil, and the reference clay minerals. The linear regression is as follows:

$$K_d\,(\mathrm{DIPA})\,(\mathrm{l/kg}) = 0.10 + 0.18(\mathrm{CEC}\,(\mathrm{cmol}(+)/\mathrm{kg})) \quad R^2 = 0.805 \qquad (3)$$

The correlation is not strong, but it could be used in instances where experimental data are unavailable. The correlation should be considered an approximation because very few data points were used to develop the relationship ($N = 8$). The relationship is applicable to soils and geological materials with organic C contents of less than 1 g/100 g, near neutral pH levels, an EC of 2.7 dS/m or less, and aqueous DIPA concentrations of less than 350 mg/l.

A correlation between CEC and sorption was also developed for sulfolane to allow predictions to be made of the potential for sulfolane movement in various aquifer

materials. The reference clays were included because there were very few data points to perform the correlation. The linear regression is reported below:

$$K_d\ (\text{sulfolane})\ (\text{l/kg}) = 0.0057 + 0.012(\text{CEC}\ (\text{cmol}(+)/\text{kg})) \quad R^2 = 0.990 \tag{4}$$

Although this relationship has a relatively high R^2 value, it should only be used where no experimental sorption data is available and should be considered an approximation. Very few data points ($N = 5$) were used to develop the relationship and the K_d was very low and difficult to measure accurately in most cases. The relationship is applicable to soils and geological materials with organic C contents of less than 1 g/100 g, near neutral pH levels, an EC of 2.6 dS/m or less, and aqueous sulfolane concentrations of less than 1000 mg/l. Sulfolane has oxygen atoms that form dipoles and thus sorption may have been through dipole–dipole interaction between sulfolane and clay minerals. The correlation of sulfolane sorption with CEC may be simply because CEC is related to other factors such as clay content and surface area.

3.9. Implications for mobility in the saturated zone

Many fate and transport models use a retardation coefficient (R_d) to describe the attenuation of organic chemicals by sorption onto soil:

$$R_d = 1 + K_d(D_b/\theta) \tag{5}$$

where θ is the porosity and D_b the bulk density of soil. The velocity of contaminant movement is inversely related to R_d. The calculation of R_d involves a number of basic assumptions which are outlined by Freeze and Cherry (1979) and include the complete reversibility of sorption. Estimates for D_b and θ were made based on the particle size of the aquifer materials (Table 6). The D_b of soils typically ranges from 1.1 to 1.6 g/cm^3 and the θ from 0.3 to 0.6 cm^3/cm^3 (Hillel, 1982). Thus, the calculated R_d values are only approximations, but they can be used to make comparisons among the sites and between the compounds. The retardation of sulfolane is predicted to be from 3 to 8 times less than that of DIPA. The R_d of both sulfolane and DIPA is predicted to be lowest at site 1 and highest at site 2 (Table 6). Therefore based on abiotic attenuation, sulfolane is predicted to move 3 to 8 times farther than DIPA under the conditions at plant sites, and both compounds should be retarded relative to ground water velocities at each site as follows: site 2 > site 3 > site 1.

Table 6
Estimates of R_d values for DIPA and sulfolane at three sour gas plant sites

Site	D_b (g/cm^3)	θ (cm^3/cm^3)	R_d DIPA	R_d Sulfolane	Ratio R_d DIPA/R_d sulfolane
1	1.6	0.40	3.2	1.0	3.2
2	1.5	0.43	12	1.5	8.0
3	1.6	0.40	5.3	1.3	4.1

4. Conclusions

From the data presented in this paper, the following predictions regarding the fate and transport of DIPA and sulfolane can be made.

(1) Sulfolane sorption is very low and DIPA uptake is somewhat higher. Adsorption by clays appears to be the dominant mechanism of uptake for both compounds.

(2) At neutral pH, DIPA adsorption by montmorillonite involves cation exchange. The magnitude of DIPA adsorption by montmorillonite increases slightly as the pH decreases from 8.3 to 6.8 and as the concentration of background electrolyte increases. DIPA enters the interlayer space of montmorillonite and once adsorbed, is not readily desorbed by a 0.01 M K_2SO_4 solution. Desorption of DIPA from some aquifer materials occurs more readily than from reference montmorillonite.

(3) CEC is a useful parameter for predicting the sorption of sulfolane and DIPA in soils that contain low levels of organic C (< 1 g/100 g).

(4) Based on abiotic attenuation, sulfolane is predicted to migrate further than DIPA in ground waters.

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Determination of retardation coefficients of sulfolane and thiolane on soils by K_{ow}–K_{oc} and solubility parameter, batch and column experiments

C.G. Kim · W.P. Clarke · D. Lockington

Abstract Retardation parameters (R_f) for sulfolane and thioalne were estimated using reference values and experimentally as they were mainly observed at an aquifer underneath a waste disposal site near Brisbane, Australia. Three soil aquifer materials e.g. clay, silty clay and sand were used as sorbents. At first, R_f was obtained employing K_{oc}–K_{ow} and solubility parameter, respectively, while experimental coefficients were determined from both batch and flow-through column tests. Additionally, R_f was observed at a single- and bi-solute system through the column test. There was not found any significant difference in R_f between K_{oc}–K_{ow} and solubility parameters, but the retardation coefficient was significantly dependent on organic carbon content for solubility parameter. In contrast, using K_{oc}–K_{ow}, the coefficient correspondingly varied with an amount of clay content contained in each soil. In the same manner, the batch-determined parameters were more subject to clay content. On the other hand, the column-determined parameters can be comparable with the desk-derived values. In a bi-solute system, they did not influence each other concerning retardation coefficients while they flew though the column simultaneously. It was concluded that there was a large discrepancy in retardation coefficient of batch- against both reference-oriented estimation and column-determined values.

Key words Thiolane · Sulfolane · Retardation coefficient · Solubility parameter · Partition coefficient

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Introduction

Heterocyclic sulphur compounds have been exposed through an unconfined aquifer at a waste disposal site, Brisbane Australia since Sulfinol waste sludge has been carelessly disposed. The sludge contains sulfolane (5–20%), which is used to remove carbon dioxide from the air stream in an ammonia plant. For the past 20 years, sulfolane has been transformed into thiolane in the site by an unknown mechanism. It appears that sulfolane has been reduced by facultatively anaerobic microcosms as it is used for an electron acceptor (Zinder and Brock 1978a, b; Schrementi and Meganathan 1986, 1987). In 1995, significant contamiantion of sulfolane and thiolane was detected in the shallow unconfined alluvium underlying the weathered rock aquifer. Sulfolane is of major concern as a toxic chemical in an EPA report (Federal Register 1991). Thiolane is moderately toxic, but at low concentration, it could cause vomiting, nausea, and headache (Moschandreas and others 1982; Bradstreet and others 1985; Schmidt and Meyer-Schmidt 1985; Coy 1987). Both compounds, sulfolane and thiolane, have significantly different properties: sulfolane molecules are readily solvated into water, while thiolane is not miscible with water. Assessing the migration of sulfolane and thiolane is of great importance for site remediation to be performed in the study area. Application of solute transport models requires sorption coefficients, which can be obtained from

different methods such as literature survey and laboratory measurements. The estimated sorption coefficients can be calculated from semi-empirical equations and published sorption data (Schwarzenbach and Westall 1981) even though there is a degree of uncertainty on the applicability of estimates obtained by literature studies (Stephanatos and others 1991) in contrast to site-specific sorption properties. Sorption coefficients of organic contaminants on aquifer materials can also be determined by batch and column flow-through experiments. General agreement between batch and column results has been made, although considerable uncertainty has also been reported with respect to the application of batch-derived sorption coefficients to ground water transport models (Brusseau 1992; Roy and others 1990). Ptacek and Gillham (1992) found that laboratory scale sorption estimates produce uncertainty for inclusion in a mathematical solute transport model. Laboratory column tests have been found useful to evaluate retardation coefficients compared with values derived from measurement of site-specific plume lengths (Priddle and Jackson 1991).
The objective of this study was to compare retardation coefficients using different approaches. The parameter was indirectly determined from an equation based upon octanol-water and the fraction of organic carbon (f_{oc}) in the aquifer material. In addition, the solubility parameter was used to estimate the retardation coefficients. Laboratory batch and column tests are then performed to compare the estimation of retardation coefficients obtained in K_{oc}–K_{ow} and solubility parameters.

Materials and methods

Chemicals

A 1-Octanol (>99% GC) was purchased from Merck-Schuchardt, Germany. Sulfolane and thiolane (AR) were purchased from Aldrich Chemicals. The ground water samples used in whole adsorption studies (i.e. batch and column) were taken from the monitoring well, which is located about 2 km from the site. It was filtered (0.45 μm), purged (N_2) and then stored at 4 C until it could be used in the experiment. Thiolane standard was freshly prepared because of its potential loss from volatility (vapour pressure: 2.45 kPa at 25 C). The MilliQ water used in determining K_{ow} was purged with high purity helium gas (BOC) for 30 min at 40 ml/min to remove residual air that can cause quick diffusion of solutes into the gaseous phase.

Determination of octanol-water partition coefficient (K_{ow}) and organic carbon content (f_{oc})

A 1-Octanol (>99% GC) was rinsed with 0.1 N NaOH and 0.1 N HCl each, twice with MilliQ water, and was subsequently distilled twice. As a number of researchers demonstrated (Leo and others 1971; Craig and Craig 1950; Campbell and Luthy 1985; Marple and others 1986), the "shake flask" method was adopted to obtain K_{ow}. Solute concentration was prepared in glass vessels as low as 0.01 M as recommended by Leo and others (1971) to avoid a serious error caused by a small amount of impurities. Prior to the experiment, the glass vessels were treated by 0.01 M dichloro dimethyl silane to avoid absorption of solutes onto a glass surface. The volume ratio of water and octanol was determined as suggested by Leo and others (1971) and the OECD Guideline (1981) to consider the solubility of lipophilic (e.g. thiolane) solute into the water phase.
Duplicate glass vessels containing samples were quickly inverted so that any trapped air could escape and then repeated the 100 inversion in 5 min. Subsequently, an air-filled syringe was gently passed through the octanol layer into water phase and then the air was cautiously released through the water phase so that any residual octanol in the tip of needle would be released. Then, 20 ml of the sample were obtained from the water phase and 5 ml of it was discarded to avoid potential contamination from the tip of the needle which can occur while the needle is removed through the octanol layer. A 15-ml portion of the sample was centrifuged using Hettich (Potanta/P, Germany) at 750 rpm for 5 min to separate residual octanol molecules from the water samples.
The partition coefficient (K_{ow}) was then calculated as the ratio of the equilibrium concentration of a dissolved solute in a two-phase system consisting of pure water and octanol.

Analysis

The amount of sulfolane present in either octanol or water-phase was extracted with methylene chloride as 1:1 v/v ratio and then analysed using a Perkin Elmer AutoSystem Gas Chromatography equipped with a flame ionization detector (FID) which employs 30 m long (0.25 mm i.d.) and the 0.25-μm thick DB5 (5% phenyl methyl poly siloxane) column.
On the other hand, the concentration of thiolane was determined by injecting 25 μl of the sample into a Waters High Performance Liquid Chromatography (HPLC) equipped with a UV spectrophotometer at 215 nm.

Batch and column test

Soil sample preparation

Soil samples were obtained using a split spoon sampler while drilling with a hollow stem auger at the site. The soil samples were air-dried for 5 days, then crushed with mortar and pestle. They were subsequently passed through an 18-mesh sieve (1-mm openings). The sample was characterized for size distribution and clay content using a laser and XRD techniques. In addition, the cationic exchange capacity and organic carbon (LECO combustion method) were also determined.

Batch test

A total of 33 batch tests were carried out for three types of soils (e.g. clay, silty clay and sand) at a typical pH and

temperature observed in the study area. Proportions of stock solution were varied to achieve a range of concentrations in the adsorption tests. Prior to the experiment, 20 g of soil samples were premixed with 100 ml of filtered ground water for 10 min in a water shaker bath at 18 C to remove any air trapped in the soil samples.
After adding 100 ml of diluted sulfolane and thiolane into the bottles, they were then agitated for 24 h. Then, a 5-ml sample was collected from each bottle. The sample was centrifuged at 1500 rpm and filtered through a 0.2-μm membrane filter.
A filtered sample was directly used in analyzing thiolane employing HPLC, while it was extracted with methylene chloride at 1:1 (v/v) ratio for 1 min to quantify the concentration of sulfolane using GC-FID.
The concentration of the adsorbed phase was calculated as:

$$\bar{C} = \frac{(C_0 - C_{eq})}{W} V \quad (1)$$

where C_0: initial concentration of adsorbate in the liquid phase $\left[\frac{mmol}{l}\right]$ C_{eq}: final concentration of adsorbate in the liquid phase $\left[\frac{mmol}{l}\right]$ W: dry weight of soil samples $[g]$ V: volume of liquid phase $[l]$ $\bar{C}$: adsorbed amount $\left[\frac{mmol}{g}\right]$

Column experiments

Experimental procedures to obtain sorption coefficients in the column flow-through test are reported by Jacobson and others (1984), which are fundamentally based on pulse or frontal analysis chromatographic techniques. The entire column tests were conducted in a dark incubator (Linda and May, Australia) set at the average ground water temperature (18 C) as observed in the site.
Degassed filtered ground water was used as a leaching fluid through the column. The three major types of soils (i.e. clay, silty clay, sand) were selected for these experiments. The column (5 cm L and 3.3 cm I.D.) was constructed with stainless tube to minimize sorption losses. Both ends of the column were fitted with stainless-steel caps spouted with inlet and outlet which holds a 5.5-μm mesh glass frit that allowed the introduction and flow-through of amended ground water. Teflon o-rings were joined within stainless-steel caps to seal the ends. The column was designed to afford easy assembly and disassembly. After packing the column with air-dried soils, the trapped air was replaced by CO_2 and then prewetted with filtered ground water at the upflow to dissolve CO_2 and to obtain chemical equilibrium.
Constant low water flow was achieved at 0.4 ml/min using a gamma/4 microtubing pump (ProMinent, Germany). Flow rates were measured by collecting water at the column exit at regular intervals during the test. At first, a pulse of water (5 or 10 ml) containing the contaminants and a conservative tracer (KBr) was added just prior to the column using a glass syringe. The test was also conducted for single and combined solute systems to investigate an influence of the retardation coefficients of a solute in the presence of the other solute. The input concentrations were obtained by analyzing a sample taken at the sampling port just prior to the column. An effluent sample was collected in a specially designed sampling tube to minimize volatile loss of solutes. Samples were analyzed within an appropriate period of time.
Breakthrough curves were prepared by dividing the concentration (C) of each compound in the effluent sample by its initial concentration (C_o) to obtain a relative concentration (C/C_o). These values were then plotted against the volume of water which passed through the column. Mass recoveries were calculated using the trapezoidal rule to determine the area under each curve and comparing this value with the area obtained by the tracer (Br^-). The bromide concentration was determined by Ion Chromatography (Dionex 2010 I) equipped with a guard column (4 mm, AG4A-SC, Dionex) and an analytical column (4 mm, AS4A-SC, Dionex).
The ratio of temporal first moments (Turner 1972) at the column outlet for solutes and for bromide gave a retardation factor, R_f (Freeze and Cherry 1979), which can be used to calculate the sorption coefficient from:

$$R_f = 1 + \rho_b K_d / n = \frac{V_w}{V_c} \quad (2)$$

where ρ_b is the sorbent bulk density (M/L^3), n is the sorbent porosity (dimensionless), K_d is the sorbate distribution coefficient (L^3/M), V_w is the velocity of the unretained tracer, and V_c is the velocity of the sorbate.

Results and discussion

The study area of the waste disposal site lies in the confined alluvium aquifer overlain by weathered rock formations which consist of clay and silty interbedded with quartz sand and some gravel. The aquifer is 10–12 m thick with a 8–10-m thick saturated zone overlain by a thick aquitard clay layer. The soil samples used in the current test were characterized as shown in Table 1.
XRD analyses exposed that the clay contained in the soil subsamples was mainly composed of kaolinite and smectite.

Table 1
Characterization of clay content and CEC (Cationic exchange content) on typical soils

	Clay	Silty clay	Sand
Clay content (wt.%)	13.4	12.37	5.5
CEC(meq/100gsoil)	26.25	23.06	1.04

Theoretic calculation of retardation coefficients

A number of researchers have studied the estimation of retardation coefficients using semi-empirical equations (Karickhoff and others 1979; Hassett and others 1983; Piwoni and Banerjee 1989) as well as attempted with solubility parameter (eg. δ_o; Barton 1975; Freeman and Cheung 1981; Chiou and Kile 1994; Kopinke and others 1995). Hydrophobic organic compounds are dominantly attracted into organic materials on mineral surfaces if the organic carbon fraction consists of over 1% of the soil on a weight basis (Karickhoff and others 1979). McCarty and others (1981) found that this organic carbon content extended into the surface area and a property of a solute. In contrast, Banerjee and others (1985) found that at f_{oc} levels less than 0.2% of clay content to f_{oc} ratios greater than 60, partitioning of a nonpolar organic solute onto the mineral surfaces (Cation Exchange Capacity) may become dominant. In addition, for soil organic carbon fractions, f_{oc}, less than about 1%, sorption onto mineral surfaces is suggested as being significant (Schwarzenbach and Westall 1981). The application of carbon-based models then tends to underestimate the degree of solute retardation (Roy and Griffin 1985). Piwoni and Banerjee (1989), therefore, provide a non-carbon-based correlation equation for f_{oc} less than 1%, where the magnitude of sorption depends only on K_{ow} as presented in Eq. 3. They suggested that the correlation based on K_{ow}–K_d for f_{oc} values less than 1%.

$$\log K_d = \log K_{ow} - 3.46 \tag{3}$$

They present that for nonionic sorbates with log K_{ow} less than 3.7, the correlation yield more realistic K_d estimates than are obtained from the rigorous application of carbon-based models.

For the current study, the organic carbon contents (f_{oc}) obtained using the Leco combustion method were 0.082, 0.21, and 0.078% for clay, silty clay, and sand samples, respectively. These results indicate that the adsorption of sulfolane and thiolane onto soils may possibly comply with correlation presented by Piwoni and Banerjee (1989).

The octanol-water partition coefficients for thiolane and sulfolane can also be subject to the non-carbon-based correlation as log K_{ow} showing 1.61 and 0.093 for thiolane and sulfolane. Consequently, R_f can be calculated for three types of soils as shown in Table 2.

This non-carbon-based estimation can be comparable with the approach using the relationship between the solubility parameters. Freeman and Cheung (1981) firstly employed the single solubility parameter to describe the partitioning into nonpolar solvents. They did, however, not account for specific molecular interactions involving polar functional groups. For soil organic matters, therefore, multicomponent solubility parameters suggested by Barton (1975) can be more successfully applied for the estimation of hydrophobic partitioning (Chiou and Kile 1994). Kopinke and others (1995) introduced a modified δ concept to estimate partition coefficient as given by the Eq. 4.

$$\ln \frac{K_{om}}{K_{ow}} = \frac{V}{RT}\left[(\delta - \delta_{oct})^2 - (\delta - \delta_{som})^2\right] - \ln \rho_{som} \tag{4}$$

where the molar volume, V[cm^3], dry density of soil organic matter, ρ_{som}, 1.2 [kgl^{-1}] and δ_{som} is about 26.2 ± 1.6 Mpa$^{1/2}$ (Kopinke and others 1995). Approximating $K_{oc} = 1.724$ to 2 K_{om} (Means and others 1980; Olsen and Davis 1990). For f_{oc} greater than 0.001, partitioning into organic fraction can be defined as $K_d = K_{oc} f_{oc}$ (Lambert 1968). The retardation coefficient can eventually be calculated as shown in Table 5 using values given in Table 3 and 4.

The retardation coefficients estimated from both K_d–K_{ow} relation and solubility parameter concept yield no significant differences for each soil type concerned.

Estimatation of R_f by batch test

The soil samples were pre-wetted at the experimental temperature for 30 min, which would enhance saturation

Table 3
Solubility parameter (Barton 1991) and molar volume

	δ_o (MPa$^{1/2}$)	δ_d (MPa$^{1/2}$)	δ_p (MPa$^{1/2}$)	δ_h (MPa$^{1/2}$)	V (ml/mole)
Sulfolane	27.4	8.6	7.7	24.8	95.37
Thiolane	17.9	14.6	8.7	5.7	88.17
1-octanol	21.1	17.0	3.3	11.9	157.70

Table 4
Estimation of K_d for sulfolane and thiolane on three types of soils using Eq. 8

	K_d (L/Kg)		
	Clay	Silty clay	Sand
f_{oc} (w/w%)	0.082	0.21	0.078
thiolane	0.0057–0.0066	0.015–0.017	0.0054–0.0063
sulfolane	0.0065–0.0075	0.017–0.019	0.0062–0.0072

Table 2
R_f of sulfolane and thioalne calculated from K_d–K_{ow} correlation on three types of soils

	Clay	Silty clay	Sand
Thiolane	1.078	1.071	1.060
Sulfolane	1.002	1.002	1.002

Table 5
Calculation of R_f for sulfolane and thioane on three types of soils by solubility parameter

	Clay	Silty clay	Sand
Thiolane	1.031–1.036	1.075–1.085	1.023–1.027
Sulfolane	1.034–1.041	1.085–1.094	1.026–1.031

of air-entrapped pores in soils. The partition coefficients of non-premixed samples were resulted in about four times higher than that of premixed soils. The air entrapped in pores might drive a great mass diffusion, which causes non-equilibrium of isotherms (Benker and others 1997).

The partition coefficient can be defined as

$$k_d = \frac{V_w(C_o - C_{eq})}{m\,C_{eq}} \tag{5}$$

where V_w[l] is the volume of sorbent, C_o[kgl^{-1}] is the initial concentration, C_{eq}[kgl^{-1}] is the equilibrium concentration, m[kg] is the total mass of adsorbate.

As shown in Fig. 1 and 2, isotherms are linear over the experimental concentration range, and batch sorption coefficients presented are the slopes of linear least-squares fits to the isotherm data. Isotherm linearity permits use of a linear relation between the retardation factor and sorption coefficient in the dynamic methods using Eq. 2.

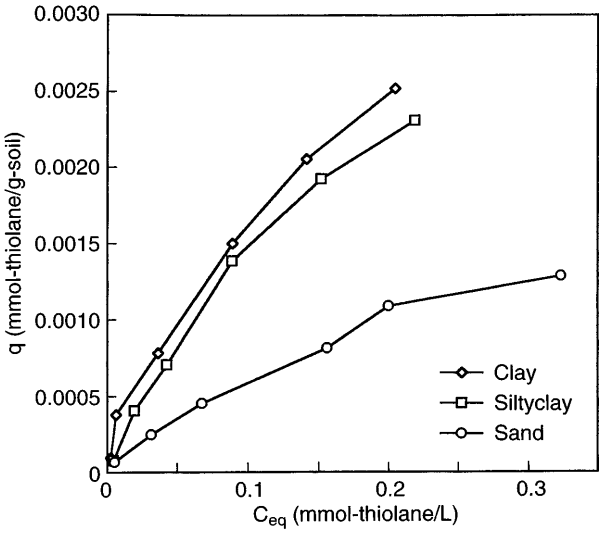

Fig. 1
Adsorbed amount of thiolane on different soils (pH 6.5 and 18 °C)

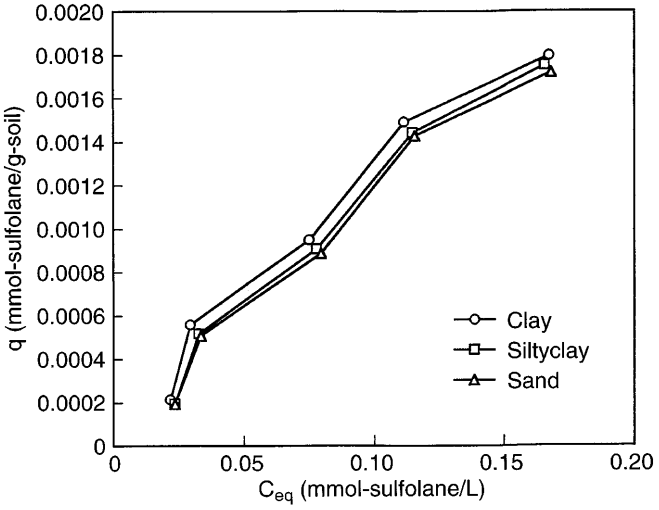

Fig. 2
Adsorption amount of sulfolane on different soils (pH 6.5 and 18 °C)

Table 6 shows the corresponding partition coefficients. R_f was then obtained as presented in Table 7.

The retardation coefficients obtained from batch adsorption tests are significantly different from those obtained from K_{ow} and δ concepts.

After the test, a dissolved organic carbon and suspended solids in the test vial were determined in the liquid phase to assess the loss of organic carbon content by contacting filtered ground water. The dissolved organic carbon, sulfur and suspended solids in triplicate were presented in Table 8.

The potential effect of the mobile phase on the coefficient can be estimated as presented by Benker and others (1997).

$$\frac{k_d^{eff}}{k_d^{true}} = \frac{k_{d1}\left[1 + \left(\frac{m}{V_w}\right)k_{d2}\right]}{k_{d1} + k_{d2}} \tag{5}$$

where k_d^{eff} is the effective partition coefficient, k_d^{true} is the true partition coefficient, k_{d1}[lkg^{-1}] is the partition coefficient between the mobile adsorbate fraction and the aqueous phase fraction, and k_{d2}[lkg^{-1}] is the partition coefficient between the mobile adsorbate fraction and the aqueous phase fraction.

Table 6
Estimated partition coefficient (K_d:L/kg) for thiolane and sulfolane on three types of soils from the batch test

	Clay	R^2	Silty clay	R^2	Sand	R^2
Thiolane	11.7	0.97	10.4	0.96	3.9	0.95
Sulfolane	10.5	0.95	10.7	0.96	10.3	0.96

Table 7
Calculation of R_f for thiolane and sulfolane on three types of soils from the batch test

	Clay	Silty clay	Sand
Thiolane	65.4	51.7	17.6
Sulfolane	58.8	54.2	44.8

Table 8
Characterization of liquid phase obtained form a batch-adsorption vessel

	Clay	Silty clay	Sand
Sulfur (mg/l)	3.1 (±0.02)	8.4 (±0.32)	7.5 (±0.16)
TOC (mg/l)	3.1 (±0.10)	32.5 (±0.21)	43.9 (±0.14)
SS (%)	12.4 (±0.20)	5.2 (±0.31)	1.3 (±0.12)

On the average, 12.42 (±0.2), 5.23 (±0.31), and 1.3 (±0.12)% of suspended solids were observed for clay, silt and sand samples, respectively, as shown in Table 8. The ratio of k_d^{eff}over k_d^{true} can be calculated as shown below for three different soil types based on a solid/liquid ratio (m/V_w) of 0.1 kgl^{-1} and an organic carbon fraction (f_{oc}) of 0.082, 0.21, and 0.078% for clay, silt and sand, respectively, and a K_{oc} of 100 lkg^{-1}.

$$\frac{k_d^{eff}}{k_d^{true}} = 0.88 \text{ (clay)}, 0.95 \text{ (silt)}, 0.99 \text{ (sand)} \quad (6)$$

The real partition coefficient for clay could expect to be less because relatively higher mobile phase has readily been released into liquid phase. It was compulsory to use a 0.2-μm membrane filter immediately after centrifugation in order to obtain reliable partition coefficients even if they still impose a potential uncertainty.

Approaches employing column experiment to estimate R_f

Application of the solute transport model using a partition coefficient obtained from a batch adsorption test has not always had satisfactory results. A flow-through column test can accommodate more accurate field estimation not only by permitting adsorbate to be in the mobile phase, but by providing an appropriate soil/aqueous phase ratio. The most currently used estimation of retardation coefficient was suggested by Freeze and Cherry (1979) as represented in Eq. 2.

Contradictory to the local equilibrium assumption given in Eq. 2, non-equlibrium may occur due to diffusion in a flow-through system (Brusseau and Rao 1989; Miller and others 1989) while a batch test is purposely designed to limit the diffusion by maximizing a contact between sorbate and sorbent. Nevertheless, laboratory column experiments are still applicable in order to evaluate retardation factors because they are relatively simple and simulate many of the solute transports observed in the field (Maclntyre and others 1991; Priddle and Jackson 1991; Benker and others 1997)

While soil was packed into the column, the vibrator was facilitated to avoid layering in the column. The remolded soil sample into the column was to yield approximately the degree of compaction as in the undisturbed soil sample obtained by split-spoon sampler (e.g. bulk density and porosity) by measuring bulk density, solid density and porosity as shown in Table 9.

Farquhar and Rovers (1976) investigated the effect of the packing column with disturbed soil on the column adsorption of leachate with an undisturbed soil sample obtained by a Shelby tube. They have not found that any significant difference in the breakthrough curve for several cation and anionic compounds from the leachate over a broad range of grain size.

Levels of thiolane were tested for three types of subsoils employing an averaged pH and temperature (18 C) range observed from the field as shown in Table 10.

For pH 4.5, thiolane is inconsiderably retarded regardless of soil types, but for pH 6.5 thiolane is retarded at a slightly greater extent compared to those observed in pH 4.5. Thiolane is not significantly retarded onto sand in the presence of sulfolane compared to those obtained for thiolane only tested. In contrast, clay and silt had thiolane retarded at a relatively slightly higher extent as it was investigated in the presence of sulfolane.

On the other hand, sulfolane showed a very low retardation coefficient regardless of soil and contaminant types compared to those estimated for thiolane. There were no differences found for 92.32 ppm of sulfolane in the presence of thiolane. In a higher concentration of sulfolane (e.g. 858.6 ppm) in the presence of thiolane, migration of sulfolane was impeded to a slightly higher extent in the presence of an enhanced concentration of thiolane by 23.09 ppm against 4.87 ppm of thiolane.

Figure 3 shows the difference between batch and column in R_f for the two components using the three soils.

In Fig. 3, R_b and R_c refer to batch- and column-determined retardation coeffficients, respectively. Figure 3 reveals that the values of retardation coefficients determined in batch tests are much higher by a factor ranging from 40 to 60 for sulfolane and 10–40 for thiolane. The retardation coefficients given in Fig. 3 are linearly increased with changes in the soil clay content. However, it is difficult to draw any conclusion why retardation coeffi-

Table 9
Bulk density, solid density and porosity of packed soil column for three types of soils

	Bulk density (g/cm^3)	C.V. (9)	Solid density (g/cm^3)	C.V. (9)	Porosity (%)	C.V. (9)
Clay	1.65	0.79	2.37	0.12	0.30	0.61
Silty clay	1.74	0.82	2.69	0.18	0.35	0.43
Sand	1.66	0.40	2.72	0.73	0.39	0.27

Table 10
Retardation coefficients (R_f) of sulfolane and thiolane on three types of soils obtained from the column experiment

	Concentration (ppm)	pH	R_f		
			Clay	Silty clay	Sand
Thiolane	4.87	4.5	1.65	1.46	1.20
	4.87	6.5	1.80	1.71	1.71
	23.09	6.5	1.79	1.72	1.72
Thiolane/sulfolane	4.87/92.32	6.5	1.80	1.76	1.69
	23.09/92.32	6.5	1.78	1.72	1.65
	4.87/858.61	6.5	1.85	1.84	1.71
	23.09/858.61	6.5	1.89	1.76	1.72
Sulfolane/thiolane	92.32/4.87	6.5	1.02	1.01	1.01
	92.32/23.09	6.5	1.05	1.02	1.01
	858.6/4.87	6.5	1.19	1.17	1.16
	858.6/23.09	6.5	1.14	1.13	1.13
Sulfolane	92.32	6.5	1.10	1.01	1.01
	858.6	6.5	1.10	1.01	1.01

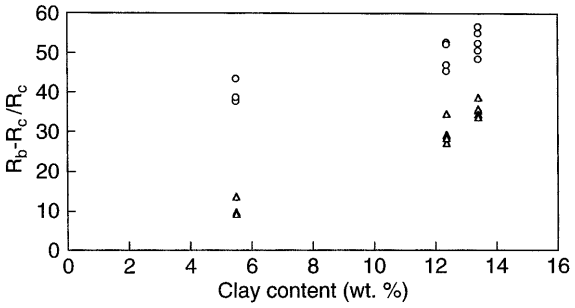

Fig. 3
Comparison between batch and column retardation coefficients for aquifer materials with different clay content: *circles* are for sulfolane and *triangles* for thiolane

cients between batch and column techniques are greatly differentiated. Recently, Maraqa and others (1998) have evaluated the previously reported factors that may cause a discrepancy between the two techniques employing benzene and dimethylphthalate for three sandy soil materials with medium to high organic carbon content. They did not make it clear why the values determined by the two techniques were different even if they have found the difference by 100% for dimethylphthalate.

Batch adsorption experiments are usually run until the partitioning of a compound has reached equilibrium between the dissolved and sorbed phases. There are much more surface area contacts so that adsorption would be maximized in the batch studies. Batch experiments can be plagued by a very slow and quite unnatural, approach to equilibrium because even quite modest levels of agitation cause particles to periodically impact against each other and thereby create still more new surfaces for adsorption (e.g. ion exchange) (Cameron and Klute 1977; Rao and others 1979; Valocchi 1985). Other chemical changes are also exerted on the system such as putting foreign species into the solution and creating unwanted colloids that can lead to experimental artifacts (Maraqa and others 1998). The equilibrium retardation coefficient calculated from the batch experiments should theoretically be similar to those calculated from column experiments that provide a continuous and constant stream of the compound to the column, assuming the adsorption-desorption mechanism is sufficiently fast that a single rate constant can accurately describe the phenomena. However, in a packed column, some sorption sites will be physically blocked by intergranular contacts that may not occur in the batch test (Elabd and others 1986). A potential preferential flow through secondary structures in the column will decrease the residence time. This will reduce the sorbed phase concentration. Aside from physical constraints, column tests that are not run to chemical equilibrium (C influent = C effluent) can skew the calculation of an equilibrium retardation factor (Cameron and Klute 1977; Rao and others 1979; Valocchi 1985).

Dissolved compounds, bacteria, viruses, and other ground water constituents can have complex sorption kinetics that cannot be accurately described with an equilibrium retardation factor. The rates of adsorption and desorption are very different and are difficult to discern in short-term column experiments (Cameron and Klute 1977; Rao and others 1979; Valocchi 1985).

Maclntyre and others (1991) explained that the differences occurring in sorption coefficients can be induced from insufficient time for batch equilibrium, failure to attain local equilibrium in columns, loss of sirbent particles through column end retainers, column flow variations (sometimes called wall and end effects), column flow channeling, and nonlinearity in sorption isotherms.

Maraqa and others (1998) assumed that the differences are ascribed to transport non-equilibrium, chemical non-equilibrium, unavailable surfaces, spatial variation occurring in column experiments and unrealistic water to soil ratio and creation of surface artifacts in batch experiments.

Despite considering the full range of speculative explanations that have been offered in their studies, the cause of the discrepancy between batch- and column-determined distribution coefficients remains unclear.

Figure 4 presents the difference in R_f for the two compounds using the three soils.

In Fig. 4, R_c and R_{sol} refer to the column- and solubility concept determined retardation coefficients, respectively. It reports that the discrepancy in retardation coefficients determined in column tests are variously ranged from as low as 0.01 up to approximately 0.8. The discrepancy obtained from the relationship between R_c and R_{sol} is much smaller than those determined from between R_b and R_c. Solubility parameters and K_{ow} concepts to obtain retardation coefficients can be comparably adopted in this study. However, it is still not valid for the retardation coefficient obtained from the concepts to be used for input parameters in modeling solute transport due to the data variability.

Conclusions

The significant discrepancy was observed in the retardation coefficient between a desk-derived calculation and

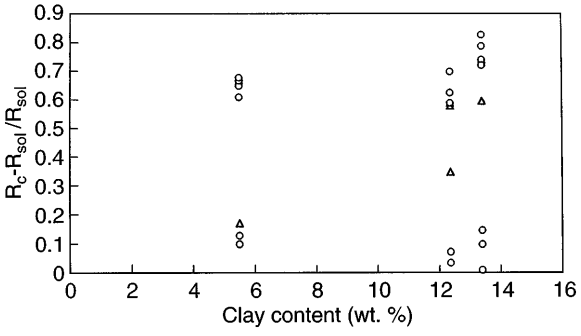

Fig. 4
Comparison between column and calculated retardation coefficients for aquifer materials with different clay content: *circles* are for sulfolane and *triangles* for thiolane

batch test for three soils. Soil materials used as sorbents; clay, silty clay and sand. On the contrary, the differences between column and K_{ow} and solubility parameter concepts were comparatively smaller than those obtained between batch and column.

On the other hand, there were no significant differences observed between the coefficients for sulfolane in both a single and co-solute system with thiolane on the three soils by employing the column. It simply indicates that sulfolane would not considerably be influenced by changing hydrogeological properties in the aquifer. In contrast, thiolane in single or the presence of sulfolane in different concentrations by the column was slightly retarded compared to those determined from the desk. Consequently, both the desk-derived and column-determined parameters would be used in modeling of solute transport within relatively smaller ranged errors than those obtained from the batch experiment.

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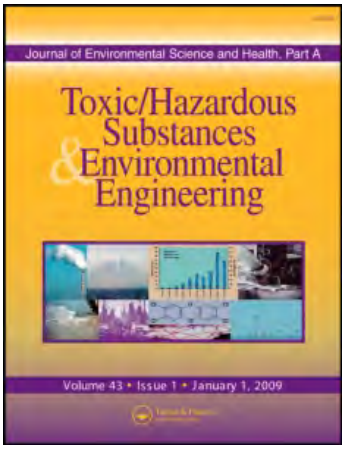

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Feasibility test of biological degradation of heterocyclic sulfur compounds in anaerobic state

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FEASIBILITY TEST OF BIOLOGICAL DEGRADATION OF HETEROCYCLIC SULFUR COMPOUNDS IN ANAEROBIC STATE

Key Words: Sulfolane, thiolane, anaerobic degradation, groundwater, biochemical methane potential

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ABSTRACT

Anaerobic biodegradability for sulfolane and thiolane was investigated in soil and anaerobically digested sludge. Biochemical methane potential was periodically quantified to assess biodegradability of microorganisms degrading the compounds prepared in the closed glass vessel. Relatively lower concentration of thiolane adopted in the test was hardly degraded in the soil. Moreover, its degradation was hindered in anaerobic digest sludge. In constrast, sulfolane was readily decomposed

in both the soil and the anaerobic sludge. It is concluded that subsequent occurrence hindered in anaerobic digest sludge. In constrast, sulfolane was readily decomposed in both the soil and the anaerobic sludge. It is concluded that subsequent occurrence of thiolane as one of intermediates generated from the reduction of sulfolane would retard the remediation of the concerned area polluted with sulfolane and thiolane.

INTRODUCTION

A biochemical methane potential (BMP) was employed to evaluate the feasibility of biodegradation of sulfolane and thiolane detected in Liquid Waste Treatment Facility (LWTF) in Brisbane, Australia. Approximately 6 hectares of the 240-hectare site have been impacted by an annual quantity of approximately 20,000 litres of a Sulfinol sludge over the last 20 years with careless disposal of sulfolane used in Sulfinol process to remove carbon dioxide from the air stream in an ammonia plant. In the following analyses of groundwater taken from the monitoring wells, sulfolane and thiolane have mainly been detected in the study area.

Sulfolane was regulated as toxic organic compound in US EPA report (Federal Register, 1991) and can be readily migrated through aquifer due to ion-dipole interaction with water molecules (Morrison and Boyd, 1987).

Thiolane is a malodorous heterocyclic sulfur compound. Although it is known to be moderate toxic, it could make an offensive effect against humans who lives closer to the site (i.e. vomiting, nausea, and headache) (Moschandreas et al., 1982; Bradstreet et al., 1985; Schmidt and Meyer-Schmidt, 1985; Coy, 1987). Boettcher et al. (1994) accomplished a feasibility test on biodegradability for 1000 mg/l of

sulfolane, by inducing aerobic bacteria, but aerobic heterotrophic bacteria could not use sulfolane as their carbon source. MITI (1987) confirmed that sulfolane is not biodegradable by microorganisms. However, Chou and Swatloski (1982) and Cowan and Stover (1984) investigated the biodegradability of sulfolane in petroleum refinery wastewater stream applying bench scale experiment. Sulfolane was biodegradable up to 200 mg/l without any inhibition in aerobic condition. Ying et al. (1994) has had three steps of biological degradation of sulfolane using Biological Activated Carbon (BAC) in aerobic condition. In their studies, the sulfolane was removed in a few days since BAC column was inoculated with petrochemical plant activated sludge. In pilot scale test, they applied groundwater contaminated with 3000 ppb of sulfolane into 6'L x 4" D of PVC column packed with Calgon F-400) and then sulfolane was significantly removed by approximately 100 ppb as fed 600 - 1500 ppb of sulfolane into reactor. Bagnall et al. (1984) investigated biological decomposition of sulfolane using Rotating Biological Contactor (RBC) at 11°C to 25^0C and pH 6.5 to 8.5. The concentrations of sulfolane introduced into the reactor ranging from 2365 to 2750 ppm at steady state were removed by 86 to 100 % after 8 to 22 days of run.

On the other hand, thiolane has been poorly studied on biodegradation even though it was detected from a number of landfill sites (Coy, 1987; Barber et al., 1988; Yasuhara et al., 1992; Yasuhara et al., 1993) as well as has been used as insecticide and herbicide (Afifi and Abdulla, 1977).

Most of works mentioned above have been devoted to biodegradability of sulfolane in aerobic condition and lack of information on thiolane degradability. This

paper contributes to investigate the feasibility of biological degradation of sulfolane and thiolane in anaerobic condition using soil innoculum and anaerobic municipal waste sludge in conjunction with biochemical methane potential technique which has been developed by Owens and Chynoweth (1993).

MATERIALS AND METHODS

Soil Innoculum

Subsurface soil innoculum was collected from the study area at depths ranging from 2 to 3 m, near water table, below the surface. In order to obtain soil samples in saturated zone, a Shelby tube (45cm L x 4.8cm I.D.) was pushed through soil once the water table was reached by excavator. Prior to sampling, the Selby tube was steam cleaned (Gerni 660 Turbo Laser, 2100 to 220 psi) and rinsed with 70% ethanol to prevent cross contamination.

Anaerobic Sludge

The sludge was obtained in cleaned and sterile glass bottles from anaerobic digestor at Oxyley wastewater treatment facility. The digestor has been operated at 35.6°C for 28 days of hydraulic retention time. The MLSS and MLVSS of the sludge were measured as 3430 and 2240 mg/l, respectively.

BMP (Biochemical Methane Potential)

The biodegradation of sulfolane and thiolane was examined in batch microcosms using the soil and anaerobic sludge innocula. Duplicate glass bottles (160 ml nominal volume, Wheaton) were used for the determination of biochemical methane potential (Owens and Chynoweth, 1993).

The stock solution of mineral salts, tracer metals and vitamin mixtures were prepared in filter sterilized (0.45 μm) groundwater as presented in Table 1, 2 and 3.

The filtered (0.45μm) groundwater containing mineral salts solution was sterilized again by autoclaving at 121°C and 15 psi for 15 min on the three consecutive days. Then, this mineral salts solution were spiked with 10 ml of stock solution of trace metals and vitamin mixtures each. Subsequently, the medium was amended with resazurin (0.0002 %, Sigma) as redox indicator (Kaspar and Tiedje, 1982) and followed by adding 0.6 g of L-cysteine hydrochloride (BDH) just before setting up serum vials. L-cysteine hydrochloride is generally used to remove dissolved oxygen in liquid phase. A 10 g of soil and anaerobic innoculum each were accommodated into serum bottle and then 90 ml of medium spiked with different concentrations of sufolane and thiolane were added into serum vials under an anaerobic environment using carbon dioxide and nitrogen (28.9 ± 0.2% and balanced nitrogen, BOC) as illustrated in Fig. 1.

Then, the vials were sealed with a PTFE-face butyl rubber septum and an aluminum crimp seal. The test was verified with positive controls of D-Glucose (BDH) and blank control.

Gas Analysis

The gas volume and composition were analyzed once a week for 3 months. A gas-tight syringe (Hamilton) fitted with a no. 25 sterile needle (Terumo) was used to take 100μl of gas sample in head-space of vials. The methane concentration was determined using Shimadzu GC-9A equipped with porapak Q column (220°C) and

TABLE 1
Mineral Salts [1 L of filtered (0.45 μm) groundwater] (Hobson, 1966)

Chemical names	quantity (g)
K_2HPO_4	3
KH_2PO_4	3
$(NH_4)SO_4$	6
NaCl	6
$MgSO_4 \cdot 7H2O$	1.23

TABLE 2
Trace Metals [1L of filtered (0.45 μm) groundwater] (Romli, 1993)

Chemical names	Quantity (g)
$FeCl_3 \cdot 6H_2O$	5
$MgCl_2 \cdot 6H_2O$	1
$MnCl_2 \cdot 6H_2O$	1
$CaCl_2 \cdot 2H_2O$	1
$CoCl_2 \cdot 6H_2O$	0.3
$NiCl_2 \cdot 6H_2O$	0.2
$CuSO_4 \cdot 5H_2O$	0.1
$ZnSO_4 \cdot 7H_2O$	0.1
H_3BO_3	0.1
$Na_2MoO_4 \cdot 2H_2O$	0.1
$AlCl_3 \cdot 6H_2O$	0.05

TABLE 3
Vitamin Mixtures [100 ml filtered (0.45 μm) groundwater]

Chemical names	Quantity (mg)
Biotin	20
Folic Acid	20
Pyridoyine Monohydrochloride	100
Riboflavin	50
Thiamin	50
Nicotinic Acid	50
Pantothenic Acid	50
4-Aminbenzoic Acid	50

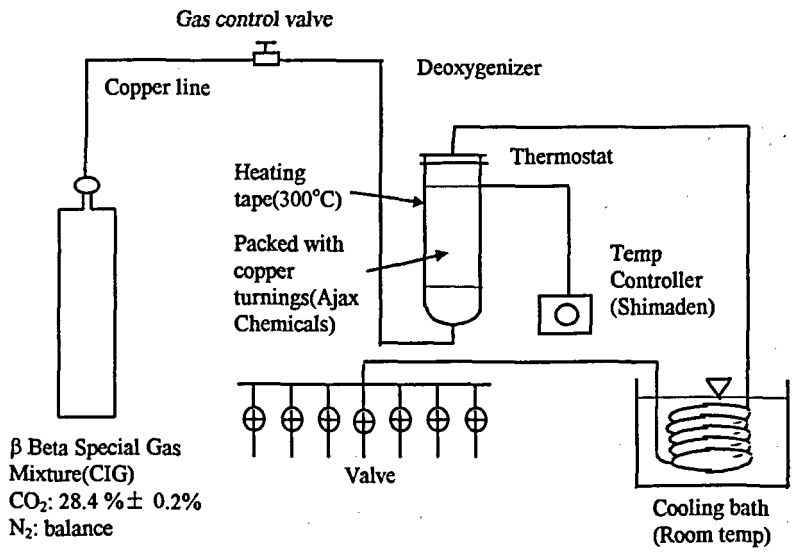


FIGURE 1

Schematic of a set-up of anaerobic environment prepared for BMP test

flame ionization detector (250°C). High purity of helium (CIG) was used as the carrier gas at a flow rate of 5 ml/min.

Calibrations have been made every 10 samples run using an external standard gas (Scotty I Analyzed Gases, CH_4=4.51, O_2=7.00, CO_2=15.01, CO=7.0 % in N_2 (v/v)±2 %). A volume of gas production was obtained using an apparatus as shown in Fig. 2.

The needle connected with Mininert syringe valve was passed through butyl rubber septum into headspace and then water column was pushed back into reservoir as much as a volume of gas produced in certain interval.

Calculations of Methane Production

An amount of methane produced at certain time was calculated as following relationshop;

V_{mt1}: $X_1V_1+X_1V_h-X_0V_h$

V_{mt2}: $X_2V_2+X_2V_h-X_1V_h$

V_{mtn-1}: $X_{n-1}V_{n-1}+X_{n-1}V_h-X_{n-2}V_h$

V_{mtn}: $X_nV_n+X_nV_h-X_{n-1}V_h$

where V_{mtn} is a volume of methane produced at certain time interval since test is initiated, X_n is concentration of methane (v/v) at t_n, V_n is a volume of headspace gas produced at certain interval at t_n, and V_h is the headspace volume of a vial.

Since the volume of methane produced in headspace was checked using an apparatus as presented in Fig. 2 and then converted to dry gas based on 1 atm and 0°C.

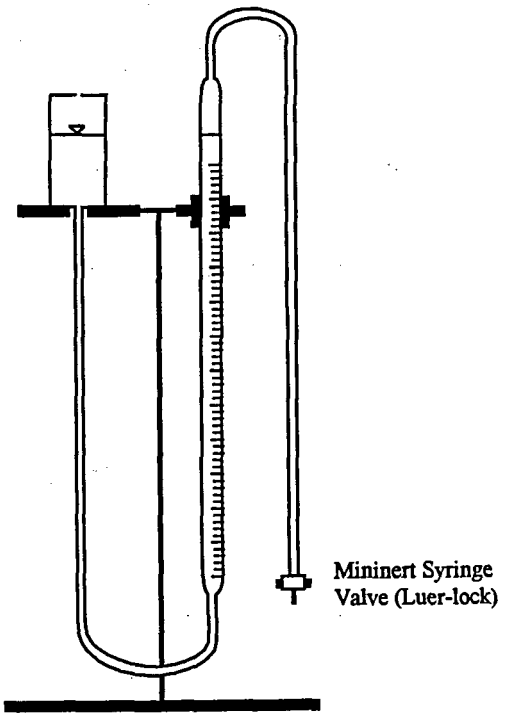


FIGURE 2

Schematic of apparatus for measurement of digested gas production

The converted dry gas volume was added up to the volume measured in the previous steps. The total of cumulative volume of methane at each time interval was corrected from the volume of gas produced from duplicate controls. The final corrected volume (m^3) was divided by a mass of MLVSS (kg) to assess the pure volume of methane produced by unit weight of biomass.

The degradation of control (e.g. glucose) were assumed to suit a first order rate of decay as presented by Owens and Chynoweth (1993).

$$y=Y_{\mu} x \{1 - \exp (-k x t)\}$$

where y is the cumulative methane yield at time t $\left[\frac{m^3}{kg}\right]$, Y_μ is the ultimate methane yield $\left[\frac{m^3}{kg}\right]$, and k is the first order decay constant $\left[\frac{1}{day}\right]$.

The parameters of Y_μ and k were estimated from the graph plotted time (t) against the cumulative yield (y).

RESULTS AND DISCUSSION

Innoculum

The characteristics of the innoculum as used in this study are shown in Table 4.

The measurement was conducted as directed in Standard Methods (1992) after the innoculum was mixed with aqueous nutrients. The amount of volatile solid of soil innocula was rather lower than that of anaerobic sludge even through total solids exceeds 16 times greater than that of anaerobic sludge.

The groundwater sample was collected from a well 2 km apart from the study area and then filtered with 0.45 μm. It was subsequently spiked with nutrients and then autoclaved. The groundwater sample used in this test was characterized as presented in Table 5.

ICPAES was used for quantitative analysis of inorganic compounds for groundwater samples. The sample was scanned for 42 elements and then determined the concentration against each of standard solution. The solution contains 21.4 ppm of TKN which shows neutral pH at 7.2. There have not been found any toxic

TABLE 4
Characteristics of Innoculum in the Slurry

	Total solids (%)	Volatile solids (% of TS)	Ash (% of TS)
Soil	5.604	45.7	54.3
Anaerobic sludge	0.348	59.5	40.5

Table 5
Characteristics of Reference Groundwater

Compounds	Concentration (mg/l)	Analytical instruments
THT	0	HPLC
$THTO_2$	0	Gas Chromatograph
S^{2-}	0.003	Hach DR/2000 spectrophotometer
SO_4	2.0	
DOC	0.001 %	
T-P	0	
PH	7.18	TPS 90-FLMV
TKN	21.35	Standard Methods
Ba	0.02	Spectro Analytical Instruments
Al	0.01	(ICPAES*), Model M+P
Ca	3.72	
Fe	0.48	
K	2.84	
Mg	4.64	
Mn	0.02	
Na	124	
P	0.04	
S	9	
Si	23.5	
Sr	0.14	

Inductively Coupled Plasma Atomic Emission Spectrophotomer

compounds, such as As, Cd, Cr, Cu, Hg, Pb, Ni, which may play a role to inhibit microorganism activities.

Soil Innoculum

The unit cumulative methane gas volume produced from degradation of thiolane and sulfolane was plotted against incubation time. In addition, the result obtained from glucose positive control for soil innoculum was also included as shown in Fig. 3A-D.

Fig. 3A shows that glucose has produced amount of methane while a blank can produce trace amount of methane due to lack of nutrients. At 40 days of incubation, the production of methane has been reached at approximately 350 cm^3 of accumulated methane and continued to be increased slightly. It simply indicates that microcosm in soil innoculum was verified to be able to use in this test as to distinguish biodegradability of sulfolane and thiolane. In addition, the estimates of ultimate yield and rate constant for the 1 g of glucose control on the soil and anaerobic sludge samples exhibited as presented in Table 6. The glucose controls for both soil and anaerobic sludge innocula showed slightly higher yields than expected, against a theoretical 373 cm^3, but were easily within a coefficient of variance of these values.

As shown in Fig. 3B, due to levels of lower concentrations of thiolane, small amount of methane can be only produced, nevertheless which means that thiolane can be degraded by anaerobic microbes. At 40.11 ppm of thiolane, amount of methane was linearly and increasingly produced during test of period while glucose was exponentially degraded. It may report that thiolane and its intermediate

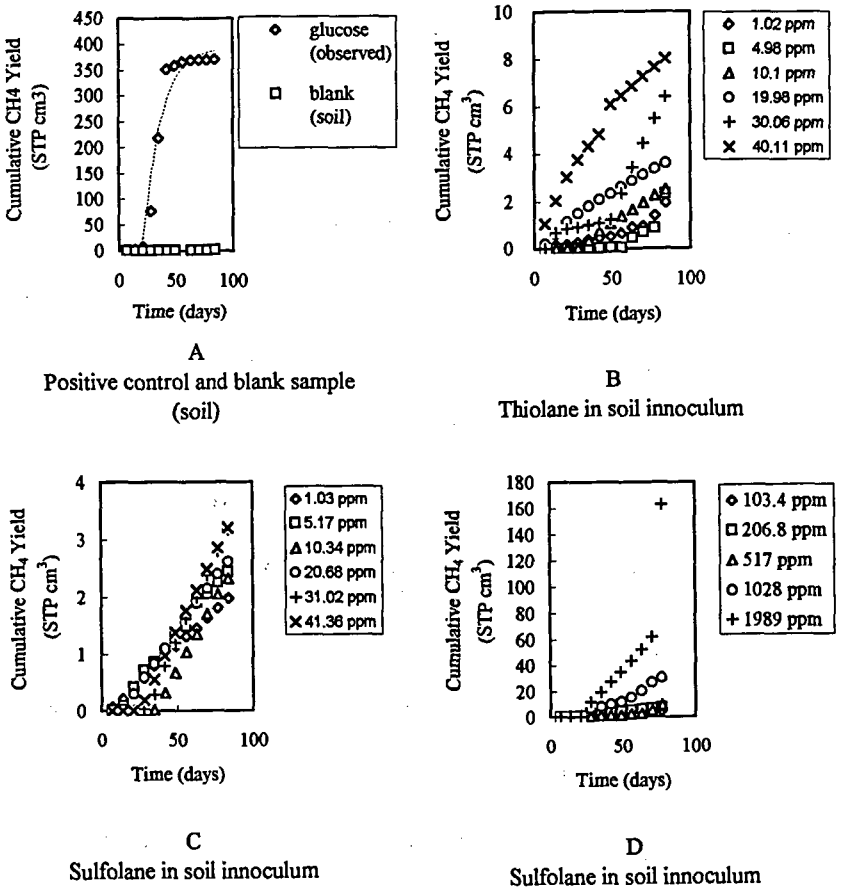


FIGURE 3

BMP cumulative methane production by soil innoculum for thiolane and sulfolane

TABLE 6

Estimates of Ultimate Methane Yield, Y_μ, and First Order Rate Constant, k, for Glucose. Values in Parentheses are Coefficients of Variances Obtained from Parameter Estimates

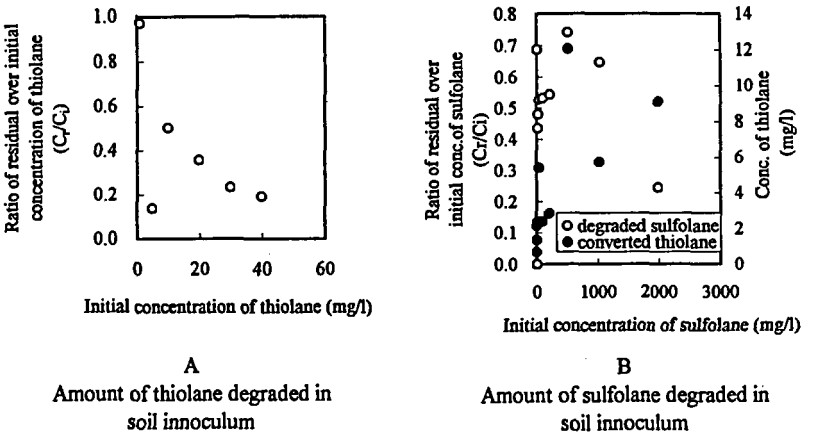
	Y_μ(cm^3 CH_4 produced)	K(d^{-1})
Soil	394.8(0.061)	0.065(0.204)
Anaerobic sludge	404.2(0.096)	0.054(0.283)

products would inhibit the activity of methane producing microorganisms. For sulfolane ranged at the same levels of concentration as tested for thiolane, relatively small amount of methane were obtained by a factor of 2 compared those produced for levels of thiolane. It is assumed that the pathway to produce methane from sulfolane would take more complex steps rather than from thiolane. At Fig. 3D, approximately 2000 ppm of sulfolane can still be degraded even though it has been lagged for approximately 30 days. Methane production for sulfolane was lineally increased with time in the same manner as observed for thiolane.

After a period of test, the residual concentrations were specified over initial concentration as presented in Fig. 4A-B.

It also verified that sulfolane would convert into thiolane. In general, thiolane was not significantly consumed at approximately 1 ppm, but it was remarkably degraded at 40 ppm with remaining only 20 % against initial concentration of thiolane. It reports that amount of carbon source can limit methane production rate as concentration has been diminished even though there may present potential inhibition in the beginning of incubation. In general, as shown in Fig. 4B, sulfolane has been increasingly degraded as the concentration was increased.

These trends were well consistent with the results obtained for methane gas production as presented in Fig. 3C-D. Fig. 4B indicates that levels of thiolane were transformed from sulfolane degradation. Regardless of concentration of sulfolane tested, the converted thiolane concentration showed less than approximately 5 ppm for 200 ppm of sulfolane, while it varied up to 12 ppm at 2000 ppm of sulfolane.



A
Amount of thiolane degraded in soil innoculum

B
Amount of sulfolane degraded in soil innoculum

FIGURE 4

Amount of thiolane and sulfolane degraded by soil innoculum during test of period

Schrementi and Meganathan (1986, 1987) demonstrates that thiolane can be occured from degradation of tetrahydrothiophene 1-oxide by facultative anaerobic bacteria. Therefore, thiolane detected in the study area would be generated as the process described above.

Anaerobic Sludge

Fig. 5A shows the result obtained for glucose control and blank sample. The innoculum seeded with anaerobic sludge produced slightly higher amount of methane compared to that generated from soil microcosm, which means that anaerobic sludge has a stronger microbial activity to produce an unit amount of methane.

Fig. 5B-D show accumulated unit methane production for thiolane and sulfolane stimulated by anaerobic sludge. In comparison with soil innoculum for degradation

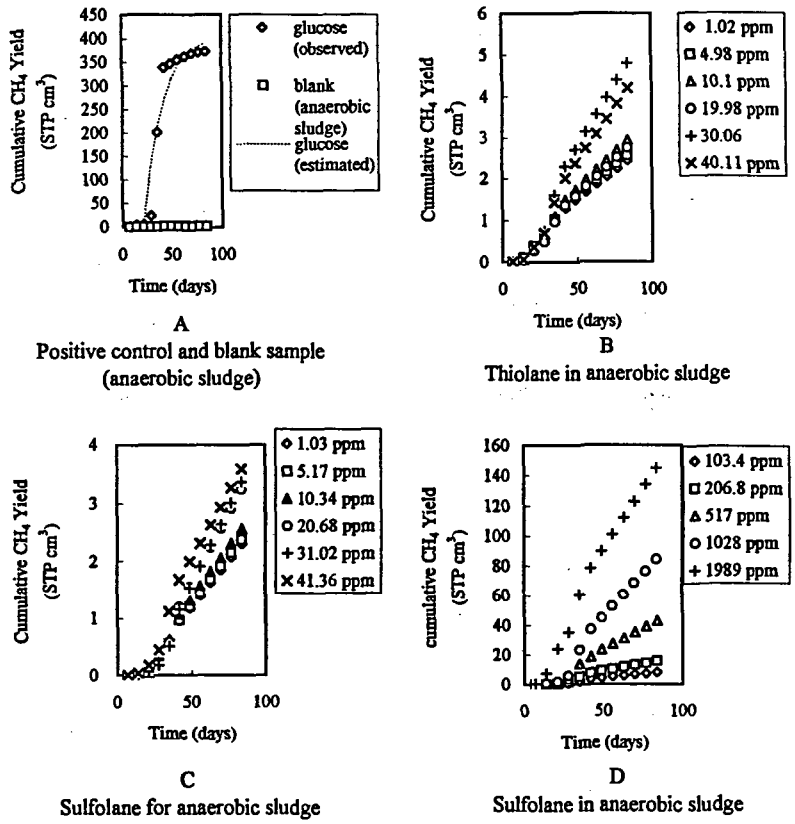


FIGURE 5

BMP cumulative methane production by anaerobic sludge for thiolane and sulfolane

of thiolane, the methane production was slightly decreased for application of anaerobic sludge. It indicates that thiolane would give a toxic effect on microcosms sustained in anaerobic sludge in the beginning of adaptation period whereas the microorganisms in soil might be more strongly resisted against of thiolane as they produce slightly higher amount of methane.

In Fig. 5C-D, the methane gas production for higher concentration of sulfolane was increased as high as by a factor of 2.3 than that obtained from introduction of

soil innoculum. Conversely, it means that sulfolane is more adaptable to be degraded by anaerobic sludge on the contrary to thiolane. At the end of test, the concentrations remained in the sample vessels were quantified and converted constituents were also characterized in the same manner as accomplished in biodegradation test for soil innoculum as shown in Fig. 6A-B.

After test of period, the amount of thiolane was still remained by a factor of approximately 3 higher (Fig. 6A) than levels of concentrations left in the soil innoculum as shown in Fig. 4A. The differences observed for residual concentration of thiolane between soil and anaerobic microcosms were well corresponded with the differences obtained from the accumulated methane production between them as indicated in Fig. 3B and 5B.

As presented in Fig. 5D, an amount of residual sulfolane was generally decreased as the initial concentration of sulfolane increased especially from concentrations of 206.8 mg/L. At more enhanced concentration from 500 ppm of sulfolane, it was remained at relatively same levels of residual concentrations except that 1989 ppm of sulfolane was left at slightly great extent. In general, sulfolane adapted in anaerobic sludge was more significantly degraded compared to that innoculated into soil mixed culture.

CONCLUSIONS

Through BMP test employing the soil and anaerobic sludge, the sulfolane was readily degradable, while thiolane was rarely decomposed in both the soil and the

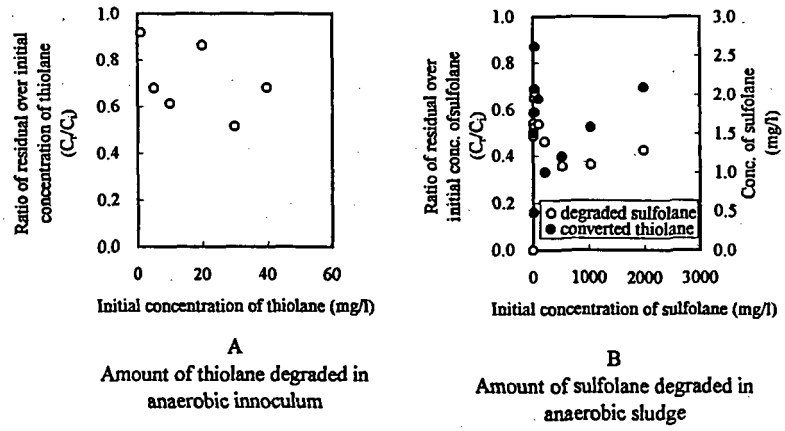


FIGURE 6

Amount of thiolane and sulfolane degraded by anaerobic sludge during test of period

anaerobic sludge. Furthermore, the introduction of thioalne into the anaerobic sludge ascribed to a possible inhibition against anaerobic microorganism. It demonstrated that there was no found any significant difference in the concentration inoculated into the vials accommodating anaerobic culture.

It was concluded that there might be a preexisted-mixed culture of microbial population to be able to degrade sulfolane in anaerobic condition. However, a possible reduction of sulfolane into thiolane (Schrementi and Meganathan, 1986, 1987) can retard degradation of sulfolane due to the inhibition of thioalne as demonstrated previously and also given evidence by Afifi and Abdulla (1977).

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Nutrient Stimulation of Sulfolane Biodegradation in a Contaminated Soil from a Sour Natural Gas Plant and in a Pristine Soil

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NUTRIENT STIMULATION OF SULFOLANE BIODEGRADATION IN A CONTAMINATED SOIL FROM A SOUR NATURAL GAS PLANT AND IN A PRISTINE SOIL

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ABSTRACT

Natural gas in western Canada can contain up to 35% H_2S. The Sulfinol® process for sour gas treatment makes use of sulfolane and an amine to remove H_2S and other sour components from natural gas. Sulfolane has leached into groundwaters at sour gas treatment plant sites, and poses a risk for off-site contamination. Sulfolane biodegradation was monitored in shake-flask cultures and air-sparged microcosms inoculated with uncontaminated topsoil or with sulfolane-contaminated soil obtained near a Sulfinol process building at a sour gas treatment facility in western Canada. For both soils, supplementation with a source of fixed nitrogen stimulated sulfolane biodegradation. Topsoil cultures and microcosms were only slightly affected by the addition of phosphate. Contaminated soil microcosms and cultures were stimulated by phosphate addition, but not to the same degree as by the addition of nitrogen. For these cultures and microcosms, amendment with both fixed nitrogen and phosphate produced an additive effect. It was possible to predict the nutrient requirements of air-sparged microcosms inoculated with each soil type using shake-flask cultures. Shake-flask cultures require less time and effort and fewer materials than the more complex air-sparged soil microcosms, and will be useful for large-scale experiments to predict the nutrient supplements required for bioremediation of sulfolane-contaminated sites.

Keywords: Biodegradation, sulfolane, sour natural gas, aerobic soil microcosm

INTRODUCTION

Some natural gas reservoirs in Alberta contain up to 35% H_2S, which is responsible for corrosion of iron-containing materials and concrete, and for a few deaths in Canada and the United States each year. Combustion of sulfur-containing compounds can also contribute to air pollution [1]. Removal of H_2S and other gas souring compounds, such as mercaptans, COS, CS_2, and CO_2, from oil and natural gas is critical for the industry.

The Sulfinol® gas sweetening process utilizes an amine chemical solvent and sulfolane as a physical solvent. It is most effective when the H_2S:CO_2 ratio is ≥1, and the sour gas has a relatively high acid gas partial pressure [2-4]. This process has been used in western Canada since its inception in the early 1960s [5]. At some Sulfinol plant sites, spills, landfilling and leaching from unlined process water storage ponds have introduced sulfolane into the soil and groundwater. Sulfolane is completely miscible with water [6] and has a very high mobility in soil [7], therefore its attenuation in contaminated aquifers is likely to depend on microbial metabolism. Detection of microorganisms active against contaminant compounds is useful for predicting the biodegradation potential at a contaminated site, and laboratory evaluations can be helpful for predicting the nutrient requirements of these organisms.

Fedorak and Coy [8] used soil columns, based on the landfarming chambers described by Mueller *et al.* [9], to examine aerobic sulfolane degradation in a field-like situation, and compared the biodegradation of sulfolane in the soil columns with activity observed in parallel shake-flask cultures. This work demonstrated that aerobic sulfolane-degrading microbial communities exist at sulfolane-contaminated sites, and that amendment with sources of N and P can increase the rate of sulfolane biodegradation and decrease the lag time before degradation commences. Greene *et al.* [10] demonstrated that sulfolane can be degraded in 2.5-l microcosms that contained sediment and groundwater, provided that the appropriate nutrient supplementation was provided. These authors also demonstrated that the required N and P supplementation could be predicted using shake-flask cultures, which require less time and fewer resources to set up and monitor.

This investigation was done to expand on initial studies of sulfolane biodegradation in soils [8, 10]. The initial research done by Fedorak and Coy [8] was limited by the analytical method for sulfolane monitoring. Using the aqueous injection GC method reported by Greene *et al.* [11], more frequent monitoring of shake-flask cultures and air-sparged microcosms was possible. The air-sparged microcosm method, originally described by Mueller *et al.* [9], was designed to imitate

landfarming or biopile remediation in the field, therefore this research will provide useful information for the design of pilot-scale sulfolane bioremediation experiments in the field. Shake-flask cultures were used to predict the microbial activity and nutrient requirements required in the air-sparged microcosms. The development of sulfolane-degrading microbial communities, and the number of total cultureable heterotrophs, were monitored to determine whether these numbers were related to sulfolane removal from the air-sparged microcosms.

MATERIALS AND METHODS

Soil samples and experimental design

Sulfolane-contaminated soil (called contaminated soil in this paper) was sampled from a depth of 7.5 m next to a Sulfinol plant building in western Canada. It was composed of sandy clay till (Table 1). The pristine topsoil sample was a commercially available composting product from Olds College (Olds, AB). Before samples were used, objects >0.5 cm were removed and the remaining materials were homogenized.

Nutrient supplementation for shake-flask cultures and air-sparged microcosms was calculated based on the C:N:P ratio of 100:5:1 [12], with respect to the carbon source described. N was added from a stock solution of NH_4NO_3; P was added as an aqueous solution of 1:1 (w w^{-1}) K_2HPO_4 and KH_2PO_4.

Shake-flasks inoculated with contaminated sediment were tested under the following conditions: N, P, or N and P supplementation calculated for sulfolane present in the cultures, and N, P, or N and P supplementation calculated for total carbon present in the cultures, and a sterile control. Cultures were inoculated with 50 g soil in 200 ml water. Analyses of the supernatants showed that the contaminated soil cultures initially contained 160 to 170 mg sulfolane l^{-1} from the soil. Topsoil cultures were spiked with an initial sulfolane concentration of 200 mg l^{-1}. The sterile control cultures were autoclaved for 30 min, then poisoned with 250 µl 37% v v^{-1} formaldehyde. Cultures were incubated shaking at 200 rpm, at room temperature (22°C).

Air-sparged microcosms (Figure 1) were designed as outlined previously [8]. Topsoil and contaminated soil were

Table 1. Soil characteristics. Topsoil was obtained commercially and the contaminated soil was obtained near a Sulfinol process building, from a depth of 7.5 m[a].

Sample	Sulfolane in soil (mg kg^{-1})	Nutrients in soil (%)			Description of soil
		C	N	P	
Topsoil	0	23.1	1.30	0.13	commercially available topsoil, compost, rich in organic matter
Contaminated soil	430	2.23	0.08	0.04	sandy clay till, 5% coarse fragments, strong odor

[a] Soil and information was provided by B. Samis, Komex International Ltd., Calgary, AB.

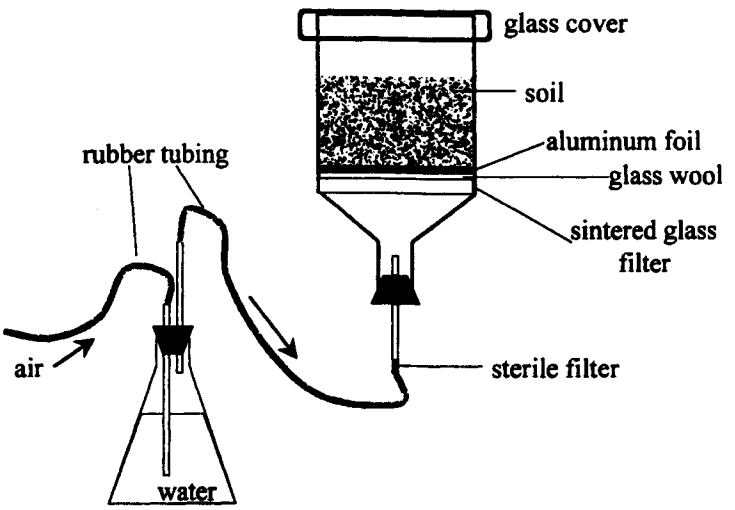

Figure 1. Diagram of an air-sparged microcosm used to simulate an aerated field situation in the laboratory. Water was used to moisten air entering the microcosms and prevent the soil from drying.

used individually as inocula. Topsoil microcosms contained 1.5 kg soil and these were studied before the contaminated soil was collected. The small amount of contaminated soil obtained allowed only 0.5 kg soil to be used in each air-sparged microcosm. Samples from the microcosms containing different soils were treated identically to minimize differences due to inoculum size; in particular, moisture and aeration of all samples was closely monitored to ensure uniformity. Topsoil was modified with either 200 mg sulfolane kg^{-1} or 1 g sulfolane kg^{-1} (initial concentration). The contaminated soil already contained approximately 400 mg sulfolane kg^{-1}. Four microcosms were incubated for each soil type: (a) unsupplemented, (b) N-supplemented, (c) P-supplemented, or (d) N- and P-supplemented. Microcosms consisted of a 3-l Pyrex Buchner funnel (Kimble), lined with glass wool and covered with perforated aluminum foil. Funnels were covered with a Pyrex dish. The bottom of each funnel was attached to an air supply (Figure 1). Microcosms were sampled by mixing, then removing 7 g soil.

Sulfolane extraction from soil

Sulfolane was extracted from 1-g soil samples by suspending the sample in 5 ml water, then centrifuging (890 x g for 10 min). The aqueous layer was recovered and the soil sample was extracted in the same manner with another 5 ml of water. The aqueous portions were combined and analyzed by gas chromatography. The efficiency of extraction ranged from 90% to 102%. These extracts were also used to measure water-extractable total organic carbon.

All values for the air-sparged microcosms were reported per g soil dry weight. The dry weight was determined by calculating the weight loss from approximately 1 g moist soil samples after heating at 105°C for 7 d. Water extraction was performed on moist soil samples, therefore the reported sulfolane concentrations represented both sulfolane in trapped pore water and sulfolane associated with dry soil.

Sulfolane and total organic carbon analysis

Sulfolane was quantified using direct aqueous injection into a gas chromatograph [10]. Total organic carbon analyses were done using an Ionics model 1505 Programmable Carbon Analyzer.

Enumeration of bacteria

Total cultureable heterotrophs and sulfolane-degrading bacteria were estimated by plating serial 10-fold dilutions of 1 g soil on PAT medium [13]. Total colony counts were done after 14 d; sulfolane-degrading colonies, which were surrounded by characteristic yellow halos, were counted at 21 to 28 d. Colony count results were reported as "colony forming units" (CFU).

Determining rate constants

Sulfolane biodegradation rates were determined using the method of Metcalf and Eddy [14]. All sulfolane degradation was found to follow zero-order kinetics more closely than first order kinetics, therefore the zero-order rates are given in this report. Lag time was defined as the time between the beginning of each incubation and the first sampling time when a decreased sulfolane concentration was observed, with continual decreases in sulfolane concentrations being observed thereafter.

Chemicals

Chemicals were reagent grade, purchased from Aldrich (Milwaukee, WI), Sigma (St. Louis, MO) or Fisher (Fair Lawn, NJ) unless otherwise indicated. Agar was obtained from Difco (Detroit, MI). Sulfolane (99%) was obtained from Aldrich. Formaldehyde solution was purchased from Fisher as a 37% w w^{-1} solution in water and 10 to 15% methanol.

RESULTS AND DISCUSSION

Air-sparged microcosms were used to predict the sulfolane degradation potential in contaminated soils being treated by landfarming or with a biopile-type bioremediation strategy [15]. Shake-flask cultures were used to predict the nutrient requirements in the more complex air-sparged microcosms. The topsoil that was used as a model soil had not previously been exposed to sulfolane but contained a high level of natural organic matter. It was hypothesized that this soil would harbor a large, diverse microbial community, and that some microorganisms therein would degrade sulfolane. Contaminated soil was used to study a system that had previously been exposed to sulfolane.

Development of sulfolane extraction method

Because of the high water solubility and negligible interaction between sulfolane and different types of soils [7], it was hypothesized that sulfolane could readily be extracted from soil samples with water. One-gram samples of sand, greenhouse soil and uncontaminated aquifer sediment, each spiked with 320 μg of sulfolane, were used to test the efficiency of the aqueous extraction method. The recoveries in triplicate determinations with the three soil types were 102 ± 2.9%, 82 ± 5.3% and 104 ± 5.3%, respectively. Sulfolane does not interact significantly with soil organic matter [7], therefore the relatively poor recovery from greenhouse soil likely reflected its capacity to retain sulfolane-containing water within porous components such as vermiculite.

In a subsequent experiment, the effects of contact time of sulfolane in soil, soil sample size, and the number of water extractions were studied. The highest recoveries were obtained when 1-g samples were extracted (90% and 102% recoveries, Table 2). Two extractions were adequate to

Table 2. Evaluation of procedures for the aqueous extraction of sulfolane from air-dried uncontaminated aquifer sediment spiked with 1 mg sulfolane g^{-1} of soil.

Time sulfolane was in contact with soil before extraction (h)	Amount of soil sample extracted (g)	Number of 5-ml aqueous extractions	Cumulative recovery of sulfolane (%)
24	1	1	65
		2	90
		3	90
	2	1	55
		2	72
		3	72
	3	1	51
		2	65
		3	74
48	1	1	67
		2	102
		3	102
	2	1	56
		2	77
		3	89
	3	1	48
		2	74
		3	82

achieve these recoveries. With larger samples, more extractions were needed to enhance the recoveries. The extraction efficiency appeared to increase when sulfolane was in contact with the soil for 48 h, rather than 24 h (Table 2). However, the reason for this is unknown. Based on these results, the extraction procedure using two, 5-ml extractions (outlined in the Materials and Methods) was adopted for this investigation. This was a vast improvement over the methylene chloride extraction used previously [8]. Headley *et al.* [16] used an aqueous extraction technique for the analyses of sulfolane in plants in a wetland near a sour gas processing facility in western Canada, and reported an extraction efficiency of 80 ± 12%.

Shake-flask cultures

Two sets of nutrient concentrations were tested: "low N and P" with sufficient N and P to account for the carbon present in sulfolane only, and "high N and P" with sufficient N and P to account for the total carbon present in the samples. The topsoil contained 23% C, 1.3% N and 0.13% P (Table 1). Considering a C:N:P ratio of 100:5:1, the topsoil contained 113% and 56% of the required N and P, respectively, however these nutrients may not have been bioavailable.

Addition of the low level of N to topsoil stimulated sulfolane biodegradation; the lag time before sulfolane removal was halved from 6 d for unsupplemented or low P-supplemented cultures to 3 d for low N-supplemented or low N- and P-supplemented cultures (Table 3). Supplementation of the cultures with higher levels of nutrients resulted in longer lag times before the commencement of biodegradation (Table 3). No net loss of sulfolane from the sterile control was observed over the incubation time. Overall, for biodegradation in the topsoil shake-flask cultures, the lag time was shorter with low level N supplementation and the rate of sulfolane biodegradation increased with the high level P supplementation (Table 3).

The total carbon in the contaminated soil was 2.23% (Table 1) and sulfolane present at 430 mg kg^{-1} represented 14% of the total carbon. The amount of N and P in these cultures represented approximately half the N and P suggested by a C:N:P of 100:5:1. Shake-flask cultures supplemented with low N or low N and P demonstrated a lag time of 27 d, and a sulfolane degradation rate of 0.58 and 0.44 mg l^{-1} h^{-1}, respectively (Table 3). Unsupplemented and low P-supplemented cultures both had a lag time of 77 d, with degradation rates of 0.19 and 0.15 mg l^{-1} h^{-1}, respectively (Table 3). Supplementing with high N and P shortened the lag time to 2 d, and sulfolane was completely removed from shake-flask cultures at a rate of 1.9 mg l^{-1} h^{-1}. Removal of sulfolane from cultures supplemented with the high level of N occurred at 0.58 mg l^{-1} h^{-1}, after a lag time of 2 d. Sulfolane was not removed from cultures supplemented with high levels of P (Table 3) or the sterile control culture over an incubation period of 145 d. It is not clear whether high levels of P inhibited sulfolane degradation directly, or indirectly, possibly through stimulating removal of other organic carbon compounds at the expense of N or other nutrients required for sulfolane degradation. Further experimentation would be

Table 3. Removal of sulfolane from shake-flask cultures inoculated with topsoil or with contaminated soil. Low N or P refers to sufficient N or P to account for the sulfolane-carbon in a sample, according to the C:N:P ratio of 100:5:1. High N or P refers to sufficient N or P to account for the total carbon in a sample. Samples were incubated at room temperature.

Soil sample used	Type of supplementation	Lag time (d)	Biodegradation rate (mg l^{-1} h^{-1})[a]
Topsoil	none	6	1.5
	low N	3	1.5
	low P	6	1.6
	low N + P	3	1.8
	high N	24	0.14[b]
	high P	7	2.3
	high N + P	7	2.1
Contaminated soil	none	77	0.19
	low N	27	0.64
	low P	77	0.15
	low N + P	27	0.44
	high N	2	0.58
	high P	>145[c]	0.0[c]
	high N + P	2	1.9

[a] The biodegradation rate was calculated using only 3 data points as biodegradation of sulfolane occurred quickly in these cultures once the lag time was over.
[b] The biodegradation rate was calculated using 5 data points; in this sample microbial activity against sulfolane was much slower than in any of the other samples.
[c] No biodegradation of sulfolane was observed in this culture.

required to resolve this issue.

Overall, P supplementation was of little importance for sulfolane removal from the contaminated soil shake-flask cultures unless sufficient N was present (Table 3), whereas N supplementation was required to stimulate degradation of this compound. Although the soil contained less N and P than suggested by the ratio of 100:5:1 for utilization of all of the organic carbon, sulfolane was removed from the unsupplemented culture. This suggests that some of the contaminating organic compounds in this soil were more recalcitrant to microbial degradation than sulfolane.

Air-sparged microcosms

The same nutrient amendments were monitored in both the contaminated soil and the topsoil: (a) no added N or P, (b) N-supplemented, (c) P-supplemented and (d) N- and P-supplemented. No sterile control microcosms were monitored. However, there was no loss of sulfolane from the shake-flask sterile control cultures, and the boiling point of sulfolane is 285°C [6] therefore, it was unlikely that sulfolane would be lost from the microcosms by evaporation. The system used for these experiments (Figure 1) simulated biopile remediation [15].

Topsoil in air-sparged microcosms

The topsoil in the air-sparged microcosms was supplemented with low N or low P (calculated to account for the carbon present due to sulfolane) because the corresponding shake-flask cultures had shorter lag times with the low level of N or P than with high level of N or P (Table 3). Sulfolane biodegradation commenced in N-supplemented and N- and P-supplemented microcosms after 9 d of incubation (Figure 2B, D). The rate of sulfolane removal from these microcosms was 0.31 and 0.85 mg kg^{-1} h^{-1}, respectively (Table 4). These microcosms were refed 200 mg sulfolane kg^{-1} at 14 d. This sulfolane was degraded to below detectable levels by 15 d in the N-supplemented microcosm (Figure 2B) and by 16 d the N- and P-supplemented microcosm (Figure 2D). Microcosms were reamended with sulfolane to stimulate a further increase in the sulfolane-degrading community. The microcosms were amended with 1 g sulfolane kg^{-1} at 16 d, and with no appreciable lag time, the sulfolane was removed to below detectable levels by 18 d. At 24 and 28 d, the microcosms were refed with 1 g sulfolane kg^{-1}; both times this amount of sulfolane was removed within 2 d of refeeding the microcosms (Figure 2B, D).

Microcosms that were not supplemented with nutrients or were supplemented with P only demonstrated lag times of 15 d and 14 d, respectively (Figure 2A, C), and degradation rates of 0.56 and 0.35 mg kg^{-1} h^{-1}, respectively (Table 4). After the sulfolane was removed (at 20 d), both microcosms were refed on day 22 with 1 g sulfolane kg^{-1}. After a lag time of 3 d in both microcosms (31 d after the initial inoculation), sulfolane was completely removed from the P-supplemented microcosm over the following 6 d and the unsupplemented microcosm over a period of 10 d; sulfolane removal was complete in the microcosms after a total of 38 d and 41 d of incubation, respectively (Figure 2A, C).

No sulfolane-degrading bacteria (<10 CFU g^{-1} soil) were detectable in any of the topsoil-containing microcosms at the

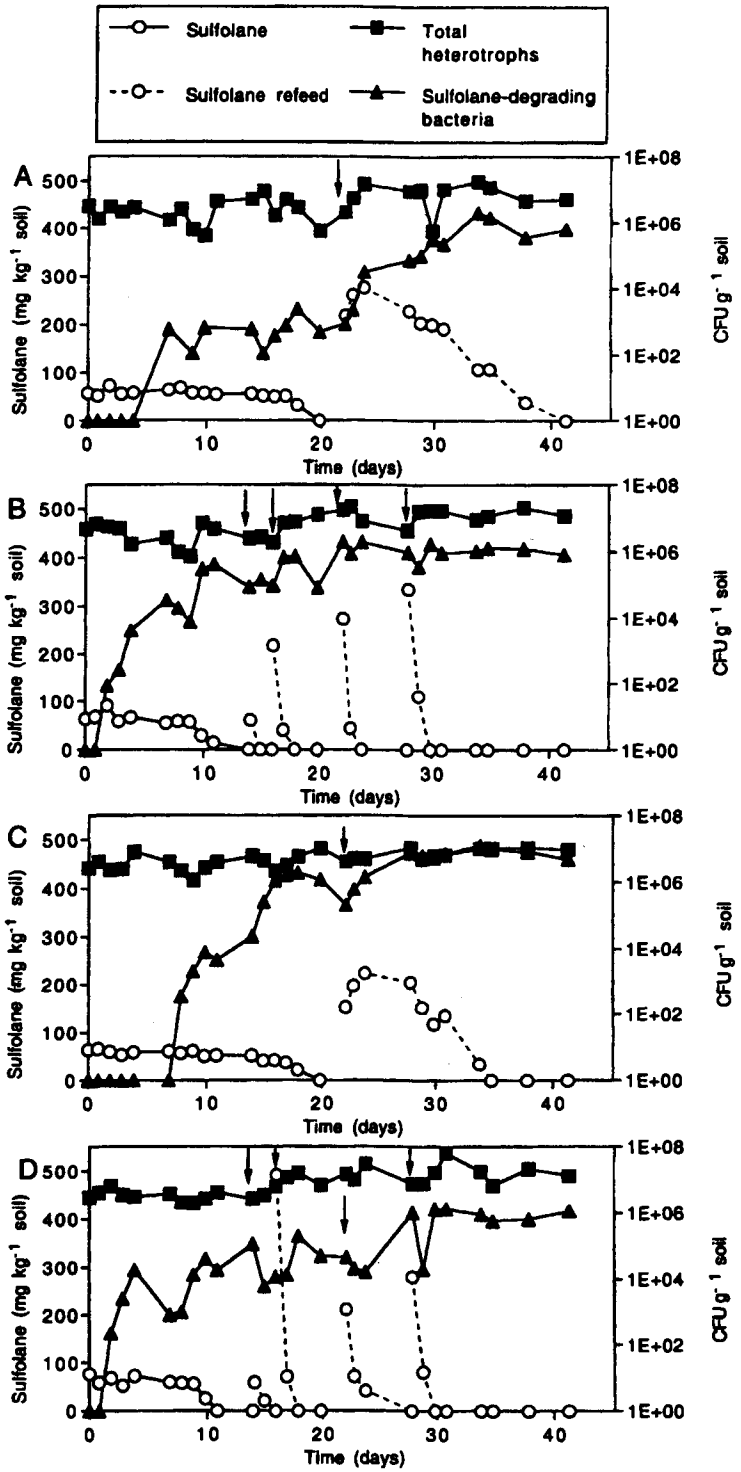

Figure 2. Removal of sulfolane from air-sparged microcosms inoculated with topsoil and incubated at room temperature, and the concurrent changes in total heterotrophic and sulfolane-degrading microbial populations. N and/or P were added to account for the carbon from sulfolane in a sample, according to the C:N:P ratio of 100:5:1. Arrows indicate when microcosms were refed with N, P and sulfolane. Either 200 mg sulfolane kg^{-1} or 1 g sulfolane kg^{-1} were added. A. Unamended microcosm. B. N-supplemented microcosm. C. P-supplemented microcosm. D. N- and P-supplemented microcosm.

Table 4. Removal of sulfolane from air-sparged microcosms inoculated with topsoil or contaminated soil, and the total increase in the heterotrophic and sulfolane-degrading microbial populations. Microcosms were incubated at room temperature.

Soil used	Type of supplmentation	Lag time (d)	Initial degradation rate (mg kg^{-1} h^{-1})	Initial change in total heterotrophs (CFU g^{-1} soil)	Initial change in sulfolane degraders (CFU g^{-1} soil)
Topsoil[a]	none	15	0.56	ND[b]	10^3
	N	9	0.31	ND[b]	10^5
	P	14	0.35	10^1	10^6
	N and P	9	0.85	ND[b]	10^5
Contaminated soil[c]	none	63	0.18	10^2	10^5
	N	56	0.32	10^3	10^4
	P	63	0.19	10^3	10^4
	N and P	35	0.96	10^4	10^4

[a] Sufficient N or P to account for the sulfolane-carbon in each sample, according to the C:N:P ratio of 100:5:1, was added at the same time as the sulfolane.
[b] ND: no change in cell numbers was detected.
[c] N and/or P were initially added at concentrations sufficient to account for the sulfolane-carbon in a sample (i.e. the "low" level) the appropriate microcosms were amended to contain N or P to account for the total carbon (i.e. the "high" level) in the samples after 32 d of incubation.

beginning of this experiment (Figure 2). After sulfolane amendment, N-supplemented and N- and P-supplemented microcosms developed sulfolane-degrading communities within 2 d (Figure 2B,D); 7 d before sulfolane biodegradation was detectable. Removal of the initial dose of sulfolane resulted in the development of 10^5 CFU g^{-1} soil (Table 4). In both microcosms, the population was first detected at 10^2 to 10^3 CFU g^{-1} soil (dry weight); this population increased steadily to approximately 10^6 to 10^7 CFU g^{-1} soil. At this point the numbers remained stable for the remainder of the incubation, although sulfolane was added after this stable population had been reached (Figure 2B,D). Over the 41-d incubation period, the number of total cultureable heterotrophs in all four of the topsoil-containing microcosms remained stable, at approximately 10^7 to 10^9 CFU g^{-1} soil (dry weight). The topsoil-containing microcosms had likely reached a population maximum before the experiment began, therefore although the proportion of sulfolane-degrading bacteria increased during the experiment, the total heterotrophic population did not increase likewise. The physical niches available for bacterial growth, and the rate of diffusion of O_2, water, substrate, or other essential factors may have limited total microbial growth to this level in the topsoil.

Biodegradation of sulfolane began after a longer lag time in the unsupplemented and P-supplemented microcosms. The sulfolane-degrading bacterial population of the P-supplemented microcosm increased significantly, to approximately 10^6 CFU g^{-1} soil (dry weight), by the end of the removal of the initial dose of sulfolane (Figure 2C, Table 4). Little increase in the numbers of either the sulfolane degraders or the total heterotrophs was observed during the removal of the second dose of sulfolane in this microcosm (Figure 2C). The change in the numbers of sulfolane-degraders in the unsupplemented microcosm was 1000-fold less than that in the P-supplemented microcosm, although the degradation rates differed by only about 60% (Table 4). The removal of the initial dose of sulfolane from the unsupplemented microcosm resulted in the development of a sulfolane-degrading population of approximately 10^3 CFU g^{-1} soil (Table 4). In contrast, the larger numbers of sulfolane-degraders (10^5 to 10^6 CFU g^{-1}) were observed in the other three microcosms early during the incubation period (Table 4). The numbers in the unsupplemented microcosm reach these elevated levels after the removal of the second dose of sulfolane was nearly complete (Figure 2A).

Overall, no nutrient amendment was required for sulfolane biodegradation to occur in the topsoil (Figure 2A). However, amendment with N decreased the lag time before sulfolane biodegradation commenced (Table 4), and the addition of P also appeared to stimulate the number of sulfolane degraders (Table 4). The biodegradation rate did not follow the same trend as the lag times before sulfolane degradation commenced, being faster in the unsupplemented microcosm than in the N- or P-supplemented microcosms (Table 4). The effects of amending the topsoil-containing microcosms with both N and P were not additive. Topsoil-containing microcosms supplemented with N and P showed no difference in lag time before sulfolane biodegradation commenced than microcosms supplemented with N alone, although the degradation rate was faster in the N- and P-supplemented microcosm.

Contaminated soil in air-sparged microcosms

Contaminated soil taken from near a Sulfinol plant building was initially supplemented with enough N or P to account for the carbon contributed by sulfolane (i.e. the "low" level), however after 32 d of incubation, no loss of sulfolane was observed (Figure 3).

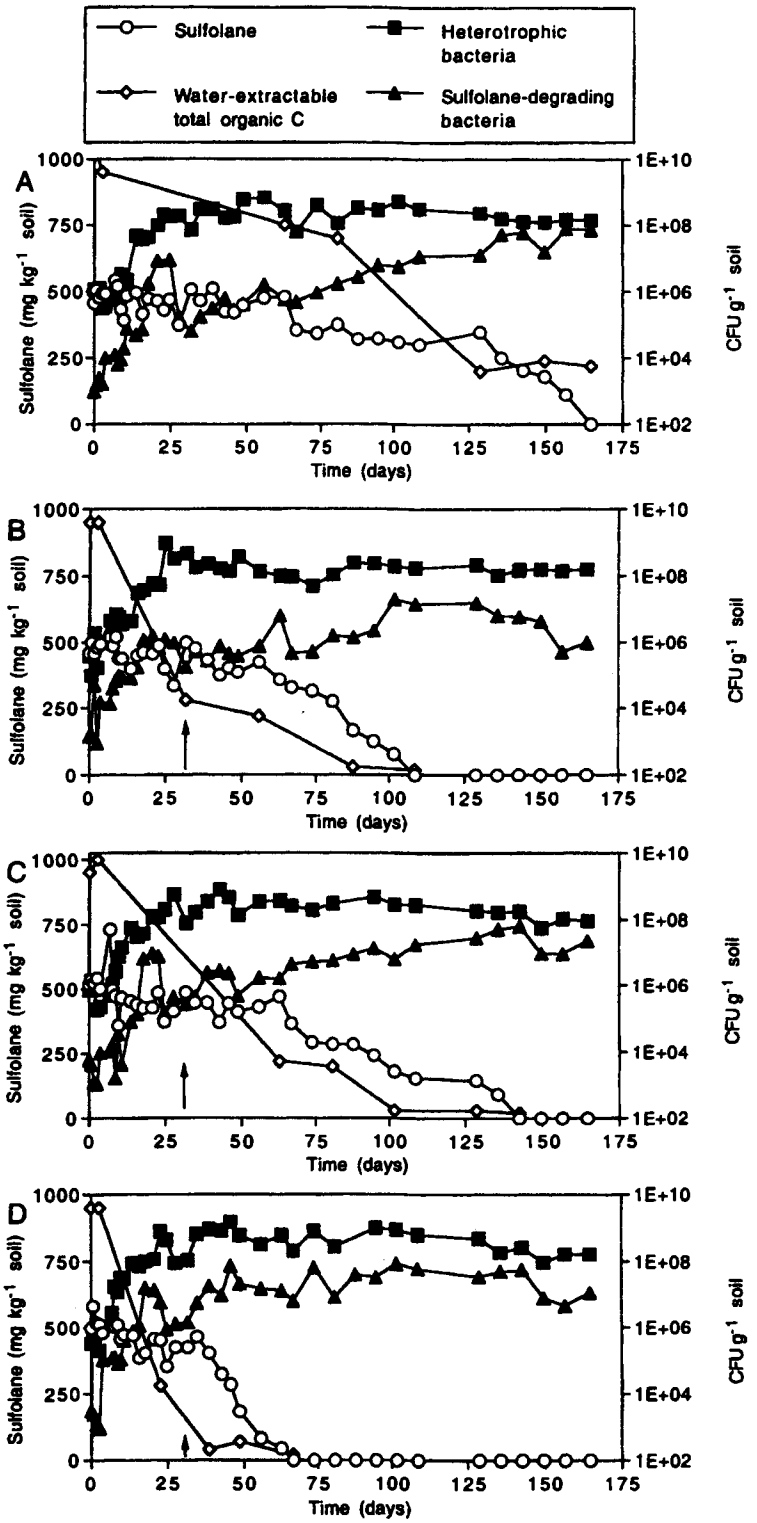

Figure 3. Removal of sulfolane from air-sparged microcosms inoculated with soil from near a Sulfinol process building and incubated at room temperature, and the concurrent changes in total heterotrophic and sulfolane-degrading microbial populations. N and P were initially added to account for the sulfolane-carbon, according to a C:N:P ratio of 100:5:1; microcosms were amended with sufficient N or P to account for total carbon after 32 d of incubation (arrows). A. Unamended microcosm. B. N-supplemented microcosm. C. P-supplemented microcosm. D. N- and P-supplemented microcosm.

At that time, the microcosms were amended with the "high" level of N and P. Shake-flask experiments suggested that sulfolane biodegradation would eventually occur with the low level of nutrients, but that it would begin sooner if high levels were provided. The lag period before biodegradation with low levels of nutrients could be estimated at >32 d but <63 d in these microcosms; high levels of nutrients were added at 32 d, and biodegradation commenced in the unsupplemented microcosm after 63 d of incubation (Figure 3A).

The N- and P-supplemented microcosm demonstrated a lag time of 3 d after the increased nutrient levels had been added (Figure 3D). After 24 d of incubation with the increased nutrient levels, the N-supplemented microcosm showed sulfolane-degrading activity (Figure 3B), and 7 d later, the P-supplemented microcosm demonstrated sulfolane degradation (Figure 3C). The addition of P had no effect on the lag time before sulfolane biodegradation, nor on the rate of sulfolane removal when compared with the unsupplemented microcosm (Table 4). In addition, biodegradation commenced sooner, and at a greater rate, in the N- and P-supplemented microcosm than in the N-supplemented microcosm (Table 4). These results suggest that N was likely the major limiting nutrient for sulfolane biodegradation in this soil, but that P was also limiting. In contrast, Greene *et al.* [10] tested another sulfolane-contaminated soil and concluded that the addition of P enhanced sulfolane biodegradation, whereas the addition of N yielded little stimulation of biodegradation. Braddock *et al.* [17] observed that the addition of both N and P were required to obtain the highest observed biodegradation rate for hydrocarbons in Arctic soil.

The water-extractable total organic carbon in all four microcosms began to decrease before any decrease in sulfolane concentration was observed (Figure 3). Water-extractable total organic carbon was removed fastest from the N- and P-supplemented microcosm (Figure 3D), then from the N-supplemented microcosm (Figure 3B). In all three microcosms that received some form of nutrient supplementation, water-extractable total organic carbon was removed to below detectable levels (10 mg g^{-1} soil), however in the unsupplemented microcosm water-extractable total organic carbon removal ceased before sulfolane removal was complete (Figure 3). The addition of N and P stimulated utilization of water-extractable total organic carbon, demonstrating that there was a demand for nutrients associated with microbial removal of organic compounds other than sulfolane, thus competition must have occurred between sulfolane-degrading and other heterotrophic microorganisms in these microcosms. In general, the removal of water-extractable total organic carbon paralleled sulfolane removal from the microcosms; being most efficient in those which were able to degrade sulfolane most quickly.

The heterotrophic communities demonstrated similar population increases in all four microcosms; each community began in the 10^5 to 10^6 CFU g^{-1} soil range (Figure 3), and increased to the 10^8 to 10^9 CFU g^{-1} range by approximately 25 d of incubation, concomitant with the decrease in total organic carbon in the nutrient-supplemented microcosms and before the water-extractable carbon decreased in the unsupplemented microcosm. No further increases in viable cell counts were observed over the incubation time (Figure 3).

A sulfolane-degrading bacterial population consisting of approximately 10^3 to 10^4 CFU g^{-1} soil was present in the contaminated soil at time zero (Figure 3), in sharp contrast to the <10 CFU g^{-1} soil initially in the topsoil (Figure 2). Unlike the total heterotroph numbers which remained essentially constant over the duration of the experiment with the topsoil-containing microcosms (Figure 2), the numbers of total heterotrophs in the microcosms that contained the contaminated soil increased (Figure 3 and Table 4). The greatest increase occurred during the removal of the majority of the water-soluble total organic carbon in the nutrient-supplemented microcosms (Figure 3). Mixing and aeration provided by the simulated biopile conditions in the microcosms may have stimulated the growth of the total bacterial community. Mueller *et al.* [9] observed similar increases in heterotrophic microorganisms in a sediment sample used to inoculate landfarming chamber microcosms. Our contaminated soil sample was obtained from an anaerobic environment at a depth of 7.5 m. Therefore, the increase in heterotrophic numbers obtained on plates incubated under aerobic conditions may indicate that facultative microorganisms were acclimating to aerobic growth over time in the simulated biopiles. Increases in the sulfolane-degrading population at this time were probably part of the total population increase, rather than the result of a specific enrichment.

The sulfolane-degrading bacterial communities in each microcosm increased further when the total heterotrophic population had reached a maximum (Figure 3). The second increase in the sulfolane-degrading community was detected in each microcosm within a week of the commencement of sulfolane removal (Figure 3). At this time, sulfolane-degrading bacteria were likely selectively enriched. It is probable that fluctuations in the bacterial population took place after the initial enrichment of heterotrophs due to utilization of more recalcitrant carbon compounds.

The N-supplemented and N- and P-supplemented microcosms mostly demonstrated a single sulfolane-degrading colony morphology. The unsupplemented and P-supplemented microcosms were dominated by a different colony morphology. The colonies in the unsupplemented or P-supplemented microcosms degraded sulfolane within 14 d of plating on PAT medium, whereas the dominant sulfolane-degrading colonies from the N-supplemented microcosms required at least 21 d to demonstrate sulfolane degradation on PAT medium.

The microorganisms in the N-supplemented microcosms grew more slowly, therefore they may have initially utilized compounds other than sulfolane, or been outcompeted by other microbial populations. The population found in P-supplemented or unsupplemented microcosms

was nearly absent in the N-supplemented sediment microcosms, suggesting that the bacterium dominant in the N-supplemented microcosms was able to successfully compete against the other for substrates such as sulfolane, in the presence of added N. At time zero, only the colony morphology dominant in the unsupplemented and P-supplemented microcosms was observed.

The initial presence of a sulfolane-degrading bacterial population in the subsurface sediment is not unexpected because this sediment had been contaminated with sulfolane and other Sulfinol process chemicals for many years. The existence of this population at the sulfolane-contaminated site suggested that bioremediation, given the appropriate nutrient and aeration conditions, may be possible.

CONCLUSIONS

For both sets of shake-flask cultures and air-sparged microcosms, sulfolane biodegradation proceeded under almost all the conditions of nutrient amendment tested. Amendment with N appeared to have the greatest effect in contaminated soil shake-flask cultures and microcosms (Tables 3 and 4). Amendment with P had a lesser effect, but still increased microbial activity against sulfolane over the unamended cultures and microcosms. The differences between amendment with different nutrients were more obvious in the air-sparged microcosms, because biodegradation proceeded more slowly than in the shake-flask cultures. The results from shake-flask cultures inoculated with topsoil also suggested that low N supplementation was more effective in shortening the lag time for sulfolane degradation than P supplementation (Table 3). This observation was borne out in the air-sparged microcosms containing topsoil, where the lag phase was shorter in the N-supplemented microcosm than in the P-supplemented microcosm (Table 4). Overall, the shake-flask cultures were useful in predicting the behavior of the much slower air-sparged microcosms, with respect to nutrient amendment.

Previous experiments demonstrated the usefulness of shake-flask experiments in predicting activity against sulfolane in 2.5-l microcosms inoculated with contaminated sediment and groundwater [10]. Mueller *et al.* [9] used landfarming chamber microcosms to predict the potential for biodegradation of pentachlorophenol and creosote compounds in the field. Christensen and coworkers [18-21] determined that 2.5-l microcosms were useful in predicting *in situ* biodegradation of a number of aromatic compounds in a contaminated aquifer. Our results, which demonstrated that sulfolane biodegradation in laboratory microcosms could be predicted using shake-flask cultures, may be extrapolated to allow predictions of the potential for microbial activity against sulfolane *in situ*. It is important to realize, however, that the microbial sulfolane degradation observed in the air-sparged microcosms, as in the other laboratory cultures and microcosms, occurred under aerobic, nutrient-supplemented conditions. Such conditions are unlikely to occur in contaminated soils or aquifers. Our results suggest that bioremediation would only be successful if forced aeration combined with nutrient amendment were applied.

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ORIGINAL PAPER

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Sulfolane degradation by mixed cultures and a bacterial isolate identified as a *Variovorax* sp.

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Abstract Sulfolane (tetrahydrothiophene-1,1-dioxide) is used in the Sulfinol process for natural gas sweetening. At many sour-gas processing plants spills, landfills and leakage from unlined surface storage ponds have contaminated groundwaters with sulfolane. Due to its high water solubility and mobility in aquifers, sulfolane poses a risk for off-site contamination. This study investigated the aerobic biodegradation of sulfolane by two mixed microbial enrichment cultures and by three bacterial isolates. Sulfolane served as the sole C, S and energy source for these cultures. In the two mixed cultures, 60% and 80% of the sulfolane C was recovered as CO_2, whereas in cultures of the three isolates only 40–42% of the substrate C was recovered as CO_2. In the mixed cultures, 81% and 97% of the sulfolane S was converted to sulfate, and in the pure isolates, 55–90% of the substrate S was converted to sulfate. Thus, the mixed cultures were capable of greater mineralization than the pure isolates. One isolate, strain WP1, was identified using a combination of 16S rRNA gene sequencing, physiological traits and cell morphology. WP1 was determined to be most similar to *Variovorax paradoxus*.

Key words Biodegradation · Natural gas · Sulfolane · Tetrahydrothiophene-1,1-dioxide · *Variovorax*

Introduction

Natural gas that contains greater than 1% H_2S is called sour gas. Sweetening processes, which typically use amines with other solvents to remove the H_2S, are required before the natural gas can be marketed. Sulfolane (tetrahydrothiophene-1,1-dioxide, Fig. 1) has been used in the Sulfinol process for natural gas sweetening since the early 1960s (Fitzgerald and Richardson 1966). Spills, landfills and unlined process water storage ponds have allowed sulfolane to leach into the groundwater at Sulfinol plants. Contaminated plumes containing sulfolane at concentrations up to 680 mg l^{-1} have been reported (Greene et al. 1999).

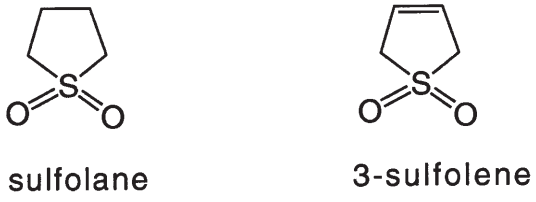

Fig. 1 Structures of compounds used in this study

The toxicity of sulfolane has been investigated. Mice, rats and guinea pigs all demonstrated an LD_{50} of 1.8–2.5 g (body weight kg)$^{-1}$ for orally administered sulfolane, and of 0.6–1.5 g kg^{-1} for subcutaneously injected sulfolane (Alexander et al. 1959; Andersen et al. 1976; Brown et al. 1966). Sulfolane did not have toxic systemic or irritant effects when applied to guinea pig skin (Brown et al. 1966). Ursin et al. (1995) found that living human skin showed little permeability to sulfolane (0.2 g m^{-2} h^{-1}). Sulfolane therefore exhibits low levels of toxicity.

Luther et al. (1998) determined that sulfolane mobility in soil is very high. It does not interact significantly with soil organic matter or with the clay mineral portion of soil, and it is relatively inert. It is therefore likely that, at sites with sulfolane in the groundwater, this compound would migrate off-site and contaminate nearby domestic wells and surface waters. The attenuation of sulfolane in contaminated aquifers will depend on biodegradation or biotransformation. Aerobic sulfolane degradation has been demonstrated in laboratory and field-scale studies (Chou and Swatloski 1984; Greene et al. 1998, 1999); however

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anaerobic sulfolane biodegradation is unlikely to occur in the environment (Greene et al. 1998).

Groundwater contamination problems with sulfolane have some similarities to the groundwater contamination with methyl tertiary butyl ether (MTBE), a gasoline additive (Cullen 1998). Both compounds are very water-soluble, move rapidly in groundwater, and are resistant to anaerobic biodegradation.

Lee and Clark (1993) isolated a strain of *Pseudomonas maltophila*, able to degrade aromatic sulfonic acids, which could grow on minimal agar with sulfolane as a C source. Juhl and Clark (1990) developed a series of *Escherichia coli* mutants with sulfone oxidase activity that was also stimulated by sulfolane; these mutants were able to utilize sulfolane on tetrazolium agar indicator plates.

Greene et al. (1998, 1999) and Greene and Fedorak (1998) have reported sulfolane biodegradation by bacterial cultures enriched from sulfolane-contaminated sediments. This paper describes the characteristics of sulfolane biodegradation by two mixed bacterial cultures, and by three pure isolates obtained from the enrichment cultures. The extent of sulfolane mineralization to CO_2 and sulfate, and conversion to biomass, was determined for mixed and pure sulfolane-degrading bacterial cultures. The identity of the most active sulfolane-degrading bacterium, isolate WP1, was determined using 16S rRNA gene sequencing, physiological traits and cell morphology.

Materials and methods

Media and growth conditions

Two different liquid media were used. The composition of one, called B+N8P in this report, is given by Kropp et al. (1994). Sulfate-free medium (Fedorak and Coy 1996) was also used. Sulfolane was added to the medium before sterilization by autoclaving, or after autoclaving as a sterile solution. 3-Sulfolene and 2,4-dichlorophenoxyacetic acid (2,4-D) were filter-sterilized and added to the medium after autoclaving.

The solid, differential PAT medium was described by Greene and Fedorak (1998). The API 20E and API 20NE kits (bioMérieux, Marcy-l'Etoile, France) and selective and differential media were used to determine the substrate utilization and growth profile for isolate WP1.

Sources of microbial inocula

Two sour gas plants in Alberta, Canada, were sampled to obtain aquifer materials from plumes contaminated with sulfolane. Detailed descriptions of the sites and the sampling methods are given by Gieg et al. (1998). Site 1 yielded two mixed enrichment cultures, designated M1 and M2, and one isolate, designated P1. Site 2 yielded two isolates, designated WP1 and P2. The mixed cultures were incubated aerobically in shake flasks that contained B+N8P medium with 500 mg sulfolane l^{-1}. M1 was enriched at 28 °C and M2 was enriched at 8 °C. The mixed cultures were maintained on B+N8P with sulfolane as their sole C and energy source.

P1 was isolated from the mixed culture M1, and P2 was isolated from an enrichment culture that contained contaminated sediment from site 2. These bacterial strains were obtained from plating the enrichment cultures onto PAT medium. Isolated colonies were picked and tested for growth on sulfolane in liquid cultures. Strain WP1 was isolated from plates of PAT medium inoculated with a portion of an enrichment culture that contained contaminated sediment from site 2 incubated at 8 °C with sulfolane as the sole C source. Although strain WP1 was isolated at 8 °C, it grew at 28 °C and all experiments with this isolate were done at the higher temperature.

C and S balance

The inocula were grown in sulfate-free medium with sulfolane as the sole C and S source for at least three consecutive transfers before use in C and S balance experiments. Bacterial cultures for C and S balance experiments were grown in 158-ml sealed serum bottles containing 50 ml sulfate-free medium with 100 mg sulfolane l^{-1}. The headspace gas contained sufficient O_2 for complete mineralization of sulfolane to CO_2 and sulfate based on the following equation:

$$C_4H_8O_2S+6.5O_2 \rightarrow 4CO_2+3H_2O+2H^++SO_4^{2-} \quad (1)$$

Nine replicates of each culture were prepared for the C balance experiments. Triplicate cultures were used to analyze each of the three different parameters: CO_2, sulfate and organic C. The cultures used for organic C analyses were separated into biomass and supernatant fractions by centrifugation (12,000×*g* for 20 min). The collected cells were resuspended in deionized, distilled water for biomass C analysis. The supernatant fraction was filter-sterilized to ensure that all cells were removed prior to analysis. Similarly, the cultures used for sulfate analysis were centrifuged at 12,000×*g* for 20 min and the supernatant was filter-sterilized before sulfate analyses. The treatment of the cultures for CO_2 analysis is given in the "Analytical techniques" section.

The time course of sulfate release during sulfolane degradation was also monitored in sulfate-free medium in triplicate, 200-ml shake-flask cultures. Inocula were 10 ml of culture freshly grown in sulfate-free medium. Samples from the cultures were centrifuged at 12,000×*g* and the supernatants were filter-sterilized before sulfate analyses were performed.

Detection of sulfite from sulfolane

Seventy millilitres of sulfate-free medium were dispensed into 158-ml serum bottles that contained approximately 0.5 g of $CaCO_3$ for added buffering capacity. The medium in each serum bottle was supplemented with 500 mg sulfolane l^{-1} and inoculated with isolate WP1 grown in sulfate-free medium. The bottles were sealed and incubated at 28 °C with shaking. Appropriate sterile controls were also established. Samples were removed at various times and analyzed for sulfolane and sulfite.

Growth of isolate WP1 on 3-sulfolene

3-Sulfolene (100 mg l^{-1}) was added to B+N8P medium, alone or with 100 mg sulfolane l^{-1}. The medium was then inoculated with freshly grown bacterial culture (10% by volume) and incubated at room temperature, shaking at 200 rpm.

Preparation of DNA for sequencing

Genomic DNA was prepared according to the method of Hopwood et al. (1985) from overnight cultures of strain WP1 or *Paenibacillus polymyxa* PKB1 (Kharbanda et al. 1999) grown in 200 ml Luria broth (LB) medium (Sambrook et al. 1989). DNA was resuspended in 10 ml water.

Two primers were synthesized for generation and partial sequencing of a PCR fragment encompassing 1378 base pairs of the 16S rRNA gene sequence. The forward primer (8f) was based on a primer described by Hauben et al. (1997), with nucleotides added to the 5′ end to introduce clearage sites for *Sac*1, *Eco*R1 and *Xba*1.

The reverse primer sequence (1403r) was based on a primer reported in Marchesi et al. (1998), with nucleotides providing the same restriction sites added to the 5′ end. Other sequencing primers were designed based on a series of 16S rRNA primers described by Hauben et al. (1997). The six primers used were 8f: 5′-GAGCTCTAGAATTCAGAGTTTGATCATGGCTCAG-3′; 704f: 5′-TGTGTAGCGGTGAAATGCGTAGA-3′; 1176f: 5′-AGGAAGGGGGGGAGGAGGT-3′; 358r: 5′-CCCACTGGTGCCTCCCGTA-3′; 1106r: 5′-CGCCCTTTTCGGGACTTAACCC-3′; 1403r: 5′-TCGAGCTCTAGAATTCGGGCGGTGTGTACAAGGC-3′.

PCR reactions were done in an MJ Research Minicycler. The thermocycler was programmed to perform an initial 5-min denaturation step at 94 °C, then 30 cycles of 94 °C for 30 s, 55 °C for 30 s, and 72 °C for 1.5 min. This was followed by a final extension step at 72 °C for 5 min.

Reactions contained: 0.6 ng genomic DNA ml^{-1}; 0.4 pmol ml^{-1} each of primers 8f and 1403r; 200 mM each of dATP, dCTP, dGTP and dTTP (Boeringher Mannheim); PCR buffer [50 mg KCl, 848 mg tris(hydroxymethyl)aminomethane hydrochloride, (pH 8.8), 0.1 ml 1% Triton X-100 per 100 ml] ; 1.5 mM $MgCl_2$; and 0.1 units Taq DNA polymerase ml^{-1}. PCR product was purified by neutral phenol:chloroform (1:1 v/v) extraction and ethanol precipitation. DNA fragments were separated on a 0.8% ultrapure agarose gel (ICN, Aurora, Ohio) by electrophoresis at 5 V cm^{-1}. Bands of interest were recovered using the Geneclean II kit (BIO 101, Vista, Calif.), according to manufacturer's instructions. DNA concentration was measured by fluorometry and gel electrophoresis. The Department of Biological Sciences Synthesis Service, University of Alberta, synthesized all of the primers and sequenced all the PCR fragments.

Phylogenetic analysis

The 16S rRNA gene sequence from strain WP1 was compared to nucleotide sequences from Genbank using the advanced basic local alignment search tool (BLASTN) sequence alignment system (Altschul et al. 1997) and the Ribosomal Database Project (RDP) by means of the Similarity Rank tool (Maidak et al. 1997). The websites for BLASTN and RDP are http://www.ncbi.nlm.nih.gov and http://www.cme.msu.edu/RDP. Phylogenetic trees were inferred using a variety of programs from the PHYLIP package (Phylogeny Inference Package V. 3.57c; Felsenstein 1989). These include: the distance matrix method with the algorithm of Fitch and Margoliash (1967) or the neighbor-joining method (Saitou and Nei 1987), and the maximum likelihood method (Felsenstein 1989). Bootstrap analysis of 100 data resamplings was performed with the programs Seqboot and Consense (Felsenstein 1993). A previously identified environmental isolate, *P. polymyxa* PKB1 (Kharbanda et al. 1999), was used as a positive control for the 16S rRNA gene amplification and sequence alignment.

Tests for identification of isolate WP1

API 20E and API 20NE identification tests (bioMérieux, Marcy-l'Etoile, France) were used following the manufacturer's instructions. Both isolates, WP1 and *P. polymyxa* PKB1, were grown at room temperature on selective and differential media; the results were interpreted as suggested by the Difco Manual (1984). Flagellar stains were done following a modified version of the Gray staining method (Mayfield and Inniss 1977).

Analytical techniques

The gas chromatography (GC) method used for sulfolane was described by Greene et al. (1998), except that a 1.3 m×2.8 mm stainless steel column and a 15-cm-long guard column, both packed with Tenax-TA (Alltech Associates, Deerfield, Ill.) coated with 5% polyphenyl ether (6-ring), were used in this study. The oven temperature was 200 °C for sulfolane and 50 °C for 3-sulfolene.

Soluble organic C and biomass C were analyzed by the method of Gieg et al. (1999). Carbon dioxide production was measured by adding 1 ml of 10 M HCl to each 50-ml culture in a sealed 158-ml serum bottle. These were incubated with shaking overnight to allow CO_2 to partition into the headspace. Samples (0.1 ml) of the headspace gas were analyzed by the GC method of Bressler et al. (1999). A calibration curve was prepared by adding known amounts $NaHCO_3$ in 25 mM borate buffer (pH 9.2) into 50 ml of sulfate-free medium in 158-ml serum bottles. The contents of these sealed serum bottles were acidified and treated in the same manner as the cultures prior to sampling for GC analyses.

Degradation of 2,4-D was monitored by high performance liquid chromatography using a Hewlett Packard Series 1050 HPLC with a C_{18} reverse phase column (Waters, Milford, Mass.). The mobile phase was 70% deionized water, 20% acetonitrile and 10% 1 M K_2HPO_4 (pH 7.0). The flow rate of the mobile phase was 1.5 ml min^{-1}, and 2,4-D was detected at 283 nm.

Initially, sulfate was quantified by the turbidimetric method described in Standard Methods (APHA 1989), modified to suit a 25-ml sample size. Filtered culture supernatant was mixed with 5 ml of a solution that contained (per 1 l) 30 g $MgCl_2 \cdot 6H_2O$, 5 g CH_3COONa, 1 g KNO_3, 20 ml 99% CH_3COOH and stirred continuously while 2 g $BaCl_2$ was added. After 1 min, the absorbance at 420 nm was measured. Later, in the studies, sulfate was quantified by ion chromatography using a Dionex Series 2000i/SP ion chromatograph equipped with a Dionex IonPac AS4A 2×250 mm anion exchange column (Dionex, Sunnyvale, Calif.).

Sulfite was also detected by the ion chromatography method. To verify the presence of sulfite, samples of the culture supernatants were added to a solution of 40 μg malachite green l^{-1}. Sulfite decolorizes this dye (Feigl and Anger 1972), and the decrease in color was measured spectrophotometrically at 617 nm.

A Philips Model PU 8740 UV/VIS spectrophotometer was used to measure OD_{600} and turbidity for sulfate analyses. DNA quantification was done using a Unicam UV3 UV/VIS Spectrometer at 260 nm. DNA primers and DNA for sequencing were quantified by fluorometry. Fluorometry was done using a Hoefer Scientific Instruments Model TKO 100 fluorometer; 2-μl samples were mixed with 1 ml Hoefer Scientific H33258 fluorometry dye, according to the specifications of the manufacturer.

Chemicals

Chemicals were reagent grade, purchased from Aldrich (Milwaukee, Wis.), Sigma (St. Louis, Mo.) or Fisher (Fair Lawn, N.J.) unless otherwise indicated. Chloroform (99.7%) was from BDH and phenol was from Anachemia (Montreal, PQ). Sulfolane (99%) and 3-sulfolene (98%) were obtained from Aldrich; 2,4-D was obtained from Sigma.

Results

Mineralization of sulfolane by mixed cultures and single isolates

Mass balances for C and S from sulfolane were done with two mixed cultures and three bacterial isolates in sulfate-free medium that contained 100 mg sulfolane l^{-1} (Table 1). Equation 1 indicates that complete oxidation of sulfolane would yield the stoichiometric release of S as sulfate. The results in Table 1 show that the mixed cultures released 81% and 97% of S as sulfate, whereas the bacterial isolates P1 and P2 released only 71% and 55% of S as sulfate. In contrast, 90% of S from sulfolane was found as sulfate in the cultures of isolate WP1 at the end of the incubation period.

Table 1 Conversion of 100 mg sulfolane l^{-1} to CO_2, biomass, soluble organic C and sulfate by two mixed cultures and by three single isolates. Conversion is described as the percent of total C or S added as sulfolane at time zero that was detected as the various components at the end of the experiment. Mean and standard deviation of triplicate cultures are reported

Culture	Incubation time (days)	SO_4^{2-} (%)	CO_2 (%)	Soluble organic C (%)[a]	Biomass C (%)	Total C recovery[b] (%)
M1 (mixed)	30	81±0	60±1	6±1	20±2	86±2
M2 (mixed)	30	97±3	80±1	8±1	26±1	113±2
P1 (isolate)	30	71±5	42±0	28±1	17±0	87±1
P2 (isolate)	30	55±4	40±1	53±3	23±2	115±4
WP1 (isolate)	11	90±1	42±1	26±1	28±1	96±2

[a]All detectable sulfolane had been removed from the cultures at the time of analysis, therefore no sulfolane contributed to the reported soluble organic C

[b]Standard deviation calculated by method of Skoog and West (1976) and rounded to one figure

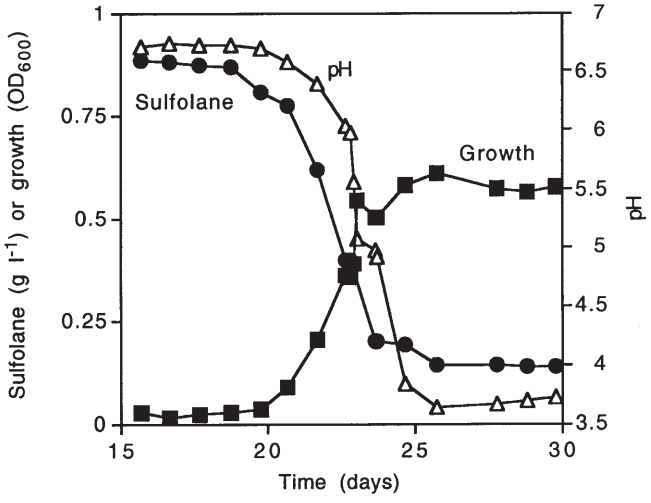

Fig. 2 Growth of isolate WP1 in B+N8P medium in a shake-flask culture with sulfolane as its sole C source

Similarly, the conversion of sulfolane C to CO_2 by the mixed cultures was more extensive than by the single isolates (Table 1); however, biomass production was alike in all five cultures, ranging from 17% to 28% of the sulfolane C incorporated into biomass. The major difference between the mixed cultures and single isolates was the amount of soluble organic C remaining after sulfolane removal, which was 28–58% in cultures of the isolates and only 6–8% in the mixed cultures. Overall, this indicates that sulfolane yielded similar amounts of C for growth in both the mixed cultures and the cultures of the isolates, but that a consortium of bacteria was more able to mineralize sulfolane to CO_2 than any of the single isolates.

The lowest release of sulfate was observed in the cultures of isolate P2 (Table 1), with only 55% of the sulfolane S being detected as sulfate. This isolate had the highest amount of soluble organic C at the end of the incubation period, and these results suggest that much of the S from sulfolane remained as unidentified organosulfur intermediates. In contrast, the mixed cultures had high sulfate release with the lowest residual soluble organic C, suggesting that little S remained as an organic form.

Although we did not specifically measure biomass S, it would not contribute significantly to the S balance. On a dry weight basis, a typical bacterial cell contains 50% C and 1%S (Stanier et al. 1970). Isolate WP1 incorporated 28% of the sulfolane C into biomass (Table 1), thus one-fiftieth of this amount of sulfolane S would have been incorporated into biomass. This would be less than 1% of sulfolane S incorporated into biomass.

Isolate WP1 was chosen for further study because of its high release of S as sulfate (Table 1), and experience showed that it gave more consistent sulfolane biodegradation than the other two isolates. Figure 2 shows the growth of isolate WP1 in B+N8P medium that contained 850 mg sulfolane l^{-1} as its sole C source. The lag time before the onset of sulfolane utilization by isolate WP1 was variable, and Fig. 2 shows a lag time of about 18 days. The consumption of sulfolane was accompanied by a sharp drop in pH, as predicted by Eq. 1, and a seven-fold increase in the OD_{600} readings. Isolate WP1 was serially subcultured on sulfolane as its sole C and S source for nearly 3 years.

A mass balance time course study was done with isolate WP1 to determine the distribution of C and sulfate during degradation of 100 mg sulfolane l^{-1} (Fig. 3). After a short lag time, sulfolane biodegradation was evident after 1 day, and the compound was completely removed after 2 days of incubation (Fig. 3). The formation of sulfate lagged behind sulfolane degradation. For example, after 1 day, 78% of the added sulfolane was removed from the cultures, but only 26% of sulfolane S was detected as sulfate. Soluble organic C decreased and CO_2 increased over the incubation period, while biomass C increased for the first 2 days of incubation, then decreased slightly by day 11 (Fig. 3).

The mixed culture M1 and isolates P1 and P2 were also monitored to determine whether the formation of sulfate lagged behind sulfolane biodegradation, as was observed with isolate WP1. All three cultures demonstrated a lag between recovery of sulfolane S as sulfate and sulfolane removal. For example, after 5 days of incubation, 100% of sulfolane was removed from the M1 culture, but only 45% of the S was detected as sulfate (data not shown). Similarly, sulfolane was completely removed from the cultures of P1 and P2 by day 11 and 7, respectively.

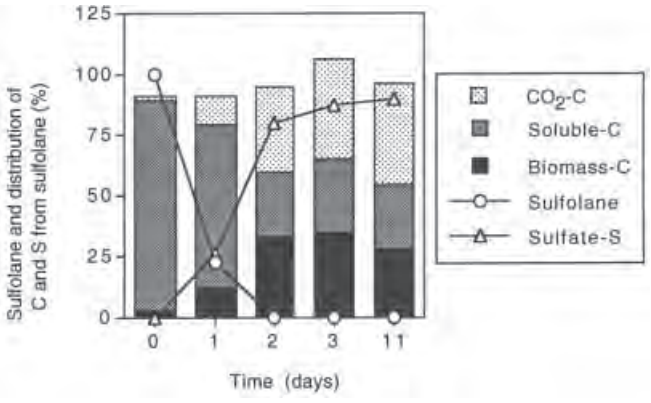

Fig. 3 Sulfolane metabolism by isolate WP1 in sealed serum bottles containing 100 mg sulfolane l^{-1} in sulfate-free medium, showing the distribution of C in the cultures and sulfate S released from sulfolane. Standard deviations for C analyses were all ≤1.1% and ≤2% for sulfate determinations

However, at these times, only 45% and 25% of the S from sulfolane was detected as sulfate. In all cases, the sulfate concentrations increased after sulfolane was depleted, as illustrated in Fig. 3.

The turbidimetric method, used in some of the experiments summarized above, is specific for sulfate, and it is not known whether sulfite was present in any of the cultures examined by this method. In later experiments, sulfite was not detected by ion chromatography. A separate experiment was done to determine if sulfite was released by isolate WP1. This isolate was incubated in sealed serum bottles containing a larger volume of medium and five times the sulfolane concentration that was used in the S balance experiments. These conditions limited the O_2 supply which would reduce the likelihood of abiotic oxidation of sulfite to sulfate. Ion chromatographic analyses of the culture supernatants showed the presence of sulfite and sulfate. The decolorization of a malachite green solution when mixed with samples of the culture supernatants verified the presence of sulfite. The sulfite concentrations were not measured.

Identification of the isolate WP1

The sequence of 1378 base pairs of the WP1 16S rRNA gene was submitted as Genbank accession number AF208386. This entire sequence was used to search for related bacterial strains within the Genbank and RDP databases. The BLAST alignment algorithm indicated that the 16S rRNA gene sequence for WP1 was most similar (96%) to that of *Variovorax paradoxus* type strain 16S rRNA. Other similar 16S rRNA sequences included the following environmental isolates: an unidentified 2,4-D-degrading bacterium, strain HW1 (95%; Kamagata et al. 1997) and a trichloroethylene-degrading strain of *V. paradoxus* (96%; Hamada and Harayama, unpublished data). The similarity matrix results showed that the 16S rRNA gene sequence in the RDP database most similar to that of isolate WP1 was from *Variovorax paradoxus*, at 0.934. This *V. paradoxus* strain was metallotolerant (Anzai et al., unpublished data). Thus, strain WP1 was genetically similar to environmental isolates capable of degrading or tolerating xenobiotic compounds.

The positive control, *P. polymyxa* PKB1, was most closely related to a *P. polymyxa* strain according to both BLAST and the RDP analysis. Both nucleotide database search results suggested that isolate WP1 was most closely related to *V. paradoxus*.

Phylogenetic trees were generated using the 1378-bp sequence of strain WP1 and the 16S rRNA gene sequences from the bacteria determined to be most similar to that of strain WP1 from the Genbank and RDP nucleotide databases after alignment. The distance matrix method of Fitch and Margoliash, the neighbor joining method and maximum likelihood all suggested that the 16S rRNA sequence of strain WP1 was most closely related to the 16S rRNA of *Citrobacter freundii*. Bootstrap analysis of these trees showed a high bootstrap value of 100% for the branch node of strain WP1 and *C. freundii*. This is in contrast to the similarity matrix results from RDP, which gave a poor similarity (0.833) rating between strain WP1 and *C. freundii*.

Therefore, a morphological and biochemical profile of WP1 was done to compare these characteristics to those of *V. paradoxus* and *C. freundii*. Selected characteristics are summarized in Table 2. Based on those taxonomic tests, isolate WP1 more closely resembles *V. paradoxus* than *C. freundii*. WP1 cells were gram-negative rods. No spores or endospores were observed in WP1 cells. A flagellar stain detected no flagella on isolate WP1, and live cells were not motile when observed with a phase contrast microscope or in motility agar. *V. paradoxus* is motile and has two to four degenerate peritrichous flagella (Holt et al. 1994; Kersters and De Lay 1984). This was the major difference between strain WP1 and *V. paradoxus*.

Many described strains of *V. paradoxus* were capable of degrading 2,4-D; therefore strain WP1 was tested for its ability to degrade this compound. Strain WP1 did not degrade 100 mg 2,4-D l^{-1} after 24 days of incubation, al-

Table 2 Comparison of physiological characteristics of *Variovorax paradoxus*, isolate WP1 and *Citrobacter freundii*

Characteristic	*V. paradoxus*[a]	Isolate WP1	*C. freundii*
β-Galactosidase	≥90%–	–	≥90%+
Citrate	≥90%+	–	≥90%+
Lactose	≥90%–	–	26 to 75%+
Maltose	≥90%–	–	≥90%+
Methyl red	U[b]	No growth	≥90%+
Motility	+[c]	–	≥90%+
Oxidase	≥90%+	Weak+	≤10%+
Sucrose	≥90%–	–	26–75%+
Yellow pigment	Present	Present	Absent

[a] Formerly *Alcaligenes paradoxus* (Willems et al. 1991)
[b] Unknown
[c] Degenerate peritrichous flagella

though it degraded 100 mg sulfolane l^{-1} in cultures that also contained 2,4-D. Inoculation of the cultures with 2,4-D-exposed soil resulted in complete removal of the compound within 3 days.

Growth of WP1 in the presence of 3-sulfolene

Although the biodegradation of sulfolane has been reported (Chou and Swatloski 1984; Lee and Clark 1993; Greene et al. 1998), its metabolic pathway has not been elucidated. In an attempt to slow sulfolane biodegradation and possibly cause the accumulation of some intermediates, isolate WP1 was grown in the presence 100 mg 3-sulfolene l^{-1}, a sulfolane analogue. 3-Sulfolene was completely removed from the culture medium by isolate WP1 over the 21-day incubation period, with an increase in OD_{600} indicating that this compound supported growth of isolate WP1.

3-Sulfolene was degraded more slowly than sulfolane, and its presence in cultures with sulfolane slowed sulfolane degradation. In a series of cultures that contained only sulfolane, the lag time before degradation commenced was <1 day, and the degradation rate was near 100 mg l^{-1} day^{-1} (data not shown). When sulfolane and 3-sulfolene were both present at 100 mg l^{-1}, the lag time for sulfolane degradation was approximately 4 days, and the degradation rate fell to about 5 mg l^{-1} day^{-1}.

Discussion

Slater and Lovatt (1984) reviewed several studies in which single isolates and mixed microbial communities degraded organic compounds. In many of these studies, the substrates were degraded more extensively by mixed cultures than by single isolates. This was true for sulfolane mineralization by our cultures, as summarized in Table 1. The single isolates mineralized only 40–42% of the C from sulfolane, whereas the mixed cultures mineralized 60% and 80% of the C from sulfolane to CO_2. Slater and Lovatt (1984) listed several mechanisms for the enhanced biodegradation by mixed cultures, including the provision of specific nutrients, the removal of growth-inhibiting products, and the combined metabolic attack on the substrate. It is not known which mechanism resulted in the increased mineralization of sulfolane by our mixed cultures.

The aerobic biodegradation of sulfolane by mixed cultures and single isolates has been documented (Chou and Swatloski 1984; Lee and Clark 1993; Greene et al. 1998). However, this is the first report of its degradation by a bacterium that was specifically isolated on sulfolane as a sole C, S and energy substrate. As indicated by Eq. 1, the mineralization of sulfolane leads to the release of acid, which was observed by Chou and Swatloski (1984) and was the basis for the development of the PAT medium (Greene and Fedorak 1998). When grown in B+N8P containing 850 mg sulfolane l^{-1}, strain WP1 decreased the pH of the medium to below 4, which caused sulfolane degradation to stop. We have observed that sulfolane degradation resumes after the pH is adjusted back to near neutrality.

Greene (1999) tested isolate WP1 on several sulfolane analogues, including 3-methylsulfolane, 2,4-dimethylsulfolane, 3-hydroxysulfolane and tetrahydrothiophene sulfoxide as potential growth substrates. None of these supported growth of isolate WP1, nor was growth observed on thiophene or tetrahydrothiophene (data not shown).

3-Sulfolene was degraded and supported growth of isolate WP1. This degradation would likely not occur as a result of adding H_2O across the double bond, because this would yield 3-hydroxysulfolane, which does not support growth of isolate WP1 (Greene 1999). 3-Sulfolene metabolism may occur via the reduction (hydrogenation) of the double bond to yield sulfolane; however, the sulfolane was not detected in the GC analyses of the culture supernatants. Reduction of double bonds in aerobic cultures has been documented. For example, a *Pseudomonas* sp. reduces cinnamic acid (3-phenylpropenoic acid) to 3-phenylpropionic acid (Blakley and Simpson 1964).

In general, the mechanisms by which microorganisms cleave the heteroatomic rings of sulfur heterocycles are poorly understood (Bressler et al. 1998). The detection of inorganic S, typically as sulfide, sulfite or sulfate, has been used as a means of evaluating the biodegradation of sulfur heterocycles (for review see Bressler et al. 1998). The release of sulfate from dibenzothiophene by *Rhodococcus* sp. strain IGTS8 is the best-studied system (Gray et al. 1996). The reaction proceeds by the so-called 4S pathway, which is proposed for use in biodesulfurization of petroleum (Rhodes 1995; Shennan 1996). Gray et al. (1996) have shown that two monooxygenations yield dibenzothiophene sulfone as an intermediate, and another monooxygenase then produces 2′-hydroxybiphenyl-2-sulfinic acid (Fig. 4). A novel desulfinase releases sulfite, which spontaneously oxidizes to sulfate. The carbon skeleton remains unbroken yielding 2-hydroxybiphenyl. In contrast, *Brevibacterium* sp. strain DO completely mineralized dibenzothiophene via its sulfone (Van Afferden et al. 1990). In this case, 99% of the S from dibenzothiophene sulfone was recovered as sulfate. These examples illustrate that some bacteria must oxidize dibenzothiophene to its sulfone prior to ring cleavage. Of course, sulfolane is a sulfone (Fig. 1), and we observed sulfate in our culture supernatants as a result of its biodegradation. Isolate WP1 is not able to grow on tetrahydrothiophene or tetrahydrothiophene sulfoxide, demonstrating that it cannot oxidize either of these compounds to the sulfone, which is essential for isolate WP1 to attack the ring structure.

In their mixed-culture studies, Chou and Swatloski (1984) observed stoichiometric release of sulfate from sulfolane. Our mixed cultures yielded near stoichiometric amounts of sulfate, whereas the yields of sulfate in the cultures of isolates P1 and P2 were much lower (Table 1). In contrast, 90% of the sulfolane S was found as sulfate in the cultures of isolate WP1.

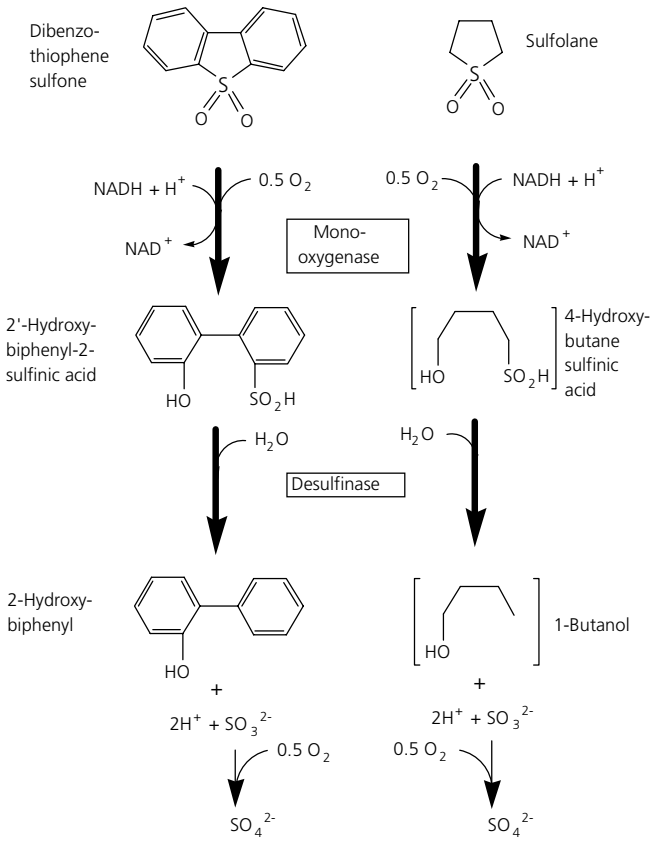

Fig. 4 The release of sulfite from dibenzothiophene sulfone and the hypothesized release of sulfite from sulfolane by strain WP1. The pathway from dibenzothiophene sulfone has been established for *Rhodococcus* sp. strain IGT8 (Gray et al. 1996). An analogous pathway for the release of sulfite from sulfolane is hypothesized. The compounds in *square brackets* have not been detected in cultures of strain WP1

Despite the numerous studies of the biodegradation of organosulfur compounds, few have attempted a C and S balance. In their pure-culture studies, Van Afferden et al. (1990) observed that about 9% of the C from dibenzothiophene remained as dissolved organic C, which they attributed to lysis products of cells or biodetergents in the culture fluid. The proportions of soluble organic C in our mixed-culture studies were 6% and 8% of the sulfolane C (Table 1). However, our single isolates left substantially more soluble organic C in the medium after the sulfolane was degraded (Table 1).

There are no reports on the extent of mineralization of sulfolane, but some data exist on the degradation of thiophene-2-carboxylate. Kanagawa and Kelly (1987) described a *Rhodococcus* strain that grew on this compound as its sole C and S source. They observed a stoichiometric recovery of the S as sulfate from this culture. Cripps (1973) demonstrated that an unidentified microorganism converted 74% of thiophene-2-carboxylate C to CO_2, approximately 4% to biomass C and 100% of the S from this compound to sulfate. These findings are similar to our results for mixed-culture sulfolane biodegradation in which 60% and 80% of the substrate C was found as CO_2 (Table 1). Our biomass yields were higher than that observed by Cripps (1973), ranging from 17% to 28% (Table 1).

Bressler et al. (1999) described a *Pseudonocardia* sp. that used the sulfones of benzothiophene, 3- and 5-methylbenzothiophene, as sole C, S and energy sources. It grew better on the first two compounds, and mass balance experiments showed that 57% and 62% of the substrate C was converted to CO_2, 17% and 19% to biomass C, and 17% and 35% to soluble organic C. Our single isolates produced considerably less CO_2 from sulfolane (Table 1) than the *Pseudonocardia* sp. did from benzothiophene and 3-methylbenzothiophene. In general, the pure sulfolane degraders yielded about the same amount of biomass C and more soluble organic C than the *Pseudonocardia* sp.

Sulfate and sulfite were detected in the cultures of *Pseudonocardia* sp. (Bressler et al. 1999). These two anions accounted for 44% and 77% of the S from benzothiophene sulfone and 3-methylbenzothiophene sulfone, respectively. The *Pseudonocardia* sp. would not grow on sulfolane (Bressler et al. 1999).

Sulfite was detected in cultures of isolate WP1 grown on sulfolane. This is consistent with the observation of sulfite release in the desulfurization of dibenzothiophene via its sulfone (Fig. 4). By analogy, we hypothesize a similar two-step pathway for the cleavage of the sulfolane ring and the release of sulfite (Fig. 4). Bressler et al. (1998) summarized the strengths of various C–C and C–S bonds and illustrated that the C–S bonds are typically weaker than C–C bonds. In addition, the oxidation of the S atom to a sulfone further weakens the C–S. For example, the C–C bond strength in $H_3C–CH_2CH_3$ is 330 kJ mol^{-1}, whereas the C–S bond strengths in $H_3C–SCH_3$ and $H_3C–SO_2CH_3$ are 308 and 280 kJ mol^{-1}, respectively. Thus, the weakest bond in the sulfolane ring would be the C–S bond, and cleavage between the S and a C atom would be more likely than between two C atoms. Further research is required to determine whether 4-hydroxybutane sulfinic acid and 1-butanol are produced by isolate WP1, as suggested in Fig. 4. However, this isolate does grow on 1-butanol.

V. paradoxus was formerly known as *Alcaligenes paradoxus* (Holt et al. 1994). The only species that has been described in the genus *Variovorax* is *V. paradoxus* (Willems et al. 1991). Although the results of biochemical and morphological tests and 16S rRNA gene sequencing indicated that isolate WP1 may be a strain of *V. paradoxus*, its relatively low similarity to the type organism shown by the RDP analysis suggests that it may represent a new species in the genus *Variovorax*.

Di Giovanni et al. (1996) obtained 32 different *V. paradoxus* isolates capable of degrading 2,4-D. Kamagata et al. (1997) detected a number of 2,4-D-degrading strains of *V. paradoxus* in a pristine soil. The inability of isolate WP1 to degrade 2,4-D sets it apart from the *V. paradoxus* isolates described by Di Giovanni et al. (1996) and Kamagata et al. (1997).

This study provides another example showing that mixed microbial communities may be better suited to

completely degrade organic contaminants than a single bacterial isolate. It describes many characteristics of isolate WP1, which is likely a species of *Variovorax*. This bacterium is capable of releasing most of the S from sulfolane as sulfate and is an excellent candidate for further studies to elucidate the pathway of sulfolane metabolism. Adding 3-sulfolene to culture medium should slow the biodegradation rate of sulfolane, allowing detection of the proposed intermediates.

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Laboratory Evaluations of Factors Affecting Biodegradation of Sulfolane and Diisopropanolamine

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Abstract: Sulfolane and diisopropanolamine (DIPA) are used in the Sulfinol® process to remove hydrogen sulfide from sour natural gas. This process has been used in western Canada since the early 1960s, and contamination of groundwater has occurred from surface spills and from seepage from landfills and unlined process water storage ponds. Aquifer sediments from contaminated and uncontaminated areas, and muds in a wetland downgradient from the contaminated plume, were collected from a gas plant. Vigorously agitated shake-flask cultures and gently agitated 2.5-L microcosms consisting of contaminated sediment, mud and groundwater, or wetland water were used to study the biodegradation of sulfolane and DIPA. The aerobic shake-flask method showed that all five of these materials contained microbial communities that biodegraded both compounds. Microorganisms in all samples, except the uncontaminated aquifer sediment, degraded both compounds in the aerobic 2.5-L microcosms. In general, the biodegradation occurred more rapidly in the shake-flask cultures. The addition of P greatly enhanced the degradation of sulfolane and DIPA, whereas the addition of N yielded little stimulation.

Introduction

Natural gas reserves in western Canada can contain up to 35% hydrogen sulfide (H_2S). The Shell Sulfinol® gas sweetening process is particularly useful at high H_2S concentrations (Goar, 1971), and therefore it has been applied in western Canada since the early 1960s (Fitzgerald and Richardson, 1966). Contamination of Sulfinol® plant sites has occurred through spills, landfills, and seepage from unlined process water-storage ponds, leading to the presence of the major components, sulfolane and diisopropanolamine (DIPA) (Figure 1), in the groundwaters at these sites.

Sulfolane and DIPA are very water soluble and therefore are able to migrate through the groundwater for long distances. Luther et al. (1998) showed that DIPA interacts with clay minerals through cation exchange; however, little or no interactions between sulfolane and soil were detectable. Thus, sulfolane in particular poses a potential risk for off-site contamination due to its high mobility in groundwater.

Aerobic sulfolane biodegradation has been reported previously. Chou and Swatloski (1983) observed sulfolane degradation in an activated sludge system, McLeod et al. (1992) reported sulfolane removal from wastewater using a biological-activated carbon system, and more recently Fedorak and Coy (1996) demonstrated the biodegradation of sulfolane in soil and groundwater samples taken from a sour gas plant site. Greene et al. (1998) also reported aerobic sulfolane

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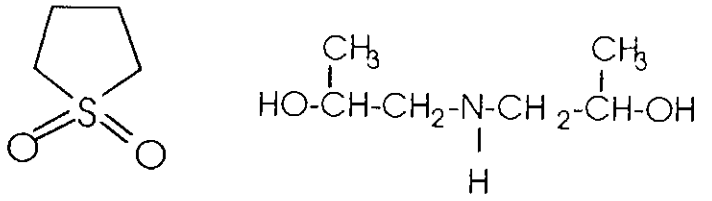

Sulfolane Diisopropanolamine (DIPA)

Figure 1. The structures of sulfolane and diisopropanolamine (DIPA).

degradation by microbial communities taken from contaminated or uncontaminated soils. Anaerobic removal of sulfolane was observed in only four of 60 microcosms taken from three contaminated sites (Greene et al., 1998). This activity was observed under nitrate- and Mn(IV)-reducing conditions. However, it was concluded that anaerobic degradation would not play a major role in sulfolane attenuation at any of the sour gas plant sites examined by these authors.

Previous work has shown that aerobic biodegradation of DIPA can occur (Bridié et al., 1979; Gieg et al., 1998; West, 1995). Studies with ^{14}C-DIPA demonstrated that much of the DIPA carbon was released as $^{14}CO_2$ (Gieg et al., 1999; West, 1995). Gieg et al. (1999) also observed anaerobic mineralization of ^{14}C-DIPA in cultures incubated under nitrate-, Mn(IV)-, and Fe(III)-reducing conditions.

Most of the research on aerobic biodegradation of sulfolane and DIPA has used shake-flask slurry cultures containing soils from contaminated sites (Fedorak and Coy, 1996; Gieg et al., 1998; Greene et al., 1998). This is a useful approach in screening for the ability of the microbial communities to degrade contaminants, but it provides very vigorous mixing and aeration that would not occur in an aquifer. Nielsen and Christensen (1994) described 2.5-L microcosms that contained fine sediment particles and groundwater. These microcosms were incubated in the dark in a slowly rotating box and were used to study the aerobic biological degradation of seven aromatic hydrocarbons. Later, Nielsen et al. (1995a; 1995b) compared the biodegradation of 19 different compounds in these laboratory microcosms with the biodegradation of the same compounds in in situ microcosms described by Gillham et al. (1990). From these studies, Nielsen and co-workers concluded that "in general, good accordance with respect to compound transformation was observed between in situ and laboratory experiments".

At the gas plant examined in this study, groundwater containing sulfolane and DIPA has migrated from the contaminating landfill cells, and low concentrations of sulfolane were detected in the surface waters of a wetland that is downgradient from the sources (Figure 2). Work by Gieg et al. (1998) and Greene et al. (1998) suggested that aerobic biodegradation was the most likely means by which sulfolane and DIPA would be removed from contaminated soils and groundwaters. Thus, the present study focussed solely on aerobic processes. No information was available on whether the microbial community in the wetland could degrade these two contaminants.

The objectives of this research were to determine the potential for aerobic biodegradation of the two compounds using samples from five locations at the plant site, and to determine whether supplementation with inorganic N and/or P would stimulate biodegradation. Many studies have shown that biodegradation of contaminants is stimulated by the addition of inorganic N and P (Braddock et al., 1997; Bragg et al., 1994; Fedorak and Coy, 1996; Lai et al., 1996; Piehler and Paerl, 1996). Our study was done using a shake-flask method and the 2.5-L microcosms described by Nielsen and Christensen (1994) so that the results from these two approaches could be compared. It was hypothesized that the shake-flask cultures would give a relatively rapid indication of the sulfolane and DIPA biodegradation potentials of the various samples, and the 2.5-L microcosms would more closely mimic the field conditions, based on the findings of Nielsen et al. (1995a; 1995b). All incubations were done at 8°C, a typical groundwater temperature in western Canada.

Materials and Methods

Aquifer Sediments, Muds, and Water Samples

Aquifer sediment, groundwater, wetland mud, and wetland water samples were taken from five locations at a gas plant site in western Canada (Figure 2). Sediment cores from the east and west plumes and the

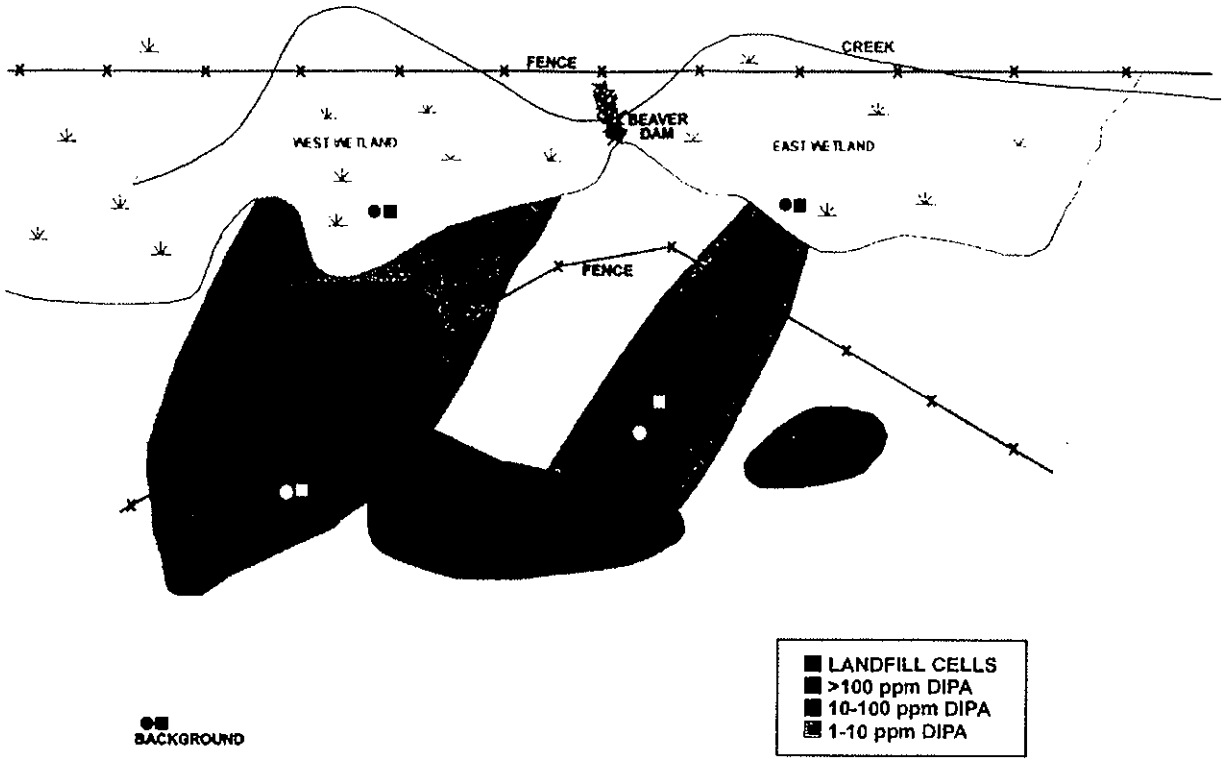

Figure 2. The contaminated landfill cells, the DIPA plumes, and the sampling locations at the sour gas treatment plant that was studied. Locations from which groundwater and surface water samples were taken are marked with circles. Locations for corresponding sediment and mud samples are marked with squares.

uncontaminated sample were taken from depths of 2.5 to 4.7 m using an auger rig. The cores were placed in 6.4-cm-inner-diameter plastic sleeves in 76-cm sections. Groundwater samples were taken from piezometers adjacent to each drilling site where sediment samples were obtained. Wetland mud samples were taken at the surface of the wetland, and surface water samples were taken from an area adjacent to where the wetland mud samples were obtained (Figure 2). The wetland mud and all groundwater and surface water samples were placed in sterile, 4-L plastic bottles. Samples were transported to the laboratory in ice-filled coolers and stored at 4°C until used.

Subsamples of each soil core were mixed aseptically in a 4-L plastic beaker to ensure that uniform samples were used for all inoculations. One 76-cm segment of sample core was used in the experiment for each location.

Chemicals

DIPA was obtained from TCI America (Portland, OR) as a 98% pure mixture of isomers. Sulfolane was obtained from Aldrich (Milwaukee, WI) and was 99% pure. Formaldehyde solution was purchased from Fisher (Fair Lawn, NJ) as a 37% w/w solution in water and 10 to 15% methanol. All chemicals used in microbiological studies were reagent grade and purchased from BDH or Aldrich.

Analytical Methods

Sulfolane analyses were done using a model 5890 gas chromatograph (Hewlett Packard) equipped with a flame ionization detector. The column was 120 × 0.32 cm stainless steel packed with 5% polyphenyl ether 6-ring (Chromatographic Specialties, Brockville, ON) coated Tenax-GC, 60/80 mesh (Alltech Associates, Deerfield, IL), and had an additional 15-cm segment of column material added to the front end as a guard column. The carrier gas was helium with a flowrate of 25 mL/min. The oven temperature was 200°C; injector and detector temperatures were 250°C. Using a 2-µL direct aqueous injection, the detection limit of the method was 1 mg/L.

DIPA was analyzed by direct aqueous injection into a gas chromatograph with a N-selective detector (Gieg et al., 1998). A modified temperature program was 150°C for 2 min, heating at 12°C/min to 168°C,

which was held for 2 min. The injection port and detector were maintained at 250 and 300°C, respectively. To reduce peak tailing, the injector split ratio was 20:1 and the carrier gas flow was 20 mL/min.

Unidentified co-contaminants in the groundwaters from the east and west contaminated plumes caused severe problems for the DIPA analysis. After as few as four injections of east plume samples, DIPA peak tailing increased and the peak areas decreased. This analytical problem was lessened by switching to the base-deactivated Cyclosplitter® liner (Restek Corp., Bellefonte, PA) and the use of methanol injections between sample injections. Each liner could be used for 15 to 25 injections of samples from the contaminated plumes before it had to be replaced. Because the DIPA peak areas decreased as more injections of the contaminated groundwaters were made, calibration standards were frequently injected to ensure that the best possible quantitative data were obtained. This method was very time consuming; thus, many fewer DIPA analyses than sulfolane analyses were done.

Soil pH was measured in distilled water and 0.01 M $CaCl_2$ (McLean, 1982). Dissolved oxygen was measured using a YSI Model 59 oxygen meter. For each sample, the probe was immersed in the shaking culture for 1 to 2 min before the dissolved oxygen reading was recorded. Sulfide analyses were done using the method of Ulrich et al. (1997).

Total organic C was measured using an Ionics Model 2000 Total Organic Carbon Analyzer. Samples were diluted to a total organic C concentration of 10 to 50 mg/L with deionized, distilled water before analysis.

Shake-Flask Cultures

Shake-flask cultures were comprised of 50 g (wet weight) of sediment or mud and 200 mL of the corresponding groundwater or wetland water sample in sterile 500-mL shake-flasks closed with foam plugs. East and west plume groundwaters contained sufficient sulfolane and DIPA to be monitored during the experiment. The uncontaminated and wetland water samples contained very little sulfolane or DIPA, so these were spiked with sterile sulfolane and DIPA solutions to give a final concentration of approximately 120 mg/L of each compound.

For each sampling location, three cultures were monitored: one sterile control, one culture without N and P supplementation, and one culture with N and P supplementation. The sterile solution of N and P supplement contained 1.2 g NH_4Cl, 2.0 g KNO_3, 32 g KH_2PO_4 and 48 g K_2HPO_4, per L of water. Each supplemented 200-mL culture received 10 mL of this solution providing 30 mg N/L and 790 mg P/L. Control cultures were autoclaved for 30 min at 121°C, then formaldehyde was added at a final concentration of 500 mg/L to prevent any microbial growth. Cultures were incubated shaking at 200 rpm in the dark at 8°C.

2.5-L Microcosm Studies

The 2.5-L microcosms were modeled after those described by Nielsen and Christensen (1994) and Holm et al. (1992). Each microcosm consisted of 1 kg (wet weight) of aquifer sediment and 1.3 L of groundwater, or 1 kg (wet weight) of wetland mud and 1.3 L of surface water from the wetland added to a sterile 2.5-L bottle sealed with a foam plug. Before the groundwaters or surface water were added to the microcosms, they were aerated by bubbling air through the water sample until the dissolved oxygen concentration was approximately 10 mg/L. Groundwater added to the sterile controls was not aerated. The groundwater from the east and west plumes contained sufficient sulfolane and DIPA for the purpose of the experiment. Water added to the uncontaminated and wetland microcosms was spiked to give a final concentration of approximately 120 mg/L of each of these two compounds.

The east plume, west plume, and both wetland microcosms had a corresponding sterile control. For the sterile controls, the soil and groundwater were autoclaved for 30 min at 121°C. Sterile controls also received formaldehyde to give a final concentration 500 mg/L. All 2.5-L microcosms were incubated in the dark at 8°C, shaking at 40 rpm.

Effects of N and P Supplementation on Biodegradation

The effects of N and P supplementation on biodegradation were examined using the shake-flask culture method. A C:N:P ratio of 100:5:1 in weight units (Alef and Nannipieri, 1995) was selected as the basis for the N and P concentrations that were tested. The C concentration used for this calculation was the total amount of C contributed by sulfolane and DIPA only. The mean sulfolane and DIPA concentrations in the west plume groundwater samples were 680 and 70 mg/L, respectively (Table 1). These were equivalent to organic C concentrations of 272 mg/L and 38 mg/L, respectively, giving a total of 310 mg C/L from these two compounds in the groundwater. The concentrations of added N were 0Nr, 1Nr, and 2Nr, where Nr is the ratio of N required based on the C:N:P ratio of 100:5:1. Similarly, the concentrations of added

Table 1. Some characteristics of the samples taken from the sour gas treatment facility

Sample location	Sulfolane in aqueous samples (mg/L)	DIPA in aqueous samples (mg/L)	TOC in aqueous samples (mg/L)	TOC from sulfolane (mg/L)	TOC from DIPA (mg/L)	Other TOC (mg/L)	Soil type
Soil type							
East plume[a]	490	350	650	197	188	265	Silty clay and silty sand
West plume[a]	680	70	550	272	38	240	Silty clay
Uncontaminated[a]	<1	<1	<1	<1	<1	<1	Sandy silt
West wetland[b]	0.0024[c]	<0.05[c]	ND	ND	ND	ND	Clay loam
East wetland[b]	0.013[c]	<0.05[c]	ND	ND	ND	ND	Loam sand

Note: ND = Not determined

[a] Groundwater sample.
[b] Surface water sample from wetlands.
[c] Results obtained from previous analyses of samples from this site (J.H. Sevigny, unpublished data).

P were 0Pr, 1Pr, and 2Pr, where Pr is the ratio of P required based on the C:N:P ratio of 100:5:1. A total of nine cultures were incubated in order to test every possible combination of N and P, using these added concentrations. A sterile control without N and P addition, and a positive control that contained 30 mg N/L and 790 mg P/L, were also incubated.

A second set of cultures was comprised of sediment and groundwater from the east plume and was supplemented with the same concentrations of N and P as the west plume cultures. DIPA contributed 188 mg C/L to the cultures, and sulfolane contributed 197 mg C/L (Table 1), giving a total of 385 mg C/L. Therefore, concentrations of N supplementation were 0Nr, 0.8Nr, or 1.6Nr and the concentrations of P supplementation were 0Pr, 0.8Pr, or 1.6Pr, based on the C contributions from sulfolane and DIPA. Nine cultures were incubated, using a matrix of the N and P concentrations that tested all the possible combinations of N and P. Five additional cultures were incubated as part of this experiment: a sterile control, a culture supplemented with 1.6Nr and 205Pr, and three cultures containing 1.6Nr and with 2.4Pr, 3.2Pr, or 4Pr.

The shake-flask cultures consisted of 50 g of sediment sample taken from the east or west plume plus 200 mL of the corresponding groundwater sample. N was added as a sterile solution of 0.648 g NH_4Cl and 10.8 g KNO_3 per 100 mL. One milliliter of this solution contained 16.7 mg of N. The sterile P solution used for supplementation contained 1.24 g KH_2PO_4 and 1.86 g K_2HPO_4 per 100 mL. One milliliter of this solution contained 6.4 mg of P.

Determining Rate Constants

The rates of biodegradation of sulfolane and DIPA were determined using the method outlined by Metcalf and Eddy (1979). Each set of substrate removal data was plotted to determine whether it was better described by zero-order or first-order kinetics. In 36 of the 38 experiments, the sulfolane biodegradation data fit zero-order kinetics better than first-order kinetics. In 29 of 38 experiments, the DIPA biodegradation data fit zero-order kinetics better than first-order kinetics. Thus, for comparative purposes, only the zero-order rate constant for each data set is given in this report.

Results and Discussion

Table 1 shows some of the characteristics of the samples used in this study. The pH of the aquifer sediment samples ranged from 7.8 to 7.9 in 0.01 M $CaCl_2$ and 8.4 to 8.6 in distilled water, which is typical for calcarious soils. When the dry sediments were treated with 0.1 M HCl, effervescence was observed due to CO_2 release from $CaCO_3$ in the soils (Miller and Donahue, 1995).

The equations for the complete oxidations of sulfolane and DIPA are given below.

$$C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO_4^= \quad (1)$$

$$C_6H_{15}O_2N + 8O_2 \rightarrow 6CO_2 + 6H_2O + NH_3 \quad (2)$$

A strong acid (H_2SO_4) and a weak base (NH_3) are formed during the aerobic biodegradation of these two

compounds. The presence of $CaCO_3$ in the sediments would provide buffering in the shake-flask cultures and the 2.5-L microcosms.

Aerobic shake-flask cultures were used to determine whether samples from the five locations at the sour gas plant contained microbial communities that were capable of degrading sulfolane and DIPA. For each of the five locations sampled, one N- and P-supplemented culture, one unsupplemented culture, and one sterile control were incubated. No loss of sulfolane or DIPA was observed from any of the sterile controls over the 120-day incubation period, and the dissolved oxygen never dropped below 8 mg/L in any of the viable cultures. The initial pH of all the cultures ranged from 7 to 8.5. During the biodegradation of sulfolane and DIPA, there was typically a drop of 1 to 2 pH units in the shake-flask cultures. The exceptions were the east wetland shake-flask cultures, in which the pH dropped to near 3 in the unsupplemented culture, and to near 4 in the N- and P-supplemented culture. Sulfolane and DIPA were still degraded at the low pH values.

The smaller pH drop in the N- and P-supplemented east wetland culture demonstrated that the addition of phosphate to the cultures can provide some buffering. The amount of phosphate added was 8.3 mM, and, according to equation (1), the biodegradation of the initial 100 mg sulfolane/L (0.83 mM) would yield 1.6 mM H^+. The sharp pH drops observed in the wetland cultures suggest that other components in these muds were degraded to acidic products, exceeding the buffering capacity of the N- and P-supplemented culture medium.

Table 2 summarizes the lag times before biodegradation of sulfolane and DIPA occurred and the rates of biodegradation in the shake-flask cultures. In the three sediment-containing cultures, both contaminants were degraded more quickly in the presence of N and P (Table 2). For example, in the east plume shake-flask cultures, the addition of N and P decreased the lag time for sulfolane biodegradation from 98 to 13 days and increased the rate of degradation from 0.6 to 3.7 mg/L-h. In the east plume-supplemented culture, the lag time for DIPA biodegradation was 7 days, whereas in

Table 2. Sulfolane and DIPA biodegradation results from shake-flask cultures and the 2.5-L microcosms

Source of inoculum	N and/or P added	Culture type	Sulfolane degradation		DIPA degradation	
			Lag time (days)	Degradation rate (mg/L-h)	Lag time (days)	Degradation rate (mg/L-h)
East plume	No	Shake-flask	98	0.6	>120[a]	0.0
	Yes	Shake-flask	13	3.7	7	0.1
	No	2.5-L	220[b]	0.0	220[b]	0.0
	P[c]	2.5-L	5	0.5	NA[d]	0.22
West plume	No	Shake-flask	34	0.4[e]	<1	0.01
	Yes	Shake-flask	12	5.2	2	0.3
	No	2.5-L	220[b]	0.0	220[b]	0.0
	P[c]	2.5-L	29	0.3	15	0.15
Uncontaminated	No	Shake-flask	88	0.4	50	0.02
	Yes	Shake-flask	24	1.7	23	0.3
	P,N[f]	2.5-L	>377	0.0	>377	0.0
West wetland	No	Shake-flask	9	0.2	4	0.4
	Yes	Shake-flask	28	0.3	22	0.2
	No	2.5-L	39	0.3	<1	0.06
East wetland	No	Shake-flask	53	0.2	10	0.02
	Yes	Shake-flask	24	0.3	26	0.06
	No	2.5-L	25	0.4	14	0.02

[a] Experiment ended at day 120.
[b] At day 221, microcosms were supplemented with P; therefore, no further incubation of the unsupplemented microcosm occurred.
[c] 1Pr was added to these microcosms at day 221; the lag time and degradation rates reported are for after the addition of P, not from time zero.
[d] Not applicable, biodegradation began before P addition on day 221.
[e] After 70 days, degradation stopped with 300 mg sulfolane/L remaining in this culture.
[f] 1Pr was added to these microcosms at day 221 and 1Nr + 1Pr at day 294; no biodegradation of sulfolane or DIPA was observed by the end of the 377-d incubation period.

the unsupplemented culture no DIPA biodegradation was detected over the 120-day incubation period.

In contrast, the onset of biodegradation of sulfolane and DIPA in the west wetland shake-flask culture and of DIPA in the east wetland shake-flask culture proceeded more quickly in the absence of N and P (Table 2). The wetland cultures contained a great deal of organic material, including grasses and peat; therefore, the addition of N and P may have stimulated the biodegradation of natural substances rather than sulfolane and DIPA, thereby decreasing the rate at which these contaminants were utilized by the microbial populations present.

In the cultures that contained the calcarious aquifer sediments, the beneficial effect of N and P supplementation was likely as added nutrients rather than as an increased buffering capacity due to phosphate. For example, the east plume groundwater contained 490 mg sulfolane/L (4.1 mM). Based on Eq. 1, its complete oxidation would yield 8.2 mM H^+. In the unsupplemented shake-flask culture, the pH remained between 8.2 and 7.5 throughout the period, while all of the sulfolane was degraded. Thus, the $CaCO_3$ in the sediment was sufficient to buffer the culture without the addition of phosphate.

The initial shake-flask experiments demonstrated that the addition of N and P to aquifer sediment-containing cultures stimulated biodegradation of sulfolane and DIPA. The amount of N and P required for sulfolane and DIPA removal from groundwater was calculated using the C:N:P ratio of 100:5:1; these amounts were defined as Nr and Pr, respectively. In each of the three groundwater samples, the total N concentration from ammonium, nitrate, and nitrite was ≤0.13 mg/L, and P as orthophosphate was <0.003 mg/L (J.H. Sevigny, unpublished data). These low concentrations were ignored in the calculations of Nr and Pr.

Under the conditions examined, the data suggested that the presence of P increased the biodegradation of both compounds, whereas the addition of N had less effect on their biodegradation (Figure 3, Table 3). DIPA biodegradation was influenced to a greater extent by P than by N supplementation in west plume shake-flask cultures (Figure 3A). Cultures that received 0Pr showed a gradual decrease in DIPA concentration, with some of this compound remaining at the end of the 61-day incubation period. Indeed, DIPA remained in all of the west plume cultures that were not supplemented with P (Table 3). In contrast, within 30 days DIPA concentrations were below the detection limit in cultures with 0Nr; 1Pr; or 0Nr, 2Pr (Figure 3A).

The west plume shake-flask cultures all exhibited lag periods of 2 to 6 days before DIPA degradation commenced (Table 3). The cultures with 0Pr degraded DIPA at rates between 0.05 to 0.29 mg/L-h; the rates increased with increasing N supplementation. Among the three microcosms supplemented with 1Nr, there was a marked increase in biodegradation rate with 2Pr supplementation to 0.22 mg/L-h.

Figure 3B shows sulfolane biodegradation in selected west plume shake-flask cultures. Sulfolane biodegradation was observed in the unsupplemented culture (0Nr, 0Pr). The addition of P only, (i.e., 0Nr; 1Pr; and 0Nr, 2Pr) sharply enhanced the biodegradation of sulfolane, whereas the addition of 1Nr, 0Pr had a small detrimental effect.

Lag times of 20 to 22 days before sulfolane biodegradation commenced were observed in the west plume shake-flask cultures with 0Pr, regardless of the amount of N added (Table 3). The addition of 1Pr or 2Pr decreased the lag times to between 9 and 13 days. Sulfolane biodegradation rates increased more by the addition of 2Pr than of 1Pr; however, the addition of 255Pr had no further noticeable effect on biodegradation. The cultures with 0Pr exhibited sulfolane biodegradation rates between 1.0 and 1.4 mg/L-h (Table 3). When P was added at a concentration of 1Pr, the rates of sulfolane biodegradation increased to between 3.8 and 4.4 mg/L-h, and supplementation with 2Pr at 0Nr increased the rate to 6.3 mg/L-h. Amending with 1Nr, 2Pr and with 2Nr, 2Pr gave the highest sulfolane degradation rates (Table 3).

As a general rule, in a given shake-flask culture in which both sulfolane and DIPA were biodegraded, DIPA demonstrated a shorter lag time before biodegradation than sulfolane. However, once sulfolane biodegradation began, its rate and extent of removal generally exceeded those of DIPA. These results suggest that DIPA may be a better C source for a wide variety of microorganisms present in contaminated sediments; however, once a population has acclimated to degrade sulfolane, that compound is readily degraded.

Sulfolane and DIPA were not the only C sources present in the contaminated aquifer. Gas chromatography with the N-selective detector showed the presence of at least six unidentified N-containing co-contaminants in the west plume materials. With N and P supplementation, most of these compounds were removed from the shake-flask cultures after 64 days of incubations. These biodegradable co-contaminants would increase the demand for P.

The effects of P on sulfolane biodegradation were also examined in cultures containing materials from the east plume (Figure 3C). As with the west plume cultures, the addition of P increased the biodegrada-

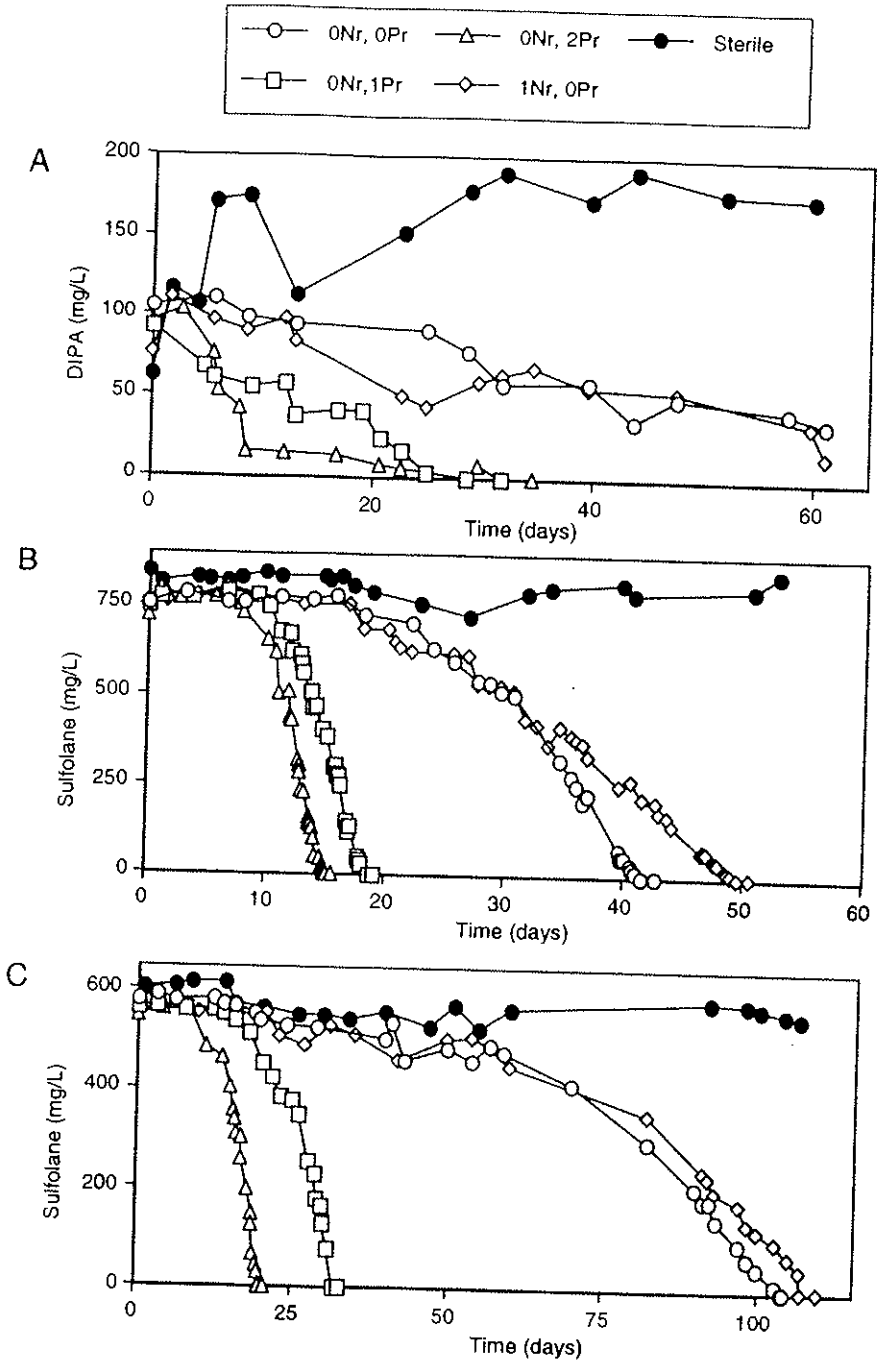

Figure 3. Loss of DIPA or sulfolane from shake-flask cultures consisting of contaminated sediment and the corresponding groundwater sample. Cultures were supplemented with various amounts of N and P: (A) DIPA degradation by the microbial population from west-contaminated plume materials; (B) sulfolane degradation by the microbial population from west-contaminated plume materials; (C) sulfolane degradation by the microbial population from east-contaminated plume materials.

tion rate and decreased the lag times (Table 3). With 0Pr, there was no sulfolane biodegradation for 57 days. When 0.8Pr was added, the lag times decreased to between 19 and 27 days (Table 3). Addition of 1.6Pr decreased the lag times to between 12 and 14 days. Addition of 3.2Pr and 4Pr decreased the lag times to 8 and 9 days, respectively. However, 205Pr increased the lag time to 15 days. Overall, for the east plume

Table 3. Biodegradation of sulfolane and DIPA in west plume shake-flask cultures and of sulfolane in east plume shake-flask cultures supplied with various amounts of N and P and incubated at 8°C. No loss of either sulfolane or DIPA was observed in the corresponding sterile control cultures

N, P added (mg/L)		West plume culture identity	West plume sulfolane degradation		West plume sulfolane degradation		East plume culture identity	East plume sulfolane degradation	
N	P		Lag time (days)	Degradation rate (mg/L-h)	Lag time (days)	Degradation rate (mg/L-h)		Lag time (days)	Degradation rate (mg/L-h)
0	0	0Nr, 0Pr	6[a]	0.05[a]	22	1.4	0Nr, 0Pr	58	0.5
15	0	1Nr, 0Pr	2[a]	0.12[a]	20	1.0	0.8Nr, 0Pr	58	0.4
30	0	2Nr, 0Pr	6[a]	0.29[a]	21	1.0	1.6Nr, 0Pr	57	0.6
0	3.1	0Nr, 1Pr	6	0.14	12	4.4	0Nr, 0.8Pr	21	1.5
15	3.1	1Nr, 1Pr	2	0.09	12	3.9	0.8Nr, 0.8Pr	19	2.1
30	3.1	2Nr, 1Pr	2	0.22	13	3.8	1.6Nr, 0.8Pr	27	2.0
0	6.2	0Nr, 2Pr	3	0.15	10	6.3	0Nr, 1.6Pr	14	3.0
15	6.2	1Nr, 2Pr	2	0.22	9	10	0.8Nr, 1.6Pr	12	1.8
30	6.2	2Nr, 2Pr	2	0.22	12	12	1.6Nr, 1.6Pr	13	2.9
30	9.3		ND	ND	ND	ND	1.6Nr, 2.4Pr	13	3.0
30	12.4		ND	ND	ND	ND	1.6Nr, 3.2Pr	8	4.6
30	15.5		ND	ND	ND	ND	1.6Nr, 4Pr	9	4.8
30	790	2Nr, 255Pr	2	0.30	10	6.2	1.6Nr, 205Pr	15	4.5

Note: ND = Not done.

[a] After a short lag time there was a brief period of DIPA biodegradation which slowed drastically when approximately one-half of the DIPA remained. The rate shown is for the initial DIPA biodegradation that occurred. By the end of the 61-day incubation period, DIPA still remained in these shake-flask cultures.

shake-flask cultures there was a strong linear correlation ($r^2 = 0.92$) between the rate of sulfolane biodegradation and the concentration of P, up to 4Pr.

At comparable concentrations of P, the rates of sulfolane biodegradation in the shake flasks containing materials from the west plume were nearly always greater than in those containing east plume materials (Table 3). The only exception was in the cultures supplemented with 790 mg P/L. These differences in rate may be attributable to the differences in total organic C concentrations in the two groundwater samples. The east plume groundwater contained 650 mg/L organic C, of which 197 mg/L (31%) came from sulfolane (Table 1), whereas the west plume groundwater contained 550 mg/L, of which 272 mg/L (49%) came from sulfolane. The higher organic C concentration relative to sulfolane in the east plume may have resulted in a higher demand for P for the biodegradation of compounds other than sulfolane, causing a lower sulfolane biodegradation rate in these shake-flask cultures. However, other unknown factors may also contribute to the differences between sulfolane degradation rates.

Some of the P added to the shake-flask cultures would have precipitated as a calcium phosphate in the calcarious aquifer sediments (Miller and Donahue, 1995). Thus, the concentrations of added P given in Table 3 were likely higher than the actual concentrations of soluble phosphate in the cultures. Nonetheless, the addition of P did stimulate the biodegradation of sulfolane and DIPA.

The results in Figure 3 and in Table 3 clearly demonstrate that the biodegradation of sulfolane and DIPA by microbial communities in the contaminated sediments was limited by the supply of P. Other examples of P limitation of biodegradation have been reported. For example, in aerobic laboratory microcosms used to study the biodegradation of benzene, toluene, ethylbenzene, and xylenes (BTEX) and some trimethylbenzenes, Grainger (1997) reported that microcosms amended with N alone showed a negligible amount of biodegradation over a 62-day incubation period. The lag times and substrate utilization rates in the microcosms amended solely with P were similar to those observed in microcosms supplemented with both N and P.

Lai et al. (1996) studied the biodegradation of naphthenic acids in tailings pond water from the extraction of bitumen from oil sands. They found that the degradation rate of these acids was increased by the addition of phosphate. They also observed that the acute toxicity of tailings pond water to fathead minnows, which is thought to be due to the presence of naphthenic acids, was decreased by the addition of phosphate.

In the case of the sour gas treatment plant site studied in this project, the intrinsic P concentration was lower than the amount of P required for sulfolane and DIPA biodegradation in the east and west plume contaminated sediments and groundwaters. The N concentration present, however, did not appear to be too low for removal of these compounds. Gieg et al. (1999) showed that between one-third and one-half of the N from DIPA was released as ammonia-N in aerobic batch cultures. Thus, once DIPA biodegradation begins, DIPA itself will contribute to the amount of available N.

The 2.5-L microcosms were used to determine whether results from biodegradation studies in shake-flask cultures could be related to results obtained using microcosms modeled after those described by Holm et al. (1992). These microcosms were not initially supplemented with N or P. At the shaking speed of 40 rpm, the solids settled to the bottom of the microcosms during the first 2 days of incubation, forming a sediment layer overlaid with a nearly clear water layer about 10 cm deep in the wetland microcosms and 15 cm deep in the aquifer sediment microcosms. The relatively large amount of plant detritus and peat in the wetland samples prevented their settling as tightly as the sediment samples, which were comprised of clay, sand, and small rocks.

The sterile control microcosms showed no loss of sulfolane or DIPA during the 377-day monitoring period. Examples of microbial degradation of sulfolane and DIPA and the dissolved oxygen in the aqueous portions of the 2.5-L microcosms are shown in Figure 4.

In general, the slow shaking of the microcosms was adequate to maintain the high dissolved oxygen concentrations between 7.5 and 10 mg/L during the experiment (Figure 4A). However, there was a sharp decrease in dissolved oxygen in the east wetland microcosm between days 10 and 14. On day 15, air was bubbled into this microcosm to replenish the oxygen content. Subsequently, no further decreases in the oxygen concentration occurred (Figure 4B). This drop in dissolved oxygen was not observed in any of the other 2.5-L microcosms.

During the rapid biodegradation of sulfolane and DIPA in the east plume microcosm after the addition of 1Pr (Figure 4A), the rate of sulfolane removal was 0.5 mg/L-h (4.2 µmol/L-h), and the rate of DIPA removal was 0.22 mg/L-h (1.6 µmol/L-h) (Table 2). Based on Eq. 1 and 2, the oxygen demands for these biodegradations were 27.3 and 12.8 µmol/L-h, respec-

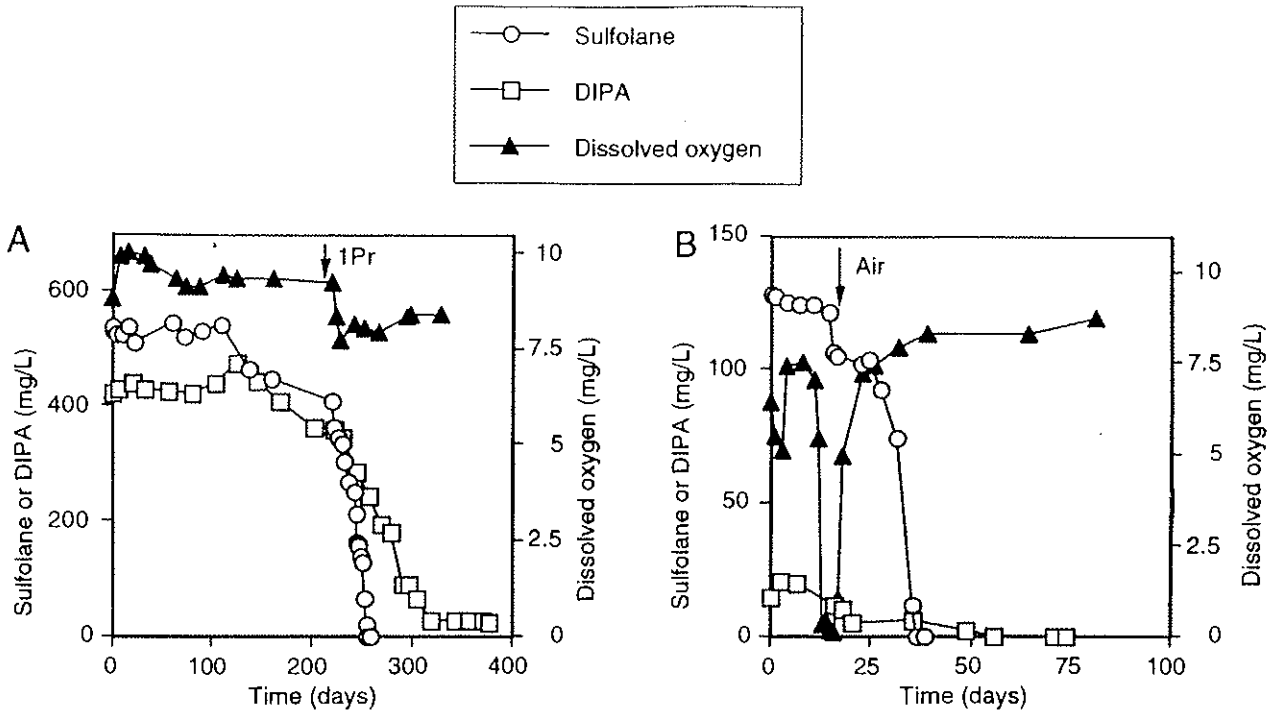

Figure 4. Loss of sulfolane and DIPA from 2.5-L microcosms consisting of contaminated aquifer sediment and groundwater from (A) the east-contaminated plume or of (B) wetland mud and the corresponding surface water from the east wetland region and the concurrent changes in dissolved oxygen concentrations in the aqueous portion of the microcosms. The arrow on the east plume microcosm graph (A) indicates the time that the microcosm was supplemented with 1Pr. The arrow on the east wetland microcosm graph (B) indicates the time at which air was bubbled into the east wetland microcosm to replenish depleted dissolved oxygen.

tively. Thus, the total oxygen demand for the mineralization of these two compounds was 40.1 μmol/L-h. There was little decrease in the dissolved oxygen concentration during this time, so the rate of O_2 replenishment in the aqueous phase must have been at least 40.1 μmol/L-h.

Between days 10 and 14, there was a decrease in the sulfolane and DIPA concentrations in the 2.5-L microcosms containing east wetland material (Figure 4B). The mean rates of removal during this time were 0.69 mg/L-h (5.8 μmol/L-h) for sulfolane and 0.42 mg/L-h (3.2 μmol/L-h) for DIPA. Based on Eqs. 1 and 2, these biodegradation rates would require O_2 to be replenished at a rate of 63.3 μmol/L-h, which is greater than the replenishment rate estimated from the data from the east plume microcosm. Thus, the consumption of sulfolane and DIPA may have contributed to the sharp decrease in dissolved oxygen concentration observed between days 10 and 14. However, the east wetland mud also contained 26% organic matter, and biodegradation of this material likely contributed to the severe drop in dissolved oxygen.

After 220 days incubation, there was no apparent sulfolane biodegradation in the 2.5-L microcosms that contained sediments from the uncontaminated aquifer or the west plume. However, after a lag time of 100 days, sulfolane biodegradation began in the east plume microcosm (Figure 4A), and about 20% of the sulfolane was removed by day 220, giving a removal rate of 0.04 mg/L-h. Similarly, there was no DIPA biodegradation in the former two microcosms by day 220, whereas approximately 15% of the DIPA had been degraded in the east plume microcosm between days 126 and 220 (Figure 4A), corresponding to a removal rate of 0.06 mg/L-h. The shake flask studies demonstrated that the addition of P would stimulate sulfolane and DIPA biodegradation, so on day 221 phosphate was added to the three aquifer sediment-containing microcosms to give a final concentration of 1Pr.

After the addition of phosphate to the west plume microcosm, sulfolane biodegradation began within 28 days and DIPA biodegradation began within 14 days, and there were marked increases in the rates of sulfolane and DIPA biodegradation in the east plume microcosm

after P supplementation (Figure 4A). Similarly, the sulfolane concentration decreased to below the detection limit of the analytical method after 33 days in the east wetland microcosm, after 53 days in the west wetland microcosm, after 255 days in the east plume microcosm, and after 319 days in the west plume microcosm. There was no decrease in sulfolane or DIPA concentrations in the microcosm that contained uncontaminated sediment, even after the addition of N and P (Table 3).

Table 2 summarizes the results obtained from monitoring the 2.5-L microcosms. On days 221 and 294, P and/or N were added to selected microcosms to stimulate biodegradation of sulfolane and DIPA. The west wetland and east wetland microcosms did not require nutrient supplementation. In those two microcosms, sulfolane biodegradation began after 39 and 25 days of incubation, respectively, and the rates of degradation were 0.3 and 0.4 mg/L-h, respectively. DIPA biodegradation started after a lag times of <1 day for the west wetland microcosm and 14 days for the east wetland microcosm. The DIPA biodegradation rates were 0.06 and 0.02 mg/L-h, respectively.

After 60 days, a black precipitate was detected in the viable contaminated aquifer sediment microcosms, suggesting that sulfate-reducing bacterial activity was producing iron sulfides. At the end of the experiment, the sediment in the sterile east plume microcosm contained 1 μg sulfide/g (wet weight), whereas the sediment in the viable east plume microcosm contained 510 μg sulfide/g. No sulfide was detected in the sediment from the sterile west plume microcosm, but 760 μg sulfide/g (wet weight) was found in sediment from the viable west plume microcosm. The east plume and west plume groundwaters contained 1470 and 600 mg/L sulfate, respectively (J.H. Sevigny, unpublished data), which could support sulfate-reducing bacteria.

The sulfide production in sediments in the 2.5-L microcosms in this study indicated that although the dissolved oxygen concentrations in the aqueous layer remained above 7.5 mg/L, the settled sediment layer became anaerobic. Gieg et al. (1998) demonstrated that sulfate-reducing bacteria were present at this gas treatment plant site, but there was no evidence for sulfolane or DIPA biodegradation by these bacteria (Gieg et al., 1998; Greene et al., 1998).

The results from the 2.5-L microcosms that contained uncontaminated sediment differ from those obtained from the shake-flask experiments (Table 2), which showed that the microorganisms in this sediment could biodegrade both sulfolane and DIPA in the absence or presence of N and P. Using the shake-flask method, Gieg et al. (1998) demonstrated that DIPA could be biodegraded by microorganisms in three soils that had no known history of DIPA or sulfolane contamination. Greene et al. (1998) used these same three uncontaminated soils and observed sulfolane biodegradation in shake-flask cultures. Thus, the shake-flask method can readily detect biodegradation potentials in uncontaminated soils. Further experimentation is required to determine if these potentials can be detected using the procedure with the 2.5-L microcosms.

Sulfolane was biodegraded to below detection limits in all of the shake-flask cultures and all but one of the 2.5-L microcosms. DIPA removal to below the detection limit was observed in only two of the 2.5-L microcosms. This occurred after 70 days in the east wetland and after 48 days in the west wetland microcosms. At the end of the 377-day experiment, 7 mg/L DIPA remained in the west plume microcosm and 22 mg/L remained in the east plume microcosm (Figure 4A). At the end of the shake-flask experiment (after 120 days of incubation) the remaining DIPA concentrations in the unamended east plume and west plume shake-flask cultures were 200 and 28 mg/L, respectively.

The results from all the shake-flask cultures and from the 2.5-L microcosms indicate that once sulfolane biodegradation started, it was removed to concentrations <1 mg/L. These results are consistent with previous aerobic studies of sulfolane biodegradation (Chou and Swatloski, 1983; Greene et al., 1998). DIPA removal was not complete in many of the shake-flask cultures and 2.5-L microcosms in the present study, whereas no residual DIPA was observed in other aerobic studies (Gieg et al., 1998, 1999). The stronger sorption of DIPA than sulfolane to soils (Luther et al., 1998) would be expected to reduce the bioavailability of DIPA and thereby contribute to its incomplete removal from the cultures. However, this cannot be the only factor leading to residual DIPA in the cultures because soil extraction to recover sorbed DIPA was not part of our analytical method. The residual DIPA concentrations measured were in the aqueous phase, and this DIPA should be bioavailable to the active microbial community.

Table 2 compares the lag times and biodegradation rates observed in the shake-flask cultures and the 2.5-L microcosms. For sulfolane biodegradation, seven direct comparisons of the lag times can be made (no comparison can be made for the east plume with N and P added). In five of these cases, the shake-flask method produced much shorter lag times, but in one case (east wetland without N and P) the 2.5-L microcosm exhibited a shorter lag time. The lag times for sulfolane biodegradation were essentially the same for the east plume without N and P. For DIPA biodegradation, six direct comparisons of the lag times can be made (no

comparisons can be made for the east plume material with or without N and P). In five of the six cases, the lag times for DIPA biodegradation were shorter in the shake-flask cultures. The exception was the west wetland sample, which gave a longer lag time in the shake-flask culture than in the 2.5-L microcosm. In general, the shake-flask method yields shorter lag times than the 2.5-L microcosms (Table 2).

The data in Table 2 allow the direct comparisons of the biodegradation rates for all eight pairs of results for sulfolane and for sevens pairs of results for DIPA degradation (no comparison can be made for the east plume without N and P). Conservatively, the rates were considered to be the same if they differed by less than a factor of three. Applying this criterion, the shake-flask method yielded higher sulfolane biodegradation rates in six of eight cases, and higher DIPA degradation rates in four of seven cases. In no case was the biodegradation rate in the 2.5-L microcosm threefold greater than that in the corresponding shake-flask culture. Thus, as was observed with the lag time data, the shake-flask method generally hastened the biodegradation of these two compounds.

The enhanced biodegradation in the shake-flask cultures would not be due to superior aeration because, with the exception of the brief decline in dissolved oxygen in the 2.5-L microcosm containing the east wetland material (Figure 4B), the dissolved oxygen concentrations remained high in the water layer of all these microcosms and in the shake-flask cultures.

The key difference between these two experimental approaches is the extent of mixing. The shake-flask cultures essentially were completely mixed by shaking at 200 rpm throughout the duration of the experiment. In contrast, the sediments in the 2.5-L microcosms settled quickly at the beginning of the experiment, and remained as a phase distinct from the overlying groundwater as the bottles were incubated at 40 rpm. The extent of mixing would have a profound effect on the contact between the active microorganisms and their growth substrates, including sulfolane, DIPA, and oxygen. The aerobic biodegradation of sulfolane and DIPA in the 2.5-L microcosms would have occurred mainly at the sediment-liquid interface.

The shortest lag times for sulfolane and DIPA biodegradation in the 2.5-L microcosm study were the microcosms that contained wetland mud (Table 2). These materials were much less dense than the aquifer sediments and did not compact as tightly as the sediments when they settled. This would allow more transport of the overlying water within the mud and provide a greater supply of nutrients to the microorganisms. This is best illustrated by comparing the results from the uncontaminated sediment with the west wetland material (Table 2). These two microcosms had the same initial concentrations of sulfolane and DIPA, and the dissolved oxygen concentrations remained high throughout the experiment. Biodegradation of sulfolane and DIPA began within 40 days with the wetland material, but no biodegradation was observed with the uncontaminated sediment over 377 days.

Fu et al. (1996) used electrolytic respirometry to compare oxygen uptake rates during phenol degradation in slurry, wafer, and compacted soil tube reactors. Our shake-flask method was equivalent to their slurry reactors, and our 2.5-L microcosms were similar to their compacted soil tube reactors. In the two experiments described by Fu et al. (1996), the lag times before phenol biodegradation were longer for the compacted soil tube reactor than for the slurry reactor. Our data for sulfolane and DIPA biodegradation (Table 2) showed that the 2.5-L microcosms generally had longer lag times, consistent with the observations of Fu et al. (1996). The observed rates of phenol degradation, as measured by oxygen uptake, were greater in the slurry reactors than in the compacted soil tube reactors (Fu et al., 1996). Similarly, our data in Table 2 showed that the biodegradation of sulfolane and DIPA was generally faster in the shake-flask cultures than in the 2.5-L microcosms.

The 2.5-L microcosms more closely mimic conditions in an aquifer than do the shake-flask cultures. However, these microcosms were not complete replicates of the aquifer. For example, although the solids settled in the microcosms during incubation, the soil architecture was disturbed during the preparation of the microcosms. Also, the contaminated aquifer from which the samples were taken was essentially devoid of O_2. However, because little or no biodegradation of sulfolane occurred under anaerobic conditions (Greene et al., 1998), we chose to use aerobic conditions in this investigation. During the first 220 days of incubation, no biodegradation of sulfolane or DIPA occurred in any of three aquifer samples in the 2.5-L microcosms (Table 2). This is very likely the most accurate estimate of what would happen in the aquifer. Biodegradation in two of these microcosms began after the addition of P. Thus, the degradation rates from these 2.5-L microcosms reported Table 2 would be representative of what might occur if nutrients and O_2 were injected into a contaminated aquifer.

Conclusions

This investigation demonstrated that microbial communities capable of degrading sulfolane and DIPA were present in all the sediment and mud samples taken from five locations at a sour gas processing

plant. It showed that a shake-flask method provided a faster, and likely more sensitive, means of assessing their biodegradation potential than 2.5-L microcosms, although the rates of biodegradation obtained from the shake-flask method undoubtedly exceeded those that occurred in the environment. The higher biodegradation rates observed in the shake-flask cultures were attributed to the vigorous mixing that maintained contact between the active microorganisms and their growth substrates. This intense mixing did not occur in the 2.5-L microcosms. The shake-flask method established that supplementation with P gave a greater stimulation to biodegradation of these two compounds than did the addition of N. Studies with the 2.5-L microcosms verified that supplementation with P-enhanced biodegradation of sulfolane and DIPA. In general, DIPA biodegradation commenced before sulfolane biodegradation in the various cultures studied. DIPA biodegradation is known to release ammonia-N, which would serve as an N source. The availability of this N source from DIPA is likely the reason that the shake-flask cultures were not stimulated by the addition of exogenous N.

The results from previous studies suggest the biodegradation of sulfolane and DIPA in the anoxic contaminated plume is not likely to occur. However, if oxygen and nutrients, especially P, are available, DIPA and sulfolane degradation should occur. Also, if these two contaminants slowly seep into the adjacent wetland at the study site, and aerobic conditions are maintained, their intrinsic bioremediation in this natural wetland may occur.

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SULFOLANE BIODEGRADATION POTENTIAL IN AQUIFER SEDIMENTS AT SOUR NATURAL GAS PLANT SITES

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Abstract—Sulfolane is used in the treatment of sour natural gas. It is a highly water soluble compound that has been introduced into soils and groundwaters at a number of sour gas processing plant sites. Aquifer sediments from contaminated locations at three sites in western Canada were assessed for microbial activity and their ability to degrade sulfolane under aerobic and five anaerobic (nitrate-, Mn(IV)-, Fe(III)-, sulfate- and CO_2-reducing) conditions. The microcosms were supplemented with 200 mg/L sulfolane and adequate supplies of N, P, and the appropriate terminal electron acceptor. Microcosms containing contaminated aquifer sediments from each of the three sites were able to degrade sulfolane aerobically at 8°C and 28°C, and the biodegradation followed zero-order kinetics. The lag times before the onset of sulfolane biodegradation were shorter when sulfolane-contaminated sediments were used as inocula than when uncontaminated soils were used. No anaerobic sulfolane biodegradation was observed at 28°C, nor was sulfolane biodegradation observed at 8°C under Fe(III)-, sulfate- and CO_2-reducing conditions. At 8°C, anaerobic degradation of sulfolane coupled to Mn(IV) reduction was observed in microcosms from two sites, and degradation coupled to nitrate reduction was seen in a microcosm from one of the contaminated sites. © 1998 Elsevier Science Ltd. All rights reserved

Key words: aerobic biodegradation, diisopropanolamine, groundwater, manganese-reduction, nitrate-reduction, sulfolane.

INTRODUCTION

Sour natural gas can contain undesirable compounds, including H_2S, COS, CS_2 and mercaptans (Goar, 1971). The Shell Sulfinol® process uses a physical solvent, tetrahydrothiophene sulfone (sulfolane) and a chemical solvent, diisopropanolamine (DIPA) to remove H_2S and other contaminants from sour natural gas. This process is particularly effective at high H_2S concentrations (Goar, 1971), therefore is useful in western Canada, where natural gas reserves can contain up to 35% H_2S.

The Sulfinol® process was first used to treat sour natural gas in western Canada in the early 1960s (Fitzgerald and Richardson, 1966). Over the past few decades, landfills, spills and evaporation ponds containing sulfolane and DIPA have contaminated surface and subsurface soils at sour gas plant sites. Sulfolane and DIPA (Fig. 1) are both highly water soluble compounds, and they have become groundwater contaminants with the potential to migrate from the sour gas plant sites.

Only a few studies on sulfolane degradation are reported. These studies were mainly concerned with wastewater treatment or the ability of activated sludge to degrade sulfolane (Bridié *et al.*, 1979; Chou and Swatloski, 1983; Juhl and Clark, 1990; McLeod *et al.*, 1992). During sulfolane biodegradation by an activated sludge system, acid was produced through the near stoicheometric release of the sulfur from sulfolane as sulfate (Chou and Swatloski, 1983). There have been no reports of anaerobic sulfolane biodegradation.

The toxicity of sulfolane has been evaluated. Andersen *et al.* (1976) reported acute toxicity data for mice, rats and guinea pigs with LD_{50} values ranging from 632 to 1846 mg/kg body weight. Lewis (1992) reported LD_{50} concentrations of 1080 mg/kg for mice via intravenous injection, 1540 mg/kg by oral administration to rats, and 3180 mg/kg by dermal application to rabbits. It appears that sulfolane is not very toxic, however operators of sour gas plants want to understand the fate of this compound and prevent its migration away from the plant sites.

The major objective of this investigation was to determine whether microbial populations indigen-

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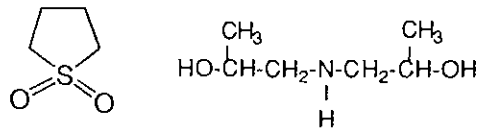

Sulfolane Diisopropanolamine (DIPA)

Fig. 1. Structures of sulfolane and DIPA, which are the two major components used in the Sulfinol® process.

ous to sulfolane- and DIPA-contaminated aquifers at three sour gas treatment plants in western Canada were capable of biodegrading sulfolane. Incubations were done under aerobic and anaerobic conditions, because both these conditions exist in the contaminated plumes under investigation. Geochemical evidence suggests that nitrate, Mn(IV), Fe(III), sulfate, and CO_2 are the primary terminal electron acceptors for organic matter degradation in anaerobic environments (Lovley and Phillips, 1988), so anaerobic studies were done using each of these five terminal electron acceptors. Experiments were conducted at incubation temperatures of 28°C and 8°C; the lower temperature approximates the groundwater temperatures of aquifers in western Canada and the higher temperature was predicted to give faster biodegradation so that the presence of sulfolane degraders could be assessed more quickly.

MATERIALS AND METHODS

Sediment samples

Sediment samples and groundwaters were taken from the anaerobic zones of sulfolane- and DIPA-contaminated aquifers at three western Canadian sour gas treatment sites (Table 1). All samples were shipped on ice to the laboratory and stored at 4°C until they were used.

Site 1 represents one of the largest gas plants in Alberta, and has been used in the recovery of natural gas liquids since 1961. The sources of sulfolane contamination include landfill cells, and evaporation and surface runoff ponds. The sample consisted of sandstone, siltstone and shale bedrock, which was ground during the sampling procedure.

Site 2 is in southwestern Alberta, and has also been in operation since the 1960s. Contamination of groundwater can be traced to a landfill containing construction debris, Sulfinol® filters and spent catalyst. A contaminated core was taken downgradient from the landfill and an uncontaminated core was taken above the landfill site. The core material was made up of silty-clay till (Luther *et al.*, 1998).

Site 3, in eastern British Columbia, has been in operation since 1980. This site was sampled at a contaminated zone downgradient from a filter and catalyst dump containing sulfolane and DIPA. The sample consisted of sandstone bedrock and was ground to a sandy material by the drilling process.

Uncontaminated, humus rich soil was taken from the Dh horizon of a region 6 km north of Lacombe Park in St. Albert, Alberta. This soil had been sifted and air dried and was stored at room temperature until cultures were inoculated. Uncontaminated soil was obtained from a greenhouse at the University of Alberta.

Culture media

The compositions of the media used for the microcosms incubated under aerobic, or nitrate-reducing conditions are described by Gieg *et al.* (1998). Sulfate-reducing studies were done using the freshwater composition medium described by Collins and Widdel (1986). Medium used for the methanogenic microcosms is described by Fedorak and Hrudey (1984). Viable microcosms and sterile controls were supplemented with a final concentration of 200 mg/L sulfolane (99%, Aldrich, Milwaukee, WI).

Anaerobic media were prepared under a 30% CO_2 balance N_2 headspace. For all but the Fe(III)- and Mn(IV)-reducing media, 75 mL of medium were added to a 158-mL serum bottle, which was then sealed with a butyl rubber stopper and autoclaved at 121°C for 20 min. The Fe(III)- and Mn(IV)-reducing media were dispensed in 65-mL volumes, to allow the addition of 10 mL of a slurry of $Fe(OH)_3$ or MnO_2 prepared as outlined by Lovley and Phillips (1986). The slurry was added to the medium at the same time as the anaerobic sediments.

Inoculation with sediments

Microcosms prepared with uncontaminated materials and aquifer sediments from sites 1 and 2 received 50 g (wet weight) of soil. Due to the limited supply of aquifer sediment from site 3, only 35 g wet weight were added to each microcosm. Detailed procedures for inoculating the microcosms are given by Gieg *et al.* (1998).

For each test condition, sterile controls were prepared by autoclaving at 121°C, 15 psi for 30 min on 3 consecutive days. Aerobic sterile controls were then supplemented with mercuric chloride at a final concentration of 2.5 mg/L (Fedorak and Coy, 1996), and the anaerobic sterile controls were given 0.5% (v/v) chloroform (Albrechtsen *et al.*, 1995).

Microcosms were incubated at 8°C and at 28°C. For each temperature, duplicate cultures of each condition and a single sterile control were prepared. Aerobic cultures were incubated in the dark, shaking at 200 rpm.

Table 1. Characteristics at the sampling locations at the three sour gas plant sites that were investigated during this study

Site	Groundwater sulfolane concentration (mg/L)	Groundwater DIPA concentration[a] (mg/L)	Characteristics of sediment used in the microcosms
1	4	< 1	crushed sandstone bedrock
2	320	< 1	clay rich glacial till
3	30	6	fine to medium grain sand

[a]Detection limit was 1 mg/L, from Gieg *et al.* (1998).

Anaerobic cultures were incubated statically in the dark, and for sampling, the volume was replaced by additional headspace gas. Samples were stored at −20°C.

Analytical methods

For sulfolane analysis, soil and sediment slurry samples were centrifuged at 14,000 rpm for 10 min in an Eppendorf microfuge, and a 2-μL sample of supernatant was injected into a Hewlett Packard HP5890 gas chromatograph (GC) equipped with a flame ionization detector. The column used was 2 m × 0.3-mm diameter stainless steel tubing packed with 5% polyphenyl ether 6-ring (Chromatographic Specialties, Brockville, Ontario) coated Tenax-GC, 60/80 mesh (Alltech, Deerfield, IL). The carrier gas was He at a flow rate of 24 mL/min. Analysis was isothermal with the oven temperature held at 210°C. Injector and detector temperatures were both 250°C. The detection limit for sulfolane was 0.5 mg/L.

Methods used for methane, nitrate, Mn(II), Mn(IV), Fe(II), and Fe(III) analyses are given by Gieg *et al.* (1998). The method outlined by Budwill *et al.* (1996) was used to detect N_2O.

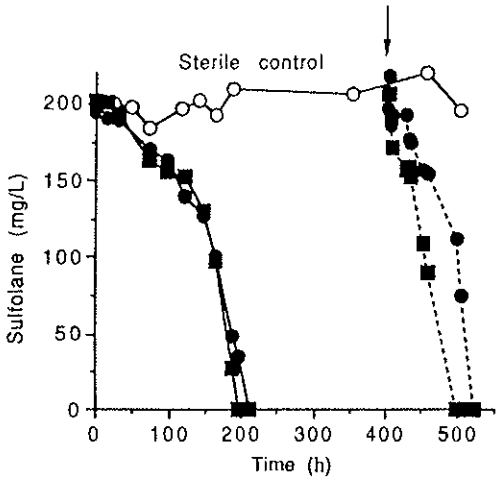

Fig. 2. Removal of sulfolane from aerobic microcosms containing contaminated sediment from site 1 incubated at 8°C. Solid circles and squares represent the replicate microcosms. The arrow indicates when microcosms were refed sulfolane.

RESULTS AND DISCUSSION

Aerobic sulfolane biodegradation

Aerobic sulfolane biodegradation was observed in all the microcosms containing contaminated sediments incubated at 8°C and 28°C. No sulfolane loss was observed from any of the sterile controls. The typical data for substrate loss are illustrated in Fig. 2, which shows the activity in shake flasks containing sediment from site 1 incubated at 8°C. After 30 h of incubation, the sulfolane concentrations in the viable microcosms were below that in the sterile control. Sulfolane was no longer detectable after about 200 h of incubation in these shake-flask cultures. At 402 h, the active microcosms were refed sulfolane and biodegradation began after a very short lag time (Fig. 2). There were some differences between the sulfolane biodegradation by the two replicate microcosms after the second feeding, however biodegradation of the second portion of sulfolane was faster than the initial portion in both microcosms. Similar results were seen in microcosms from all three sites.

The lag times before aerobic sulfolane biodegradation commenced are summarized in Table 2. In most of the duplicate microcosms, the onset of sulfolane degradation was detected at the same sampling time, giving the same lag time. In a few cases, the lag times differed between replicates, which likely reflected the heterogeneous distribution of sulfolane degraders in the sediment samples. In each case, the lag times were shorter in the microcosms incubated at 28°C than in those incubated at 8°C. After the microcosms were refed, no significant lag times were observed in any of the cultures.

Microcosms containing three uncontaminated soils were studied to compare their sulfolane biodegradation potential with those of the contaminated soils. These were incubated at 28°C only because it was anticipated that biodegradation at 8°C would be much slower, taking longer to obtain the results. The initial lag times for microcosms that contained the uncontaminated materials were much more variable and were 7- to 17-fold longer than those that contained the contaminated sediments. These results clearly demonstrated that previous exposure to sulfolane enriches a microbial community so it is able to more rapidly begin to degrade this compound.

Kinetic analyses indicated that sulfolane degradation was more accurately described by zero-order than first-order kinetics; the zero-order rate constants are summarized in Table 2. The rate con-

Table 2. Summary of the initial sulfolane biodegradation in the aerobic microcosms containing contaminated sediments from the three sour gas plant sites investigated, or uncontaminated soils

Site or soil	Lag time (h)[a]		Zero-order rate constant (mg/L/h)[a]	
	28°C	8°C	28°C	8°C
1	16 (16–16)	30 (30–30)	6.4 (6.1–6.6)	1.3 (1.2–1.3)
2	24 (24–24)	180 (144–216)	4.6 (4.6–4.6)	2.4 (2.0–2.7)
3	29 (26–31)	50 (50–50)	4.9 (4.6–5.2)	1.9 (1.7–2.1)
Site 2 upgradient[b]	200 (187–212)	ND[c]	5 (3–7)	ND
Humus rich[b]	269 (260–278)	ND	5 (3–7)	ND
Greenhouse[b]	208 (172–245)	ND	4 (4–4)	ND

[a]Mean values of the duplicate microcosms, with the values for the duplicate microcosms given in parentheses.
[b]Uncontaminated soil.
[c]ND not determined.

stants determined from the duplicate microcosms containing contaminated sediments generally agreed; the largest difference between two values was 0.7 mg/L/h (site 2 at 8°C). For each site, the rate of degradation in the microcosms incubated at 28°C was greater than that at 8°C. After the microcosms were refed, the rates of sulfolane biodegradation were greater than the initial rates of biodegradation. These rates increased from a low of 1.3-fold for the microcosm containing sediment from site 1 and incubated at 8°C (Fig. 2) to a high of 9.6-fold for the microcosm containing sediment from site 2 and incubated at 28°C (data not shown). Rate constants determined for the microcosms containing uncontaminated soils were between 3 to 7 mg/L/h (Table 2). Although the lag times for sulfolane degradation varied greatly between the contaminated and uncontaminated soil microcosms, once biodegradation started the rates of sulfolane removal were similar among the six cultures compared.

Microbial communities in three sulfolane-contaminated sediments had the potential to biodegrade sulfolane at 8°C, a typical western Canadian groundwater temperature, given the appropriate nutrients such as O_2, N and P. Previous work demonstrated that supplementing microcosms with N and P allowed faster removal of sulfolane from aerobic soil microcosms (Fedorak and Coy, 1996). The sulfolane concentration used in this investigation was 200 mg/L. This was the shock loading concentration used by Chou and Swatloski (1983) and was substantially higher than the concentrations investigated by McLeod *et al.* (1992) and Fedorak and Coy (1996). At the three gas plants, the sulfolane concentrations near the sources of contamination are typically a few hundred mg/L (unpublished data), therefore biodegradation at high sulfolane concentrations is important.

Studies with anaerobic microcosms

At any given contaminated site, a contaminant plume will spread horizontally in the direction of groundwater flow, as well as vertically downward (Christensen *et al.*, 1994). Typically, the leading edge of a contaminated plume will be aerobic. Microbial activity at the aerobic edge of the plume will soon deplete the available oxygen, after which various other chemicals available as terminal electron acceptors may be used by the anaerobic microbial populations present in the sediment. In a stable aquatic or sedimentary environment, the reduction sequence based on thermodynamics is O_2, nitrate, Mn(IV), Fe(III), sulfate and CO_2. (Gounot, 1994; Nealson and Saffarini, 1994).

Gieg *et al.* (1998) reported that acetate utilization was observed under nitrate-, Mn(IV)- and Fe(III)-reducing conditions at both 8°C and 28°C in microcosms containing sediments from each of the three sites. Methanogenic activity was observed only in the microcosms containing sediment from site 1, whereas sulfate-reducing activity was found only in the microcosms containing sediment from sites 2 and 3.

The thermodynamics for sulfolane biodegradation under methanogenic conditions were considered by calculating the Gibb's free energy change. The free energy of formation of sulfolane was found to be -2.59×10^8 J/kmol (Aspen Technology Inc.). The biodegradation of sulfolane under methanogenic conditions can be expressed by equation 1, based on the general formula given by Symons and Buswell (1933).

$$C_4H_8O_2S + 1.5H_2O \longrightarrow 1.75CO_2 + 2.25CH_4 + H_2S \quad (1)$$

Using the free energy values given by Thauer *et al.* (1977), the ΔG° for this reaction is −233 kJ/mol sulfolane, indicating that the reaction is thermodynamically favorable, even though it is the least favorable among all anaerobic reactions with different terminal electron acceptors.

The anaerobic microcosms from sites 1, 2 and 3 were monitored for 390, 504 and 446 days, respectively. However, only 4 of the 60 anaerobic microcosms supplemented with sulfolane showed any evidence of sulfolane biodegradation. None of the microcosms incubated at 28°C showed sulfolane degradation. No anaerobic sulfolane degradation was observed in any microcosms containing sediment from site 2. Site 1 yielded the most active sediment, with evidence for sulfolane biodegradation under nitrate- and Mn(IV)-reducing conditions. There was also evidence that sulfolane was degraded under Mn(IV)-reducing conditions in one microcosm that contained sediment from site 3.

From the thermodynamic considerations with equation 1, the inability to demonstrate sulfolane degradation under Fe(III)-reducing, sulfate-reducing and methanogenic conditions in this study was due to the absence of the appropriate active microbial communities, rather than to thermodynamically unfavorable reactions.

Sulfolane biodegradation under nitrate-reducing conditions

Loss of sulfolane was observed in the one of the microcosms containing contaminated sediment from site 1 incubated in nitrate-supplemented medium at 8°C (Fig. 3). When the sulfolane concentration in this microcosm had decreased from 190 mg/L to undetectable levels after 159 days of incubation, the microcosm was refed with nitrate and sulfolane (Fig. 3), and a portion of the slurry from the microcosm was transferred to fresh medium (Fig. 4). The original nitrate-supplemented culture removed the second amount of sulfolane from 210 to 21 mg/L, without a significant lag, over a period of 50 days (Fig. 3). At this time the culture was refed sulfolane

An ample supply of nitrate was present in all microcosms. GC analyses of the headspace gases from the refed microcosm and the transfer culture showed the presence of N_2O, an intermediate or product of nitrate reduction (Firestone *et al.*, 1980; Davidson, 1991), which was not found in the sterile control. This provided evidence that nitrate reduction occurred in the sulfolane-degrading microcosms.

Other investigators working with sediment-containing microcosms have found better agreement between the expected and observed amounts of nitrate consumed. For example, Häggblom *et al.* (1990) observed that 90% of the expected amount of nitrate was used during anaerobic biodegradation of *p*-cresol by microcosms that contained pond sediment.

The lower than expected consumption of nitrate during sulfolane biodegradation suggests that sulfolane may not have been completely mineralized and that some carbon-containing metabolites may have remained in the microcosm. At the time of inoculation, the headspace gas contained 30% CO_2 and 70% N_2, precluding the accurate measurement of either of these gases. The goal of this work was to determine whether sulfolane could be biodegraded under nitrate-reducing conditions by microbial communities from contaminated aquifers at sour gas plants; this was demonstrated. Determining a mass balance and identifying the microbial products of this biodegradation will require further studies.

Sulfolane biodegradation under Mn(IV)-reducing conditions

Loss of sulfolane under Mn(IV)-reducing conditions was observed in three microcosms incubated at 8°C (Table 3). The shortest lag time (34 days) was observed in the replicate B microcosm containing sediment from site 1, where the sulfolane concentration decreased from 180 to 20 mg/L by day 91 (Fig. 5). After refeeding at day 92, this microcosm showed an immediate decrease in sulfolane (Fig. 5), and over a period of 207 days, the sulfolane concentration decreased from 160 to 5 mg/L, at a mean rate of 1 mg/L/day. This rate was substantially lower than the rate of removal of the initial sulfolane dose (5 mg/L/day, Table 3).

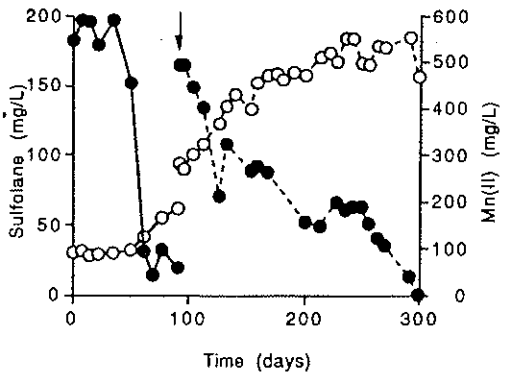

Fig. 5. Removal of sulfolane (closed circles) and production of Mn(II) (open circles) in the site 1 replicate B microcosm incubated at 8°C under Mn(IV)-reducing conditions. The arrow indicates when the microcosm was refed with sulfolane and MnO_2. The mean concentrations of sulfolane and Mn(II) in the sterile control were 180 ± 8 and 110 ± 9 mg/L, respectively.

In this microcosm, the Mn(II) concentrations increased from 90 to 190 mg/L during the initial loss of 162 mg/L of sulfolane, then increased further to 390 mg/L (Fig. 5). Over the course of the experiment, 0.18 mmol of sulfolane was consumed and 0.26 mmol of Mn(II) was produced. The color of solids in the Mn(IV)-reducing microcosms also indicated Mn(IV) reduction; as described by Lovley and Phillips (1988), the dark brown precipitate of MnO_2 added to the microcosms was converted to a grayish-white precipitate, which is consistent with the formation of the reduced product $MnCO_3$.

The replicate A microcosm containing sediment from site 1 degraded sulfolane under Mn(IV)-reducing conditions after a lag time of 160 days (Table 3). The sulfolane concentration decreased from 190 mg/L to undetectable levels (data not shown) over the next 54 days of incubation, giving a mean degradation rate of 3 mg/L/day. After refeeding, there was only a slight decrease in sulfolane concentration (15 mg/L), and no measurable increase in Mn(II) over the next 155 days of incubation. Over the 375-day incubation, the microbial community in this microcosm consumed 0.13 mmol of sulfolane and produced 0.18 mmol of Mn(II).

Mineralization of sulfolane under Mn(IV)-reducing conditions can be predicted to occur by the following equation:

$$C_4H_8O_2S + 9MnO_2 + 5HCO_3^- \longrightarrow 9MnCO_3 + 4H_2O + HS^- + 4OH^- \quad (3)$$

The two replicate microcosms containing contaminated sediment from site 1 consumed sulfolane at 8°C. For sulfolane mineralization in the site 1 microcosms, according to equation 3, the amounts of Mn(II) expected would be 1.57 and 1.15 mmol in replicates B and A, respectively. The measured formation of Mn(II) was 16% of the expected amounts in both microcosms.

The sulfolane concentration in the sterile control containing sediment from site 1 had a mean concentration of 180 ± 8 mg/L and a mean Mn(II) concentration of 110 ± 9 mg/L over the 375-day incubation period.

One site 3 microcosm showed evidence of sulfolane biodegradation under Mn(IV)-reducing conditions (Table 3). After a lag period of 168 days, this microcosm removed 200 mg/L of sulfolane at 1 mg/L/day. At day 287 this microcosm was refed and a portion was transferred to fresh medium. Sulfolane removal in the refed microcosm began

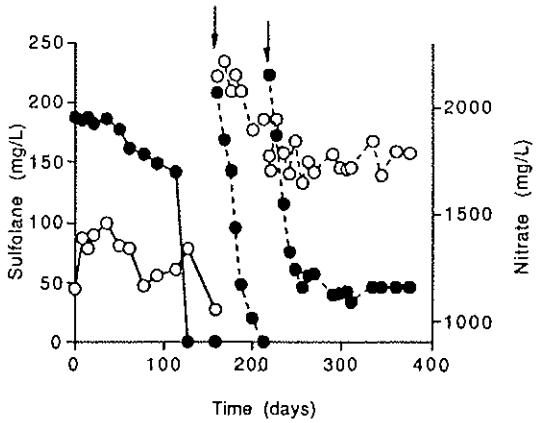

Fig. 3. Removal of sulfolane (closed circles) and nitrate (open circles) from an anaerobic microcosm (replicate B) containing contaminated sediment from site 1 incubated at 8°C under nitrate-reducing conditions. The arrows indicate when cultures were refed both sulfolane and nitrate at day 160 and sulfolane at day 220. In the corresponding sterile control, the mean sulfolane and nitrate concentrations were 190 ± 8 and 1420 ± 45 mg/L, respectively.

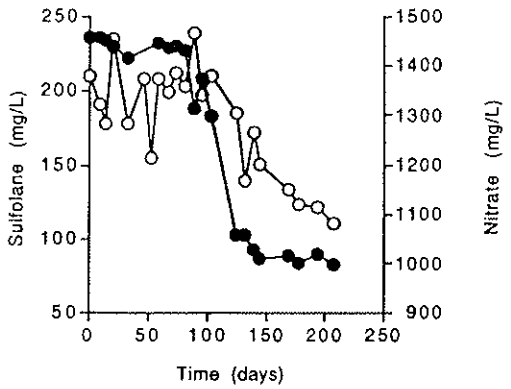

Fig. 4. Removal of sulfolane (closed circles) and nitrate (open circles) from the anaerobic transfer culture inoculated with 20 mL of slurry from the site 1 replicate B nitrate-supplemented microcosm incubated at 8°C.

without additional nitrate. The concentration of sulfolane again decreased with no significant lag period, from a starting concentration of 220 mg/L. However, once a concentration of approximately 40 mg/L sulfolane was reached, no further degradation was observed (Fig. 3). Throughout the 375-day incubation, the mean sulfolane concentration in the corresponding sterile control was 190 ± 8 mg/L (data not shown). The lag times and zero-order rate constants for sulfolane loss from the nitrate-reducing microcosm are summarized in Table 3.

During the initial loss of sulfolane, nitrate concentrations decreased from 1150 to 1060 mg/L (Fig. 3). After the culture had been refed sulfolane and nitrate, nitrate concentrations decreased from 2150 to 1950 mg/L. The third feeding of sulfolane led to nitrate concentrations decreasing from 1950 to 1780 mg/L. Overall, 0.31 mmol of sulfolane and 0.46 mmol of nitrate were consumed in this microcosm over the 375-day incubation. The mean nitrate concentration in the corresponding sterile control was 1420 ± 45 mg/L.

As shown in equation 2, complete mineralization of sulfolane under nitrate-reducing conditions is predicted to require 18 mol of nitrate per 5 mol of sulfolane, assuming that the nitrate is reduced to N_2.

$$5C_4H_8O_2S + 18NO_3^- \longrightarrow 20HCO_3^- + 9N_2 + 5HS^- + 7H^+ + 4H_2O \quad (2)$$

Based on equation 2, the microcosm utilized only 42% of the 1.11 mmol nitrate required to mineralize the 0.31 mmol of sulfolane that were consumed.

The nitrate-supplemented transfer culture showed an initial lag period of 103 days followed by a decrease in sulfolane of approximately 1.5 mg/L/day, with concentrations dropping from an initial 250 to 80 mg/L (Fig. 4). The nitrate concentration in this transfer culture decreased from 1340 to 1080 mg/L during the time that the sulfolane was removed. Overall, 0.11 mmol of sulfolane and 0.31 mmol of nitrate were consumed in this microcosm. Based on equation 2, 78% of the predicted 0.4 mmol of nitrate were consumed.

Table 3. Summary of sulfolane loss from anaerobic microcosms incubated at 8°C

Site	Terminal electron acceptor	Culture designation	Sulfolane supplementations	Lag time (days)	Rate of degradation (mg/L/day)
1	Nitrate	replicate B	First	35	5
		replicate B	Second	< 3	5
		replicate B	Third	< 3	5
		transfer B[a]	First	103	1.5
1	Mn(IV)	replicate B	First	34	5
		replicate B	Second	< 3	1
		replicate A	First	160	3
		transfer B[b]	First	157	0.2
		transfer A[a]	First	< 7	0.4
3	Mn(IV)	replicate A	First	168	1
		replicate A	Second	< 3	3
		replicate A	Third	< 3	5
		transfer A[a]	First	70	0.4

[a]20 mL of active microcosm slurry transferred to 65 mL of medium containing MnO_2 or nitrate.
[b]10 mL of active microcosm slurry transferred to 65 mL of medium containing MnO_2.

with no observed lag period, decreasing from 220 mg L to an undetectable level over 70 days at 3 mg L·day (Table 3). The culture was refed at day 392. All this substrate was removed by day 431. The mean sulfolane concentration in the corresponding sterile control was 210 ± 8 mg/L over the 431-day incubation period.

Mn(II) concentrations in the microcosm containing sediment from site 3 increased from 650 to 1000 mg/L during the removal of the initial dose of sulfolane. After the first refeeding, it increased to 1140 mg/L, and it increased further after the second refeeding to 1230 mg/L. The mean Mn(II) concentration in the corresponding sterile control was 920 ± 82 mg/L over the 431-day incubation period. During the 431-day incubation time, the microbial community in the microcosm containing sediment from site 3 consumed 0.30 mmol of sulfolane and produced 0.70 mmol of Mn(II). From equation 3, the amount of Mn(II) production predicted to occur for mineralization of 0.30 mmol of sulfolane was 2.70 mmol, therefore only 26% of the predicted Mn(II) was produced. Incomplete metabolism of sulfolane may have left organic products in the medium, thereby requiring less MnO_2 to be reduced to Mn(II) than given by equation 3, which presumes the complete mineralization of sulfolane.

The transfer cultures from the three active sulfolane-degrading microcosms (Table 3) showed little sulfolane-degrading and Mn(IV)-reducing activity. Often long lag times were observed (Table 3), and none of the transfer cultures consumed more that one-quarter of the sulfolane provided.

Microcosms from sites 1, 2, and 3 contained 85, 350 and 650 mg/L Mn(II), respectively, before Mn(IV) was added. Lovley (1991) stated that measuring the dissolved Mn(II) in interstitial waters of sediments can provide a useful indication of Mn(IV) reduction. Similarly, Gounot (1994) wrote that insoluble Mn(II) in the form of Mn_3O_4, $MnCO_3$ or adsorbed Mn(II) may constitute a significant portion of the Mn(II) generated from Mn(IV) reduction. Our measurements would detect soluble Mn(II) from interstitial waters and acid-soluble forms of insoluble Mn(II) in the sediments. The presence of Mn(II) in the time zero samples suggests that Mn(IV)-reducing activities may have been occurring *in situ* at the sampling locations of the contaminated gas plant sites.

The data collected from the microcosm studies suggest, however, that sulfolane degradation via Mn(IV) reduction was not occurring *in situ*. Only three of the six MnO_2-containing microcosms established with the contaminated sediments were able to degrade sulfolane at 8°C. Of the three active microcosms, two required lag times of ≥160 days before sulfolane degradation commenced. One would expect shorter lag times if Mn(IV) reduction coupled to sulfolane degradation was occurring *in situ*.

Relevance of sulfolane biodegradation in an aquifer

The ability of microorganisms at sour natural gas plant sites to degrade sulfolane and DIPA is of interest because these compounds are groundwater pollutants at a number of gas plant properties. Wrubleski *et al.* (1997) reported that routine monitoring of sour gas plants in western Canada showed that most plants employing the Sulfinol® process have on-site groundwater contaminations of sulfolane, and in some cases DIPA, which is often a co-contaminant with sulfolane.

Sulfolane is highly water soluble and does not sorb significantly to soils (Luther *et al.*, 1998), suggesting that it is likely to migrate from gas plant sites in the groundwater, and could eventually contaminate nearby domestic wells and surface waters. Those authors predicted that sulfolane would move 3 to 8 times farther than DIPA at the three sites investigated. It is therefore expected that sulfolane concentrations would be higher than DIPA concentrations in a plume some distance away from the contamination source.

Gieg *et al.* (1998) found lag times between 95 and 120 h before the onset of aerobic DIPA biodegradation at 28°C in microcosms that contained the same three uncontaminated soils that were used in the present study. The lag times observed in this study were significantly longer, ranging from 172 to 278 h (Table 2), indicating that sulfolane, a sulfur-containing cyclic compound (Fig. 1), was more resistant to biodegradation by microbial communities in uncontaminated soils than DIPA, a secondary amino alcohol.

The rate constants determined for the aerobic biodegradation of sulfolane in this study are substantially higher than would be observed in aquifers contaminated with sulfolane; the microcosms were supplemented with N and P and the slurries were shaken to maximize O_2 transfer to the microbial populations. In the aquifer, the sediment would be compacted. Fu *et al.* (1996) used electrolytic respirometry to compare O_2 uptake rates during phenol degradation in slurry and compacted soil tube reactors. It was hypothesized that the tube reactor would more closely represent field conditions. When the reactors were loaded with 3.75 mg of phenol, the O_2 uptake rates were calculated to be 10-fold greater in the slurry reactor than in the compacted soil tube reactor. In addition, the total O_2 uptake by the slurry reactor was double that of the other reactor, indicating that more phenol was degraded in the slurry reactor than in the compacted soil tube. Similarly, sulfolane degradation is predicted to be slower in compacted aquifer sediments.

Chou and Swatloski (1983) observed near stoichiometric release of sulfate from sulfolane. Because of the high concentrations of solids in our aerobic slurry microcosms, no attempt was made to detect

sulfate. However, sulfate release from sulfolane was observed in subsequent aerobic enrichment cultures that were devoid of the aquifer solids (E. A. Greene and P. M. Fedorak, unpublished data). Thus, the heterocyclic ring can be broken by the microorganisms from the contaminated aquifer material, and presumably much of sulfolane is eventually mineralized.

Marked differences between the biodegradability of sulfolane and DIPA under anaerobic conditions were observed. DIPA was biodegraded in each of the replicate microcosms incubated at 28°C and 8°C under nitrate-, Mn(IV)- and Fe(III)-reducing conditions in materials from the three sites (Gieg *et al.*, 1998). In contrast, few sulfolane-degrading microcosms demonstrated anaerobic activity (Table 3). Neither DIPA (Gieg *et al.*, 1998) nor sulfolane were found to be degraded at 8°C under Fe(III)-reducing, sulfate-reducing or methanogenic conditions.

In summary, sulfolane is biodegradable under aerobic conditions when sufficient amounts of N and P are supplied. It is much less biodegradable under anaerobic conditions, although some activity was observed under nitrate- and Mn(IV)-reducing conditions. These anaerobic activities were low, particularly with subsequent feeding and transfers to fresh medium. Anaerobic biodegradation of the co-contaminant from the Sulfinol® process, DIPA, was much more likely to occur.

From this study and those of Luther *et al.* (1998) and Gieg *et al.* (1998) the following predictions concerning a contaminant plume originating from the Sulfinol® process were made. Sulfolane would migrate through the groundwater more quickly than DIPA. If sufficient O_2, N and P were present at the leading edge of the plume, sulfolane biodegradation would likely occur. This would lead to anaerobic conditions behind the leading edge of the plume. In part of this anaerobic plume, sulfolane would likely be the major or only contaminant. Although anaerobic degradation may be possible, it probably would not have a marked effect on the attenuation of this compound. Closer to the contaminant source, both DIPA and sulfolane would be present in the groundwater plume. Anaerobic DIPA removal would presumably be more significant than sulfolane removal. However, because anaerobic microbiological processes are much slower than aerobic processes, the microbial attenuation of these two compounds may not be important at the high concentrations observed. These predictions have yet to be verified by field data.

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DISTURBANCES AND INHIBITION IN BIOLOGICAL TREATMENT OF WASTEWATER FROM AN INTEGRATED REFINERY

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ABSTRACT

Biological treatment of wastewater from an integrated oil refinery, containing hazardous contaminants, was studied in an on site pilot plant. The wastewater is pretreated by gravity separation, flocculation and dissolved air flotation. Biotreatment of such wastewaters poses several problems which have to be considered in planning, design and operation of the treatment system. The process rate is relatively slow, due to the inhibitory effects. The mixed liquor volatile suspended solids (MLVSS) could not be maintained at concentrations higher than 2000 mg/l. Sudden discharges of concentrated phenolic wastes disrupted the process first by impairing bioflocculation, followed by complete inhibition of the biological process.

KEYWORDS

Integrated oil refinery; biological treatment; disturbances; inhibition.

INTRODUCTION

Integrated oil refineries include many cracking processes, particularly catalytic cracking and auxiliary processes which generate wastewaters with high concentrations of hazardous contaminants such as various phenolic compounds. All refineries are significant water consumers and consequently large wastewater producers. In areas with limited water resources, reuse has to be often practiced and therefore good quality effluent is required. Also in "water rich" areas the wastewater has to be efficiently treated for removal of the hazardous contaminants, before discharge, to protect the quality of receiving waters.

Treatment schemes commonly used in refineries include gravity oil-water separation followed by flocculation and dissolved air flotation. For removal of the dissolved organics biological treatment is usually necessary.It may be applied either to pretreated refinery wastewater only, or as joint treatment with neighboring municipal wastewater.

Biological treatment of refinery wastewater has been reported for many years, with efficient stabilization in the activated sludge process requiring however, long acclimation periods for the biota to metabolize the refractory components (Dickenson and Giboney, 1970).Application of adapted mutant bacterial cultures to the treatment was suggested by Mahmud and Thanh(1978) and by McDowell and Zitrides (1979). While many report that phenol is a controlling toxicant in biological treatment (Christiansen and Spraker, 1982), (Reynolds et al., 1975), some researchers report efficient phenol removal at influent concentration up to 200 mg/l, after acclimation, but requiring long reactor residence time to achieve good biofloc settleability (McKinney, 1972). Biodegradability rate of parafinic and aromatic hydrocarbons was much lower than of municipal type organic material and adverse effects of hydrocarbons on settling characteristics of the bioflocs were encountered (Groenewold et al.,1982).

In the present work the biotreatability of wastewater from an integrated oil refinery was studied in an on-site pilot plant. It was a rather strong wastewater, due to the low specific water consumption, with significant phenols content and occasional very high phenols concentration. The phenols are contributed by the cracking process and special gasoline washeries. The specific objectives were to study the fate of phenols and hydrocarbons and their effect on the biological process, process rates, biofloc properties and to derive ways to overcome difficulties caused by these pollutants.

EXPERIMENTAL

General description. The present treatment plant in this refinery includes an API type gravity separator followed by chemical flocculation and dissolved air flotation (DAF), as described in Fig. 1. High oil, hydrocarbon and suspended solids removals are accomplished by this treatment. To meet effluent discharge standards and to prepare the effluent for reuse, the reduction of hydrocarbons (including so-called "soluble hydrocarbons") to low levels, removal of phenols and reduction of BOD are required. Biological treatment is planned as the next stage, for which this study was performed.

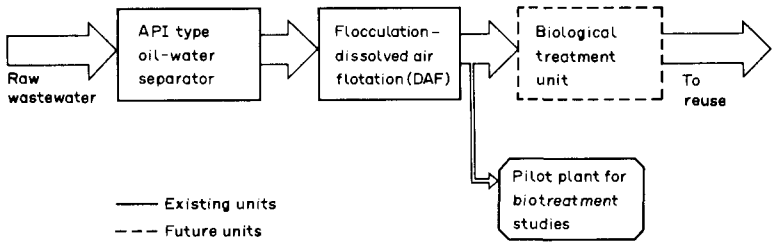

Fig. 1 Refinery wastewater treatment system

This research was done on an on-site pilot plant (see Fig. 2) consisting of an aeration tank, as bioreactor, an attached clarifier (volumes: 270 and 75 liters respectively), all the necessary piping, pumps for biosludge recirculation, flow measurements and regulation devices.

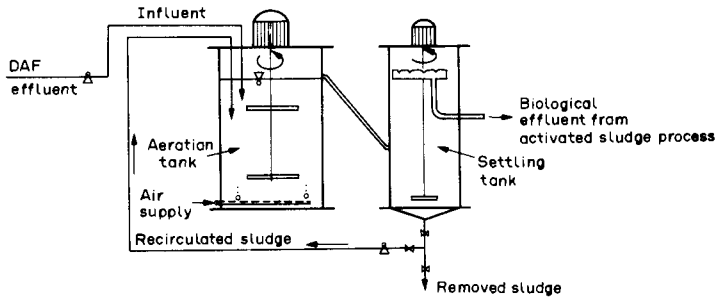

Fig. 2 Schematic description of pilot plant

Composite samples of feed and effluent were collected and stored in refrigeration for laboratory analysis while dissolved oxygen, temperatures, sludge volume index and wasted sludge were determined on site. Routine analyses were performed according to Standard Methods (1985), the hydrocarbons were analysed by CCl_4 extraction and infra red spectroscopy (U.O.P. Method 726.72), total phenols were analysed by distillation (Standard Methods, 1985) and specific phenols determination was by liquid - liquid extraction and gas chromatography using capillary column (Baird et al., 1977).

Influent to the biological reactor. The effluent of the Dissolved Air Flotation unit served as the feed to the bioreactor (see Fig. 1). The Characteristic composition of the influent to the biotreatment pilot plant is summarised in TABLE 1 .

TABLE 1 Average Concentrations of Pollutants in Oil Refinery Wastewater Before and After Biological Treatment.

CONSTITUENT	INFLUENT			EFFLUENT		
	RESEARCH PERIOD		LITERATURE	RESEARCH PERIOD		LITERATURE
	1982 - 1984	1984 - 1985		1982 - 1984	1984 - 1985	
pH	8.80	8.14	6.2 - 10.6	8.0	7.85	6.7 - 7.9
TOTAL SUSPENDED SOLIDS	46	98	15 - 85	52	47	6 - 112
VOLATILE SUSPENDED SOLIDS	25	65		34	26	
C O D - TOTAL	625	637	140 - 3340	400	230	80 - 300
C O D - SOLUBLE	561	443		330	165	
B O D - TOTAL	180	268	17 - 230	30	19	4 - 100
B O D - SOLUBLE	156	143		15	7	
PHENOLS	22	9	0.3 - 154	0.8	0.2	0.3 - 4.8
HYDROCARBONS	30	40	23 - 200	4.5	4.8	0.5 - 9.0
AMMONIA (as N)	4.7	21	0 - 120	0.5	13	0 - 43
DETERGENTS (ABS)	13.7	13.3		11.2	10.9	
CHLORIDES			19 - 1080			
SULFIDES			0 - 38			
CONDUCTIVITY (μmho / cm)		2272				

During the three years' study, two periods can be distinguished regarding influent characteristics and concentrations as shown in the Tables. The major differences are in phenols concentration, in BOD and ratios of soluble to total BOD and COD (see TABLE 2).

TABLE 2 Average Concentrations of COD and BOD in the Study.

CONSTITUENT	RESEARCH PERIOD 1982 - 1984		RESEARCH PERIOD 1984 - 1985	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
C O D - TOTAL	625	400	637	230
C O D - SOLUBLE	561	330	443	165
$COD_{SOLUBLE} / COD_{TOTAL}$	0.90	0.82	0.70	0.72
B O D - TOTAL	180	30	268	19
B O D - SOLUBLE	156	15	143	7
$BOD_{SOLUBLE} / BOD_{TOTAL}$	0.87	0.50	0.53	0.37
$COD_{TOTAL} / BOD_{TOTAL}$	3.47	13.33	2.38	12.10
$COD_{SOLUBLE} / BOD_{SOLUBLE}$	3.60	22.00	3.09	23.57

TABLE 3 Process and Operational Parameters in Experimental Work

PARAMETER	UNITS	RANGE
FLOW RATE	l / day	216 - 615
HYDRAULIC DETENTION TIME	hr	10 - 30
ORGANIC LOAD (F/M)	day^{-1}	0.09 - 1.37
CELL RESIDENCE TIME	day	5.2 - 23.5
MIXED LIQUOR VOLATILE SUSPENDED SOLIDS	mg / l	500 - 2300
DISSOLVED OXYGEN IN BIOREACTOR	mg / l	3.1 - 7.8

RESULTS AND DISCUSSION

Performance of the process. The general performance efficiency of the process in accomplishing the treatment objectives can be seen in TABLE 1, summarising the average contaminants concentrations in influent and effluent. Fig. 3 shows the variations of concentrations during the research period. When operated below a given organic loading rate, which will be discussed later, efficient reductions in concentrations of major pollutants were obtained.

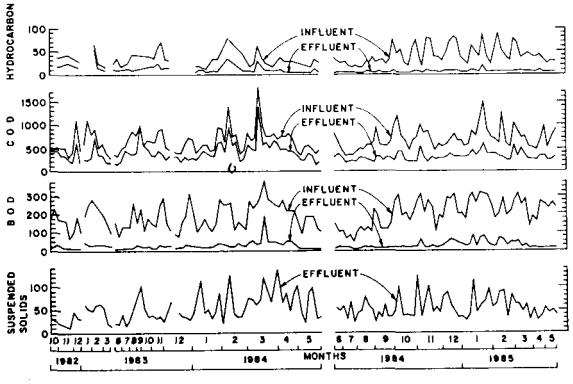

Fig. 3 Characteristics of influent and effluent in activated sludge process.

BOD: was reduced to 30 mg/l during the period 82-84 and to 20 mg/l during 84-85, with soluble values of 15 and 7 mg/l respectively, giving removals of 85 to 95 percent.

COD: residuals in the effluent were relatively high and removals of only 40 to 60 percent were obtained, indicating the refractory nature of a large part of the original organics.

Hydrocarbons: concentrations in the effluent were below 5 mg/l, half of it incorporated in the bioflocs carried over in the effluent, leaving about 2 to 3 mg/l free hydrocarbons. The hydrocarbons removal and distribution can be seen in Fig. 7 and Fig.8. Due to the variability in the influent and effluent concentrations the cumulative probability curve of hydrocarbon concentrations could be used for a better presentation of the performance of the process, as shown in Fig. 4.

A special study was performed to follow the fate and mechanisms of hydrocarbon removal.It revealed that 90 percent was removed by stripping and biodegradation and about 10 percent by entrapment in the biofloc. The magnitude of the fractions removed by stripping varies with hydrocarbons composition and their volatility, but at least 50 percent of the hydrocarbons were always removed by stripping in the aeration tank (see Fig. 5).

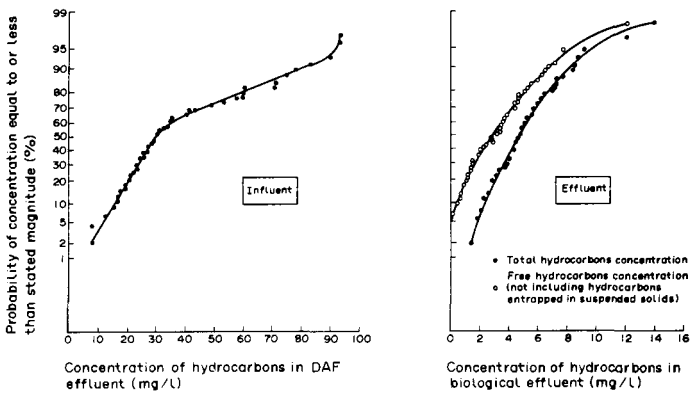

Fig. 4 Concentrations of hydrocarbons in the activated sludge process.

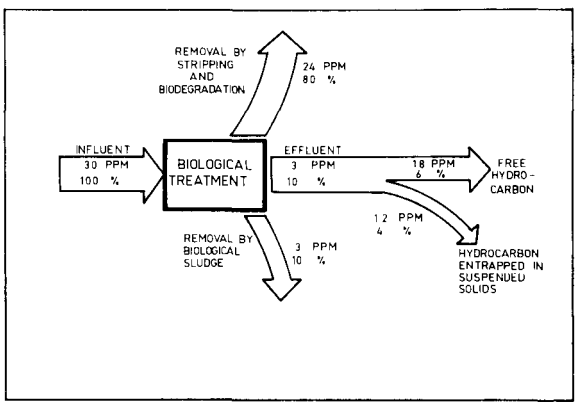

Fig.5 Removal of hydrocarbons in the activated sludge process.

Phenols: concentration was reduced by more than 90 percent, leaving average phenols concentrations below 1 mg/l, with phenols levels below 0.5 mg/l most of the time. The total phenols were composed of phenol, 3 isomers of cresol and 5 isomers of xylenol.The details and relative concentrations can be seen in chromatograms in Fig. 6.

SPECIFIC PROBLEMS AND DISTURBANCES

Process rate and inhibition. Although the process rate and kinetic analysis are not part of this paper, a short review of major findings will be given. The efficient removals of BOD and phenols, described above, could be achieved when organic loading rates did not exceed 0.15 kg BOD/kg MLVSS/day. This is a rather low specific loading rate indicating in itself slow kinetics. A more detailed kinetic analysis revealed high values of the apparent saturation constant $K_{s(ap)}$ in the Michaelis - Menten rate expression:

$$q = \frac{\hat{q}S}{K_s + S} \qquad (1)$$

$\hat{q}$ being the maximal loading rate and S the soluble organic substrate concentration.The values of $K_{s(ap)}$ were found to be directly dependent on the phenol concentration in the influent, as can be seen in TABLE 4. Analysis and interpretation of kinetic data indicates

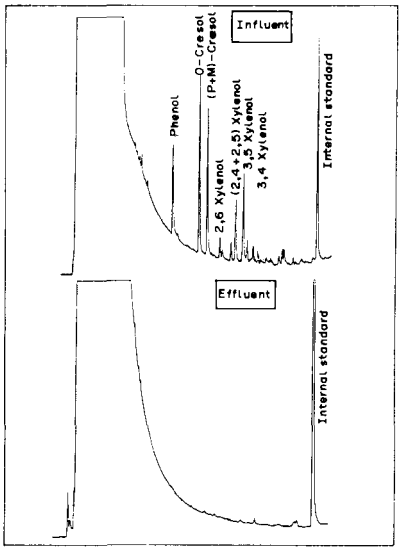

Fig. 6 Phenolic compounds in influent and effluent of the activated sludge.

inhibition by phenol via competitive type of inhibition. The apparent value of $K_{s(ap)}$ comprises the real K_s and the inhibition term:

$$K_{s(ap)} = K_s + K_I C_I \qquad (2)$$

K_I, C_I being inhibition coefficient and phenol concentration, respectively.

TABLE 4 Apparent Saturation Coefficient and Phenols Concentrations in Influent.

PARAMETER	RESEARCH PERIOD		
	LABORATORY UNIT	PILOT PLANT UNIT	
	1980 - 1982	1982 - 1984	1984 - 1985
PHENOLS CONCENTRATIONS IN INFLUENT (mg/l)	19 - 30 - 41	6 - 16 - 26	3 - 9 - 15
$K_{s(ap)}$ - APPARENT SATURATION COEFFICIENT (mg BOD / l)	151	66	32

High suspended solids in effluent and low MLVSS. As can be seen from the results, the suspended solids concentrations in the biotreated effluent were high, in the range of 40 to 50 mg/l. The secondary clarifier was working at very low surface loading and long residence time, the high suspended solids being a result of a very poor settleability of part of the bioflocs.The high suspended solids had two major negative effects:

- Adversely affecting the quality of the effluent through the high suspended solids itself and by being responsible for a great part of the hydrocarbons and BOD.
- The "escape" of solids with the effluent did not enable us to maintain MLVSS concentrations greater than 1500 mg/l to 2000 mg/l. The low MLVSS affects the required size of the bioreactor since for a given organic loading rate, q, which had to be low for this wastewater, a low MLVSS concentration requires high residence times and large reactor volumes.

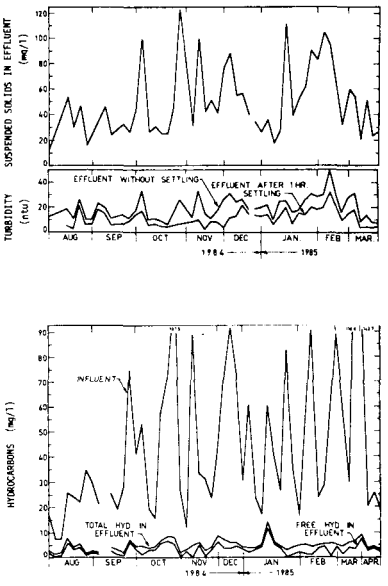

Fig. 7 Suspended solids, turbidity and hydrocarbon concentrations during experimental work.

In Fig. 7 one can see that increase in suspended solids is connected to increase in hydrocarbon concentration in the influent. One of the reasons for this effect is that with increased hydrocarbon concentrations, the hydrocarbon entrapment by bioflocs increased, thus affecting possibly the settling properties. However, high hydrocarbon content could also affect adversely bioflocculation impairing settleability of the bioflocs.

Low MLVSS in refinery wastewater treatment have been reported by Mahmud and Thanh (1978), and Dickenson and Giboney (1970), who also show high suspended solids in effluent. Banerji et al. (1974) hypothesized that the biofloc is coated by a hydrophobic layer affecting its physical properties and its biochemical performance. Microscopic observations in this research did not reveal visible coating on the floc, though on some flocs dark colored droplets(possibly hydrocarbon) could be observed. No adverse effects on oxygen uptake rate or the biotreatment efficiency were observed within the range of hydrocarbon concentrations in this study.

Sudden discharges of concentrated phenolic wastewater. Several times during the research period severe disruptions of the process were observed. The symptoms were a sudden steep rise of the effluent turbidity, discoloration of the biomass (the MLVSS), accompanied by a specific strong odor. While at initial stages of such disturbances biodegradation was still taking place (BOD removal), within a few days it was followed by complete poisoning of the system and complete inhibition of the bioactivity.
Investigations of refinery operations revealed that these disturbances occurred after sudden discharges of large volumes of concentrated phenolic wastes(15,000 mg/l of phenols) into the refinery's general wastewater system. There is a continuous low flow rate discharge of the same concentrated phenolic waste, from a gasoline washery, being responsible for the phenols in the wastewater which are normally in the range of 10 to 20 mg/l. Every few months a regeneration operation of the gasoline washery takes place, discharging in a very short period large volumes of concentrated phenols solutions. This concentrated waste contains 8,000 mg/l phenol, 5,000 mg/l para and meta cresol, 2,000 mg/l o-cresol and a few hundreds mg/l of xylenols. During such surges the total phenol concentrations in the general waste rises steeply to above 100 mg/l, disrupting the process. It seems that at first bioflocculation is impaired followed by complete disruption of the whole process. The relationship between sudden pulses in phenols and disruptions in bioflocculation can be seen in Fig. 8, where "pulses" of phenol are followed by "pulses" of turbidity and suspended solids in the effluent.

Adverse effects of sudden increases in phenols concentration on biological treatment were also reported by Reitano (1981) and Nayar and Sylvester (1979); the latter reported a steep decline in MLVSS and in substrate utilization. It seems that wastewater containing phenol even at relatively high concentrations up to 100 mg/l can be treated biologically as long as the feed is steady and continuous. In such cases there is an inhibitory effect of the phenols by reducing the process rate. When operating at the low rate the process itself is efficient including good degradation of phenols. The disruption of the process is caused by sudden discharges - surges of high phenol liquids. To prevent such disturbances, storage of the suddenly discharged concentrated wastes is necessary and their gradual, low flow rate controlled discharge to the general wastewater system.

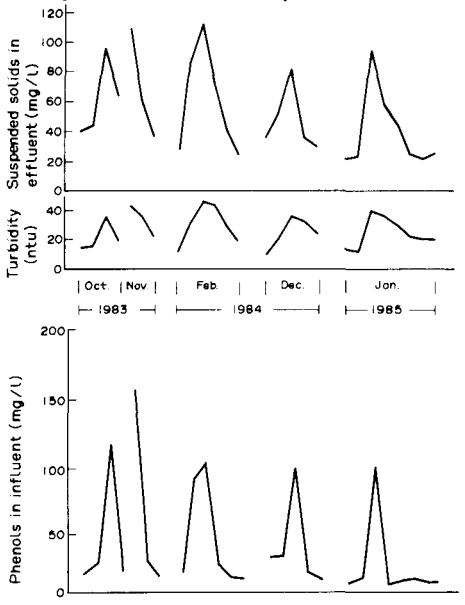

Fig. 8 Phenols in the influent, turbidity and suspended solids in effluent.

SUMMARY AND CONCLUSIONS

Biological treatment of wastewater from an integrated oil refinery, containing hazardous contaminants, was studied in an on-site pilot plant. The wastewater is pretreated by gravity separation, flocculation and dissolved air flotation.

Biotreatment of such wastewaters is feasible, but it poses several problems which have to be considered in planning, design and operation of the treatment system:

- The process rate is relatively slow, the specific loading rate should be below 0.15 day^{-1} in terms of BOD, for efficient treatment. This is due to inhibitory effects of phenols.
- The MLVSS could not be maintained at concentrations higher then 2000 mg/l and were frequently much lower. Therefore high residence times and consequently large volume reactors (aeration tanks) are required. The low MLVSS is due to poor settleability of part of the bioflocs and their "escape" from the secondary clarifier, affecting adversely also the quality of the effluent. The poor settleability of the flocs is to a great extent a result of high hydrocarbon concentrations in the influent. It is recommended to maintain the hydrocarbon concentration in influent to activated sludge units at low level by efficient opperation of the dissolved air flotation system.
- Sudden discharges of concentrated phenolic wastes disrupted the process, first by impairing bioflocculation followed by complete inhibition of the biological process. To prevent such disturbances, surges of concentrated wastes containing toxic and inhibitory compounds should be intercepted and stored. Then it can be gradually discharged from the storage facilities to the main sewerage system at a controlled predetermined flow rate not disturbing the process. Any conceptual design of refinery wastewater treatment must include regulating storage of concentrated waste in addition to equalization basins which are usually installed near the treatment plant.

- Further improvement in performance of the biological treatment is now being studied using powdered activated carbon (PAC) in the activated sludge process. The results up to now indicate that it improves the process, probably by reducing the inhibitory action of the phenols at the steady state influent concentrations.
  Powdered activated carbon combined in the activated sludge cannot be a solution for the sudden high volume discharges of concentrated phenols. This problem can be solved only through interception,storage and regulated gradual discharge.

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Biodegradation of Sulfolane in Soil and Groundwater Samplesfrom a Sour Gas Plant Site

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BIODEGRADATION OF SULFOLANE IN SOIL AND GROUNDWATER SAMPLESFROM A SOUR GAS PLANT SITE

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ABSTRACT

Sulfolane is used as a solvent in processes for the removal of H_2S from sour gas. Because of its high water-solubility, soil contamination by sulfolane quickly leads to groundwater contamination. To assess the possibility of using bioremediation to remove this compound, samples of soils, groundwaters, and sandstone from a contaminated aquifer at a gas plant were used in laboratory studies to determine if they contained sulfolane-degrading microbial populations. Aerobic shake-flask slurry cultures were incubated at 26° and 8°C, and solid phase soil bioreactors, approximating bioventing, were incubated at 8°C to test sulfolane biodegradability. Each environmental sample yielded microbial populations that degraded sulfolane. Supplementation with N and P stimulated degradation. The most rapid rates of degradation in slurry cultures incubated at 26°C and 8°C were 8 and 4 mg L^{-1} d^{-1}, respectively. In the soil column bioreactors supplemented with N and P, the rates of sulfolane biodegradation were between 0.5 and 0.7 mg kg^{-1} d^{-1}.

Keywords: Biodegradation, Groundwater, Soil, Sour gas, Sulfolane

INTRODUCTION

Sulfolane (tetrahydrothiophene sulfone) is used as a solvent in Shell's Sulfinol process to remove H_2S from sour natural gas [1]. It is extremely water soluble and therefore sulfolane contamination of soils at gas plants can lead to contaminated groundwaters.

There appear to be few reports on the microbial degradation of sulfolane. Chou and Swatloski [2] studied the biodegradation of sulfolane in a laboratory-scale completely mixed activated sludge system operated at approximately 24 ± 3°C. They used fresh activated sludge from a refinery biotreater as their source of microorganisms, and found that the sludge was not inhibited by 200 mg of sulfolane L^{-1}. A sulfolane-degrading population developed after a few days of exposure to this compound. They also found that sulfolane bio-oxidation generated acid, requiring pH control, and that there was a nearly stoichiometric release of the sulfur atom as sulfate.

McLeod *et al.* [3] investigated a biological activated carbon process for removing sulfolane from groundwater. In a bench-scale, batch air-stripping experiment, they found that when a refinery sludge, which had been obtained from an activated sludge system treating sulfolane-containing wastewater, was used as the source of microorganisms, sulfolane degradation was detected within a few days, and when activated sludge that had not been exposed to sulfolane was used as the source of microorganisms, sulfolane degradation was detected after 14 d of incubation in their test system. The concentrations of sulfolane fed to these cultures ranged from 600 to 1,500 μg L^{-1}, and the effluent concentrations were often below 10 μg L^{-1}.

Lee and Clark [4] described an isolate of *Pseudomonas maltophila* that degrades aromatic sulfonic acids. This bacterium also grew at 30°C on minimal agar containing 1,000 mg sulfolane L^{-1}.

The main objectives of this research were: (a) to determine whether soil samples and groundwater samples from a sour gas plant in Alberta, Canada contained sulfolane-degrading bacterial populations; (b) to undertake shake-flask studies with groundwater from the gas plant to determine the rates of sulfolane degradation under various incubation conditions; (c) to undertake column biodegradation studies with soil samples from the gas plant to determine the rate of sulfolane degradation under various incubation conditions.

The gas plant from which samples were taken has been using the sulfinol process since 1966.

MATERIALS AND METHODS

Sample Collection

Samples were collected in April 1995. Two groundwater samples were collected from existing monitoring wells,

denoted RW-3 and HP-8-7. From each well, two sterile, 4-L glass jugs were filled. Previous analyses of samples from these wells indicated that the water from well RW-3 typically contained 6 to 7 mg L^{-1} sulfolane, whereas water from well HP-8-7 typically contained sulfolane in the µg L^{-1} range. The water temperatures in RW-3 and HP-87 were 3°C and 5°C, respectively.

Two soil samples were collected. One, referrred to as "cut material", was from soil and bedrock cut from an area with a history of sulfolane contamination. At two locations, a backhoe dug a hole about 1.5 m deep into the cut material. At that depth, the backhoe shovel was filled with soil and samples were taken from this shovel. The samples were placed in sterile 4-L, wide-mouth plastic jugs. Each of five jugs was half-filled with soil from the first hole, and then filled completely with soil from the second hole.

The second soil sample was a core taken from a new well that was drilled at the time of sampling. This "till" material was obtained in plastic tubes, each containing a core from 0.4 to 0.75 m in length. The final depth of the new well was 3.4 m. Samples of a slurry of sandstone from a sulfolane-contaminated aquifer at the gas plant site were collected from a newly drilled well.

All samples were transported to our laboratory in coolers and stored at 4°C until they were analyzed or used in biodegradation studies.

Sulfolane Biodegradation in Aquifer Slurry Cultures

The initial incubations were done at 26°C under aerobic shake-flask conditions to provide the greatest likelihood of stimulating sulfolane biodegradation. In addition, some of the cultures were supplemented with inorganic nutrients (N and P) so that these would not be limiting. Also, most of the groundwater samples were inoculated with some of the sandstone material which was suspected to be a rich source of sulfolane-degrading bacteria. Later, groundwater samples were inoculated with sandstone material, and incubated at 8°C, a typical summer temperature of the aquifers from which the samples were taken.

Two groundwater samples were used to test for sulfolane biodegradation. One sample was from well RW-3, and the other sample was from well HP-8-7. One viable culture supplemented with N and P, one viable culture without N and P supplementation, and one sterile control were prepared for each water sample. For each of the viable cultures, 450 mL of the appropriate water sample was added to a sterile 1-L Erlenmeyer flask and 50 mL of the sandstone slurry was added as an inoculum.

Those cultures that were supplemented with nutrients received 4.5 mL of the N,P solution used by Fedorak and Westlake [5]. This solution contained (per litre) 100 g of each of the following: K_2HPO_4, KH_2PO_4 and NH_4NO_3, and was at pH 7.3.

Each sterile control was prepared by adding a 50-mL portion of the sandstone slurry to a 1-L Erlenmeyer flask. The dispensed sandstone slurries were sterilized by autoclaving for 30 min on each of three consecutive days. Water samples were filtered twice through 0.45-µm pore size HA Millipore filters. The first filtering was done with non-sterile filters and glassware, and served as a pre-filtration step to remove particulate matter. The second filtration was done with sterile filters and glassware to produce filter-sterilized water. Portions of the filter-sterilized water (450 mL) were added to flasks containing the autoclaved sandstone. As further measures to reduce the chance of microbial activity in the sterile controls, 5 mL of a solution of 100 mg $HgCl_2$ mL^{-1} was added to each flask, and the controls were not supplemented with N,P solution.

In addition, a viable culture and a sterile control containing water from well RW-3 – without the sandstone inoculum – were also prepared. The viable culture contained 450 mL of the groundwater supplemented with 4.5 mL of the N,P solution. The sterile control contained 450 mL of filter-sterilized groundwater supplemented with 5 mL of the $HgCl_2$ solution. These eight flasks containing groundwater were incubated on a shaker operated at 200 rpm in a 26°C walk-in incubator.

Samples (40 mL) were removed from of each culture at various times and each sample was transferred to a 50-mL Teflon centrifuge tube. The dissolved oxygen and pH measurements were taken on the samples in the centrifuge tube.

Sulfolane Biodegradation in Soil Slurries

Well-mixed samples of the cut material and till were used as separate inocula. The till material was taken from the core corresponding to 2.25 to 3.0 m. For each of the viable cultures, 200 g of soil were placed in a sterile 1-L Erlenmeyer flask and this was mixed with liquid medium that contained per litre: 0.5 g K_2HPO_4; 2.0 g NaCl; 0.2 g $MgCl_2$; 2.0 g KNO_3; 1.0 g NH_4Cl; a trace of $FeCl_2.4H_2O$ and 1 mL of trace metals solution [6].

To prepare sterile controls, 200-g samples of the soils were placed in 1-L Erlenmeyer flasks and these were autoclaved for 30 min on each of three consecutive days. After these were cooled following the third autoclaving, 450 mL of the liquid medium and 5 mL of stock $HgCl_2$ solution were added.

The soil slurry cultures and controls were incubated with shaking at 8°C and supplemented with approximately 10 mg of sulfolane L^{-1} at the time they were inoculated. At various times, 40-mL samples were removed and these were extracted and analyzed for sulfolane.

Sulfolane Biodegradation in Soil Columns

To approximate bioventing, soil column bioreactors were assembled and operated at 8°C. These were modifications of the device used by Mueller *et al.* [7], but no attempts were made to trap the off-gases.

Each bioreactor was a glass 2-L Büchner-type filter funnel, with sintered glass base. To prevent soil plugging the sinter glass, a layer of glass wool covered the bottom of the funnel. A sturdy piece of aluminum foil with about 15 holes (each 8 mm in diameter) punched to allow air passage was placed on top of the glass wool. A prepared soil sample (1.5 kg) was placed on top of the aluminum foil. At each sampling time, the soil was mixed prior to removing 30 g for sulfolane analysis. The aluminum foil beneath the soil prevented the disruption of the glass wool layer during mixing. The funnels were supported in a custom-made wooden box which allowed access to the bottom and top of the funnel. All of these components were housed in a walk-in incubator maintained at 8°C.

Air was supplied through the bottom of the four funnels. It was passed through an activated carbon filter to remove any contaminating oils that might be in the laboratory air supply. Next the air was moistened by bubbling through water in a 4-L Erlenmeyer flask at room temperature. Then the moistened air passed through a 500-mL Erlenmeyer flask, in the 8°C room, which allowed excess water to condense. The total air flow rate was 28 L min^{-1}, which was split among the four column reactors.

Soil preparation:

To prepare the soils for the biodegradation studies, 3 kg of the till (from depths 1.5 to 3 m) and the cut material samples were weighed into two separate stainless steel trays. Lumps in the soil samples were then crushed manually to pieces no larger than approximately 5 mm in diameter.

The soils were spiked with sulfolane to a target concentration of 10 mg kg^{-1} using the following method. Sulfolane (300 mg) was dissolved in 200 mL of distilled water. This provided a stock solution from which 20 mL was sprayed over each of the two 3-kg soil samples. The samples were mixed well in the tray to ensure even distribution of the sulfolane. Adding sulfolane to the soil at 10 mg kg^{-1} gave a concentration that was readily detectable by the analytical procedures used.

After the addition of the sulfolane, the two 3-kg soil samples were each separated into two 1.5-kg sub-samples. One of these sub-samples of each soil was supplemented with N and P, whereas the other received no N and P. The N and P supplement was prepared by diluting 2 mL of N,P solution to 20 mL. Then a 10-mL portion of this solution was sprayed onto each of two 1.5-kg sub-samples of sulfolane-spiked soils. These were mixed well to ensure even distribution of the added nutrients. This gave approximately 23 mg N kg^{-1} of soil and 14 mg P kg^{-1} of soil. To ensure equal moisture levels in all of the soil sub-samples, 10 mL of distilled water was sprayed onto each of the two samples that did not receive the N and P supplementation.

Analytical Methods

Preparation of calibration curve for sulfolane analyses:

To prepare a calibration curve, 100-mL portions of the solutions of sulfolane (0.5 to 20 mg L^{-1}) were poured into 250-mL flasks and 28.6 g of NaCl was dissolved in each sample. The resulting NaCl concentration was 80% of its saturation concentration. Then 50 µL of a dibenzothiophene solution (5 mg mL^{-1}) was added as an internal standard to each sample which was transferred to a separatory funnel. Each solution was extracted three times with 20-mL portions of dichloromethane. The extracts were pooled, dried over Na_2SO_4, concentrated on a rotovap, and transferred to a vial for storage prior to gas chromatography (GC) analysis.

The GC used for this study was a Hewlett-Packard model 5730 equipped with a flame ionization detector. A 0.25-mm by 25-m (0.25 µm film thickness) DB-5 column (J&W Scientific, Inc.) was used with a split ratio of 20:1. The injector and detector temperatures were 250°C. The oven temperature program was 90°C for 2 min, 4°C min^{-1} to 250°C which was held for 16 min. Under these operating conditions, the retention times for sulfolane and dibenzothiophene were near 8.4 min and 24.5 min, respectively. Peak areas were determined using a Hewlett-Packard model 3390A integrator.

From each GC analysis, the peak area ratio of sulfolane to dibenzothiophene was calculated and this was plotted against the total milligrams of sulfolane in the corresponding 100-mL portion of standard solution extracted. Linear regression gave the equation:

$$\text{sulfolane}(\text{mg}) = (\text{peak area ratio} + 0.14) + 2.31(\text{mg}^{-1}) \quad \text{(i)}$$

$$r = 0.979$$

However, the value of the Y-intercept (0.14) greatly affected the concentrations determined in samples with small amounts of sulfolane. Thus, the procedure was insensitive to changes in small peak ratios. For example, if peak area ratios were 0.01 and 0.001, differing by 10-fold, equation (i) gives sulfolane values of 0.065 mg and 0.061 mg, respectively, differing by 1.07-fold. Clearly this calibration curve is not well-suited to low concentrations of sulfolane. However, for the ranges of sulfolane concentrations most commonly encountered in this project, the calibration provided reliable results.

In the biodegradation studies, some samples failed to show sulfolane peaks in the GC chromatograms, so the peak area ratio was zero. In these cases, the sulfolane concentration was taken to be zero, and this value was plotted on the graphs showing sulfolane degradation over time.

As part of this project, an interlaboratory comparison of results of sulfolane analyses was done. We determined that the groundwater from well RW-3 had 18 mg sulfolane L^{-1}. Two commercial laboratories also analyzed this sample. One laboratory found a mean of 17 mg L^{-1}, and one gave a bias-adjusted mean of 18 mg L^{-1}.

Sulfolane analyses of slurries of sandstone or soil:

The 40-mL samples taken from cultures containing a sandstone or soil slurry were centrifuged at 5,000 rpm for 15 min. The aqueous supernatant was decanted into a beaker containing 12.6 g of NaCl, and this was mixed to dissolve the NaCl. Prior to extraction, 50 µL of a dibenzothiophene solution (2.5 mg mL^{-1}) was added to the aqueous sample which was then extracted 3 times with 20-mL portions of dichloromethane. Each soil pellet from centrifugation was washed twice with 30-mL portions of dichloromethane, and these washes were combined with the dichloromethane extracts of the corresponding aqueous sample. The extract was dried over Na_2SO_4, concentrated in a rotovap and transferred to a storage vial and concentrated further under a stream of N_2 prior to GC analyses.

Sulfolane analyses of soils from column bioreactors:

Duplicate 30-g samples of soil were removed from each bioreactor for sulfolane analyses. These were subjected to a 6-h Soxhlet extraction with dichloromethane. To prepare an extract for GC analysis, 0.125 mg of dibenzothiophene was added to each round-bottom flask taken from the Soxhlet apparatus. Then the extract was concentrated using a rotary-evaporator and analyzed by GC. The moisture contents of the soil samples were not determined, so the sulfolane concentrations are expressed as mg kg^{-1} wet weight.

Dissolved oxygen and pH measurements:

The dissolved oxygen measurements were taken using a New Brunswick Scientific Dissolved Oxygen (D.O.) Analyzer (model DO40) with a series 900 probe. After calibration of the apparatus, the dissolved oxygen concentrations were measured as a percent of saturation. However, the dissolved oxygen concentrations were expressed as mg L^{-1} using the value of 100% saturation of O_2 in air-saturated distilled water at 26°C and 1 atmosphere to be 8.09 mg L^{-1} [8]. The dissolved oxygen concentrations were only monitored during the first aquifer slurry studies at 26°C. Because O_2 was not limiting in these cultures, and because the solubility of O_2 increases as temperature decreases, it was felt that there was no need to monitor dissolved oxygen in the cultures incubated at 8°C.

An Accumet pH meter (model 900) was used to measure the pH of 5-mL slurry samples removed from the active cultures and sterile controls. On one occasion, the pH of the soils in the column bioreactors was measured using 4 g of soil suspended in 40 mL of 0.01 M $CaCl_2$ solution as outlined by Hendershot *et al.* [9].

RESULTS

Sulfolane Biodegradation in Aquifer Slurries

The sulfolane concentrations observed with the groundwater samples from wells RW-3 and HP-8-7 that were inoculated with 50 mL of a sandstone slurry at 26°C are shown in Figure 1. The cultures and controls were sampled at time zero and after 3 d of incubation. No sulfolane was detected in any of the day 3 samples from the viable cultures, but sulfolane was found in the controls at concentrations similar to the time zero samples (Figure 1). Analyses of the first three samples from the slurry cultures containing groundwater from well HP-8-7 (time zero to day 6), with and without N and P addition, gave virtually identical sulfolane concentrations. Thus, one curve is hidden beneath the other in Figure 1b.

To ensure that sulfolane degradation had occurred, the cultures were spiked with this compound on day 10. In each case, the controls and cultures were spiked with an amount of sulfolane that increased its concentration by about 20 mg L^{-1} (to near the 18 mg L^{-1} concentration of sulfolane that was originally found in the groundwater from well RW-3). In the case of the cultures containing groundwater from well RW-3 (Figure 1a), the control had near 20 mg L^{-1} before spiking, and the active cultures were near 0 mg L^{-1}. Spiking gave concentrations of near 40 mg L^{-1} in the control, and near 20 mg L^{-1} in the active cultures. Similarly, in the case of the cultures containing groundwater from well HP-8-7 (Figure 1b), the control had a concentration of near 2 mg L^{-1} before spiking, and the concentrations in the active cultures were near 0 mg L^{-1}. After spiking, all of the concentrations were near 20 mg L^{-1}.

Figure 1 shows that the viable cultures degraded the sulfolane added on day 10. The rates of degradation were calculated from the sulfolane concentrations measured after the sulfolane spiking, assuming a linear rate of degradation from after the end of any lag period that was observed, to the time at which the sulfolane concentration was near 0 mg L^{-1}. If there was a interval between the analyses times when the sulfolane was nearly depleted, such as between days 12 and 14 in Figure 1a for the N and P supplemented culture, the concentration of the earlier time (e.g. day 12 in this example) was the final value used for the rate calculation. This same approach was used for calculating the removal rates in all of the slurry cultures used in this study. The rates of sulfolane degradation in the cultures incubated at 26°C are summarized in column 3 of Table 1.

Between days 12 and 14, there was a marked decrease in sulfolane concentration in the sterile control shown in Figure 1a. It is unlikely that this was caused by a $HgCl_2$-tolerant sulfolane-degrading microorganism, but this possibility was not tested. Nonetheless, the sulfolane degradation was essentially complete in the viable cultures before this decrease in the sterile control was observed. The decrease was most likely due to variability in the analyses of the slurry from the control. Because of the limited volume of each slurry culture (approximately 450 mL), and the uncertainty of the number of 40-mL samples that would be removed while monitoring the time course experiments, no replicate samples were taken for sulfolane analyses. In addition, some variation in the sulfolane concentrations was presumably due to difficulties removing reproducible 40-mL samples of the slurries from the shake flasks. The relative

amounts of solids and aqueous culture varied from sample to sample causing differences in the amount of the highly water-soluble sulfolane in the samples. These two factors would contribute to the variability in the results plotted in Figures 1, 2 and 3.

The pH of the aquifer slurry cultures were monitored and they remained very near the pH of the controls over the 24-day incubation time. The initial pH values were between 7.5 and 7.8. After 3 d of incubation, the pH values were between 7.9 and 8.4, and they remained near these values for the remainder of the incubation time.

The dissolved oxygen content of the active cultures were seldom below that of the sterile controls, and never dropped below 4.5 mg L^{-1}. Thus, O_2 was not limiting in these cultures.

In a separate experiment, sulfolane concentrations were monitored in a groundwater sample from well RW-3 that was supplemented with N,P and incubated at 26°C without sandstone added as an inoculum. The initial sulfolane concentration was 21 mg L^{-1} and there was no degradation of sulfolane by day 6, however, there was a marked decrease in sulfolane concentration to 7 mg L^{-1} by day 14, which was the next sampling time. In contrast, the sulfolane concentration in the sterile control showed no decrease over the 14-day incubation time. The viable culture was much less active than those that were inoculated with sandstone (Figure 1). For example, by day 3 in the sandstone-inoculated groundwater sample, all of the sulfolane had been degraded, and a second dose of sulfolane was degraded between days 10 and 14 (Figure 1). Although the addition of

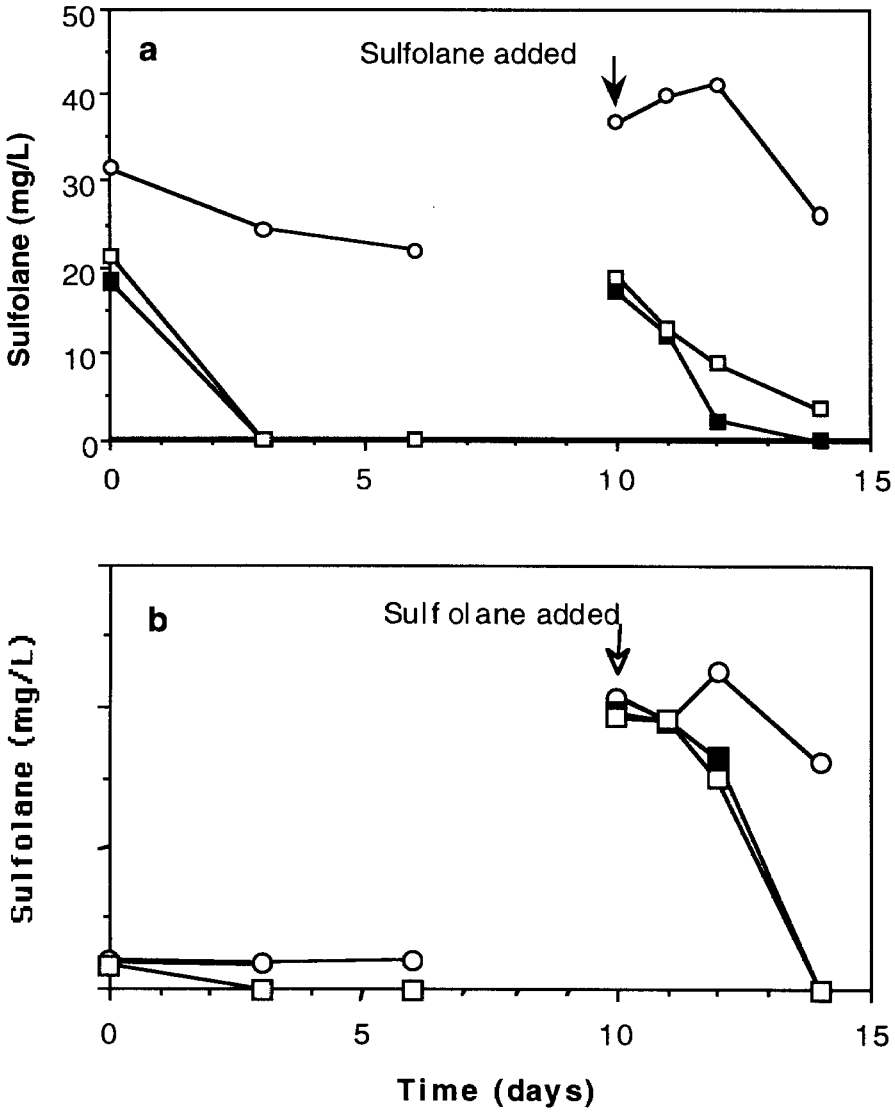

Figure 1. Sulfolane concentrations in the aquifer slurry, shake-flask cultures containing groundwater samples from wells RW-3 (a) and HP-8-7 (b) inoculated with sandstone and incubated at 26°C. Sterile control (O), N and P added (■), no N and P added (❑).

Table 1. Comparison of sulfolane biodegradation rates from aquifer slurry cultures incubated at 26°C or 8°C. The rates were calculated after the addition of sulfolane on day 10 (Figure 1) and day 9 (Figure 2), respectively.

Groundwater sample	N and P Supplementation	Sulfolane degradation rate at 26°C (mg L^{-1} d^{-1})	Sulfolane degradation rate at 8°C (mg L^{-1} d^{-1})
RW-3	No	4	0.8
RW-3	Yes	8	4
HP-8-7	No	6	1
HP-8-7	Yes	6	4

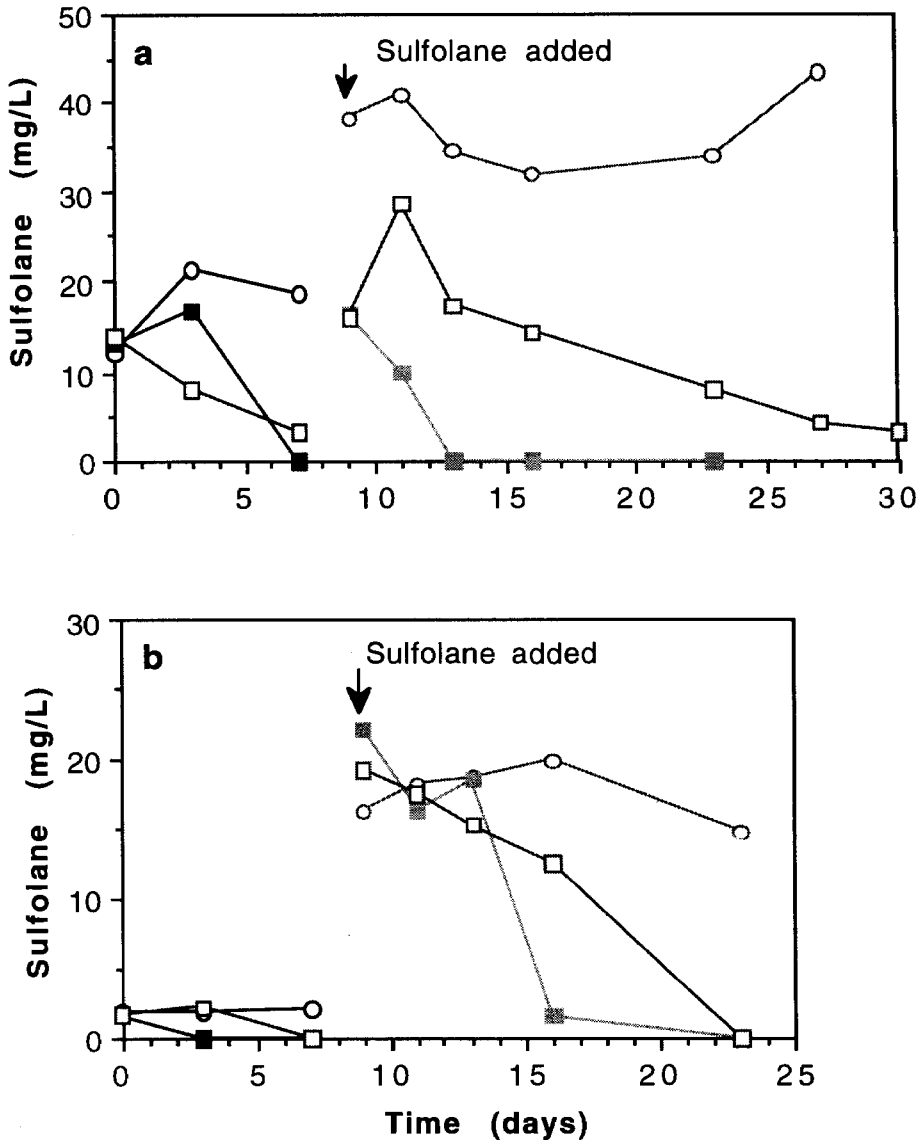

Figure 2 Sulfolane concentrations in the aquifer slurry, shake-flask cultures containing groundwater samples from wells RW-3 (a) and HP-8-7 (b) inoculated with sandstone and incubated at 8°C. Sterile control (O), N and P added (■), no N and P added (❑).

sandstone provided a much more active population of sulfolane-degrading microorganisms, this experiment showed that there were sulfolane-degrading microorganisms in the groundwater.

Figure 2 shows the sulfolane concentrations during the incubation of samples of the groundwaters that were inoculated with sandstone and incubated with shaking at 8°C. After 3 d of incubation, decreased sulfolane concentrations were observed in some cultures (RW-3, without added N,P; and HP-8-7 with added N,P). By day 7, most of the sulfolane was removed from these cultures, but no marked concentration decrease was observed in the sterile controls.

To ensure that sulfolane degradation had occurred, the cultures were spiked with sulfolane on day 9, and then the concentrations of this compound were monitored (Figure 2). The viable cultures also degraded the added sulfolane, and the degradation rates at 8°C are summarized in column 4 of Table 1.

Sulfolane Biodegradation in Soil Slurries

Preliminary studies showed that the sulfolane concentrations in the cut material and till were too low for detection by the analytical method used. Thus, soil slurry cultures were supplemented with approximately 10 mg of sulfolane L^{-1}, which was readily detected by the analytical methods used. Incubation was done only at 8°C and the soil slurries were made in medium that contained N and P, so these nutrients were not limiting. No sulfolane degradation was observed during the 14-day incubation time used for the slurry cultures inoculated with 200 g of till (data not shown). In contrast, between days 4 and 7, there was a marked decrease in the sulfolane concentration in the viable culture inoculated with the cut material (Figure 3). Subsequently, more sulfolane was added to the control and viable culture on day 11, and this was rapidly degraded between days 12 and 14, giving an average degradation rate of 6 mg L^{-1} d^{-1}. This rate was higher than the rates observed in the N,P-supplemented aquifer slurry cultures incubated at 8°C (Table 1) which were 4 mg L^{-1} d^{-1}. This may reflect the difference in inoculum sizes used. In the soil slurry cultures, 200 g of cut material was used, whereas in the aquifer slurry cultures, only about 60 g of sandstone was used.

Sulfolane Degradation in Soil Columns

The sulfolane concentrations in the soil columns are shown in Figure 4. Each data point is the mean of duplicate samples and the error bars show one standard deviation. In some cases the error bars are smaller than the symbols used. The variability among the samples of the till during the first 15 d (Figure 4) were likely due to differences in soil moisture, which could not be controlled in the bioreactor. The pH in the cut material was 7.8 and in the till was 7.9. These values were in the range of the values observed in the aquifer slurry cultures.

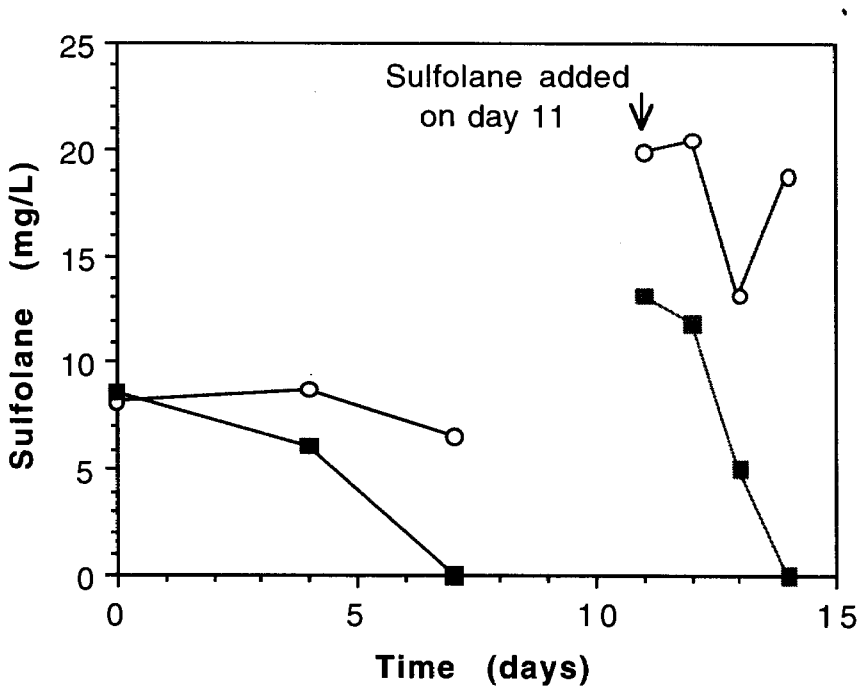

Figure 3. Sulfolane concentrations in the soil slurry, shake-flask cultures inoculated with cut material incubated at 8°C. Sterile Control (O), viable culture supplemented with N and P (■). Sulfolane was added to the culture medium at the beginning of the experiment.

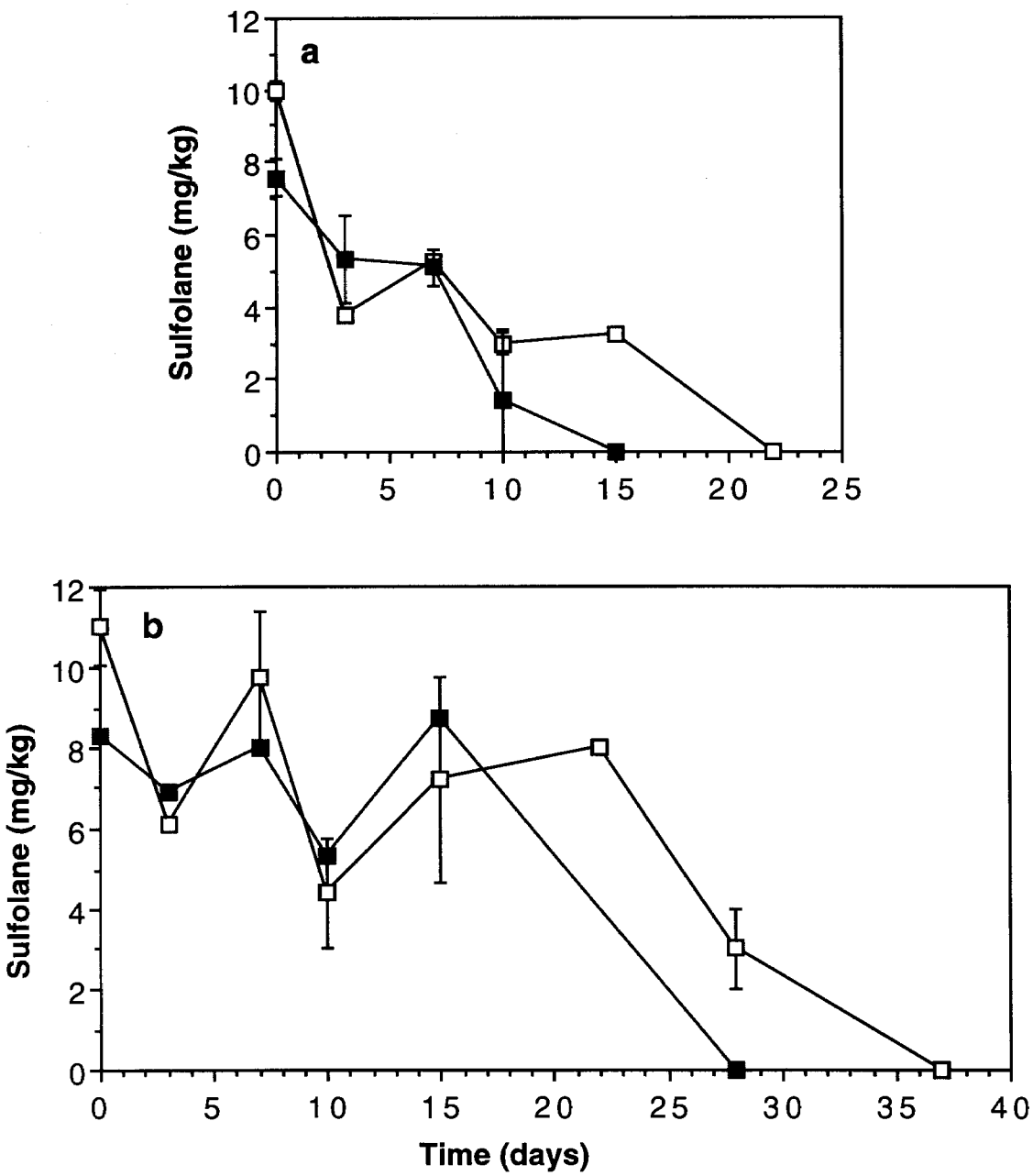

Figure 4. Sulfolane concentrations in the soil columns containing cut material (a) and till (b) incubated at 8°C. N and P added (■), no N and P added (❑). Sulfolane was mixed into the soil at the beginning of the experiment.

The data in Figure 4a clearly show that sulfolane was removed from the cut material in the column bioreactors. The mean initial concentration in the bioreactor containing cut material supplemented with N and P was 7.6 mg kg^{-1}, whereas the sulfolane concentrations on days 15 and 22 were below the detection limit of the analytical method (2 mg kg^{-1}). Similarly, the mean initial concentration in the bioreactor containing cut material without N and P supplementation was 10 mg kg^{-1}, whereas the sulfolane concentrations on day 22 was below the detection limit. Assuming a linear biodegradation rate over the sampling periods shown in Figure 4a, the rates of removal of sulfolane were 0.5 mg kg^{-1} d^{-1} in the N and P supplemented bioreactor, and 0.4 mg kg^{-1} d^{-1} in the unsupplemented bioreactor. Linear regression gave correlation coefficients of r = 0.96 and r = 0.85 for the N and P-supplemented and unsupplemented bioreactors, respectively.

Figure 4b shows that the onset of sulfolane-degrading activity by the microbial population in the bioreactors containing till was much slower than that in the bioreactor containing cut material (Figure 4a). The results from the analyses of samples taken during the first 15 days of operation

of the soil column containing till (Figure 4b) illustrate the day to day variability of the analytical method. On day 28, the sulfolane concentrations in the duplicate samples from the bioreactor containing N and P were below the detection limit of the analytical method. Between days 22 and 28, there was also a marked decrease in the sulfolane concentration in the bioreactor that was not supplemented with N and P. By day 37, no sulfolane was detected in samples from the bioreactor with N and P supplementation. These data indicate that after a lag period of 15 d, the microbes in the till material supplemented with N and P began to degrade sulfolane, and the rate of removal was approximately 0.7 mg kg^{-1} d^{-1}. Similarly, after a lag time of 22 d, the population in the unsupplemented till material, began to degrade sulfolane, and the rate of removal was between 0.5 and 0.8 mg kg^{-1} d^{-1}.

Because of limited resources, column bioreactors containing sterile soil could not be tested for the rate of sulfolane evaporation. However, the evaporative loss of sulfolane from these bioreactors operated at 8°C was expected to be insignificant for the following reasons: (a) its freezing point is 28°C, which is lower to 17°C in the presence of 1.3% water [10]; (b) sulfolane has a boiling point of 287°C, and low vapor pressure, even at elevated temperatures [for example, 1.93 kPa (14.5 mm Hg) at 150°C [10]]; and (c) McLeod *et al.* [3] demonstrated that there was no appreciable loss of sulfolane from aqueous solution by air stripping over a 10-day period, presumably at room temperature.

Thus, the loss of sulfolane observed in the soil column experiments (Figure 4) was, in all likelihood, the result of biodegradation rather than evaporation. Indeed, the manner in which sulfolane was lost from the till-containing bioreactors is consistent with a microbial population adapting to use a new substrate. That is, for 15 to 22 d, the sulfolane concentration remained fairly constant (Figure 4b). After these long lag times, there was a rapid loss of sulfolane due to biodegradation. In addition, the loss of sulfolane from the soil columns was stimulated by the addition of N and P, which is consistent with biodegradation, rather than evaporation, being the mechanism for removal.

DISCUSSION

The results of these investigations show that each of the sample types collected (i.e. groundwater, sandstone from an aquifer, till and contaminated soil) contained microbial populations that were able to degrade sulfolane. The population associated with the sandstone degraded sulfolane more quickly than the population in the groundwater sample from Well RW-3. Others have observed that solids from aquifers contain more microorganisms than the groundwaters from the same sources [11, 12, 13]. We found no previous reports of sulfolane biodegradation occurring in soils.

Chou and Swatloski [2] reported a decrease in pH accompanying sulfolane disappearance in their activated sludge-containing cultures that initially contained up to 200 mg L^{-1}. However, no significant pH drop was observed in our studies, presumably because of the high buffering capacity from the aquifer solids, and the lower sulfolane concentrations which we used (typically below 20 mg L^{-1}). Chou and Swatloski [2] also observed the release of sulfate from sulfolane. We attempted to measure sulfate release in some of the aquifer slurry cultures (data not presented), but because of the high background sulfate concentrations, the results were inconclusive. Recently, near stoichiometric sulfate release from sulfolane was observed in enrichment cultures, free from the solids that were present in the aquifer slurry cultures (E.A. Greene and P.M. Fedorak, unpublished data). Thus, the heterocyclic ring can be broken by the microorganisms from the contaminated aquifer material, and presumably much of sulfolane is mineralized.

Table 1 summarizes the sulfolane biodegradation rates in the aquifer slurry cultures at 8° and 26°C. The rates were calculated from the data obtained after the addition of sulfolane on day 10 (to the cultures incubated at 26°C) and on day 9 (to the cultures incubated at 8°C). By this time, each culture had degraded the sulfolane that was present in the groundwater sample. Thus, the cultures were acclimated to sulfolane degradation.

As expected for any biochemical reaction, the rate of sulfolane biodegradation decreased with temperature decrease. This was especially noticeable for the cultures that were not supplemented with N and P (Table 1). The rates in these cultures incubated at 8°C were 17% and 20% of the rates of the cultures incubated at 26°C. In contrast, the rates of sulfolane removal in the cultures with N and P supplementation (Table 1) incubated at 8°C were 50% and 66% of the corresponding cultures incubated at 26°C.

Comparing the degradation rates of aquifer slurry cultures with and without N and P supplementation (Table 1) shows that in all but one case (groundwater sample HP-8-7 at 26°C) the addition of N and P substantially increased the rate of biodegradation. This was most noticeable in the cultures incubated at 8°C, a temperature typical of that in the aquifer.

There do not appear to be sulfolane degradation rates reported in the literature. However, examination of data presented by Chou and Swatloski [2] and McLeod *et al.* [3] allows some estimations of rates of biodegradation. In each of the above studies, activated sludges were used as inocula, so it is very likely that there was more biomass in those batch cultures than in the groundwater samples inoculated with sandstone. Chou and Swatloski [2] incubated their cultures at approximately 24 ± 3°C. The temperature used for the studies of McLeod *et al.* [3] was not given, but it was likely room temperature.

Chou and Swatloski [2] added sulfolane to their batch culture at 100 mg L^{-1}, and after 24 h the sulfolane concentration was <1 mg L^{-1}. Thus, the biodegradation rate was ≥100 mg L^{-1} d^{-1}. McLeod *et al.* [3] used an unacclimated sewage sludge and an acclimated sludge obtained from a refinery which was treating sulfolane-containing wastewater. With the unacclimated sludge, an initial degradation rate of

0.02 mg L^{-1} d^{-1} was calculated from their data. After a 14-day exposure, the estimated degradation rate by this sludge was ≥0.11 mg L^{-1} d^{-1}. The acclimated refinery sludge was given four feedings of sulfolane over a 10-day period [3]. From the concentration data presented, the following rates for removal of sulfolane after each of the feedings were calculated to be: 0.58, 0.14, ≥0.59 and ≥1.5 mg L^{-1} d^{-1}.

The rates observed in this groundwater study (Table 1) were much lower than that calculated from the data of Chou and Swatloski [2]. However, they were in the range, or slightly higher than those calculated from the data of McLeod *et al.* [3].

The results from the soil column studies (Figure 4) were consistent with the results from the soil slurry studies at 8°C (Figure 3). For example, the viable cultures of cut material in the slurry studies (Figure 3) degraded all of the sulfolane within the first 7 days of incubation, whereas there was no degradation observed in the viable cultures of till over the 14-day incubation time. Similarly, sulfolane biodegradation was observed in the soil columns containing cut material supplemented with N and P after 10 d of incubation (Figure 4a), but no detectable degradation of sulfolane was observed in the columns containing till over the first 15 d of incubation (Figure 4b). However, sulfolane degradation was apparent in the till-containing column by day 22. Thus, if the till-containing slurry culture had been incubated longer, it is likely that sulfolane biodegradation would have been observed.

The findings of this project suggest that biodegradation may be used to remove sulfolane from contaminated soils and groundwaters in slurry bioreactors or by bioventing. Also, intrinsic bioremediation (the process by which native microorganisms degrade contaminants without engineering steps) may be an important mechanism for the attenuation of sulfolane in the subsurface environment at this site. The microbial population from this sour gas plant site will degrade sulfolane at 26° or 8°C, and the rates of degradation were stimulated by the addition of N and P.

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Uptake of sulfolane and diisopropanolamine (DIPA) by cattails (*Typha latifolia*)

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Abstract

Sulfolane (tetrahydrothiophene 1,1-dioxide, $C_4H_8O_2S$) and diisopropanolamine (DIPA) are highly water-soluble organic compounds used in the Sulfinol™ process to remove hydrogen sulfide from natural gas and have been found in samples of wetland vegetation collected near a sour gas processing facility in Alberta, Canada. Concentrations within individual plants and between plants at different locations within the wetland varied greatly but were generally higher than expected, based on exposure concentrations and plant uptake predictions using octanol/water partition coefficients. To better understand the uptake of these highly water-soluble compounds by wetland plants and to substantiate the field findings, the uptake of sulfolane and DIPA by cattails (*Typha latifolia*) was investigated in a greenhouse microcosm study. Cattails were grown hydroponically in aqueous solutions containing sulfolane and DIPA for a period of 50 days. Non-planted and non-planted poisoned hydroponic systems were run simultaneously as controls. Sulfolane and DIPA concentrations in the hydroponic solution and plant tissues were monitored throughout the study. Uptake and translocation of sulfolane and DIPA by cattails were found to be a function of exposure concentration and water transpired. However, the neutral sulfolane was translocated into the foliar portion of the cattails to a significantly greater extent than the protonated DIPA. Sulfolane concentrations were consistently greatest in the leaf tips with concentrations as high as 33,000 mg/kg dry weight for the 200 mg/L exposure. DIPA leaf concentrations were more uniform but much lower than sulfolane. The highest DIPA concentration observed was 1014 mg/kg dry weight for the 100 mg/L exposure. The average leaf to root tissue concentration ratio for sulfolane was 53 (152 for leaf tips), while for DIPA the ratio was 0.6. Normalizing the leaf concentration in each system to the amount of water transpired during exposure and dividing it by the average exposure concentration yielded approximate transpiration stream concentration factors (TSCF) that ranged from 0.1 (entire leaf) to 0.9 (leaf tip) for sulfolane and <0.01 to 0.02 for DIPA. Overall, the laboratory uptake trends matched those observed in the limited field sampling and suggest that the uptake of non-ionizable, highly water-soluble organics such as sulfolane may not be well predicted using existing relationships between TSCF and log K_{ow}. In addition, the relatively high concentrations observed in the foliar tissue suggest that wetland plants could play an important role in the natural attenuation of sulfolane, provided the sulfolane is not released by the plants during winter dormancy.

Keywords: Wetlands; TSCF; Hydroponics; Natural attenuation

1. Introduction

Diisopropanolamine (DIPA) and sulfolane are used in combination during the Sulfinol™ process to remove sour gases such as hydrogen sulfide and carbonyl sulfide from natural gas. Both compounds are highly water-soluble and have been identified in soil, groundwater and surface water near sour gas processing plants (e.g. [1,2]) as the result of

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accidental releases. Sorption to clays is the dominant retention mechanism for both compounds and sorption is more closely correlated to cation exchange capacity than organic carbon [1]. However, DIPA is a weak base (pK_a=9.7) that is protonated at most environmental pHs and is expected to be less mobile than the neutral sulfolane. Both compounds have been shown to undergo biodegradation but rates can be slow in anaerobic environments, especially for sulfolane (e.g. [2,3]). A summary of environmentally relevant physical–chemical properties for these compounds is provided in Table 1.

Sulfolane and DIPA have also been found in wetland vegetation located in areas of contaminated wetland [4,5]. For sulfolane, the highest plant tissue concentrations were generally found in the foliar sections of the plants while DIPA concentrations were typically highest in the roots. However, significant variability among plant tissue replicates and poor correlation between groundwater and plant tissue concentrations made it difficult to evaluate the uptake data [6].

For most xenobiotic organic compounds, plant uptake is believed to be a passive process related, at least in part, to the lipophilicity of the contaminant. Passive uptake occurs when a chemical is taken up directly with the water used by the plant [7]. The transpiration stream concentration factor (TSCF) has been extensively used in modeling plant uptake and translocation and is defined as the dimensionless ratio of the concentration in the xylem sap to the bulk concentration in the root zone solution [8]. Because xylem sap concentrations are difficult to measure directly for intact plants, TSCFs have been determined with detopped plants using pressure chamber techniques (e.g. [9]) and from measured shoot concentrations that are normalized to the amount of water transpired during exposure to the chemical (e.g. [10]).

With the possible exception of some hormone-like chemicals (e.g. 2,4-D), there is no evidence of active uptake (TSCF>1) of xenobiotic organic chemicals [7]. A chemical is said to be excluded (TSCF<1) when uptake is not directly proportional to water uptake (TSCF=1), although the mechanism of uptake is still thought to be a passive process. However, factors such as membrane permeability and xylem sap solubility of the contaminant may limit the extent or kinetics of passive uptake [9]. Sorption and rapid metabolism of contaminants within the plant may also reduce xylem concentrations and keep measured TSCF values from reaching one.

For organic chemicals, several empirical relationships between TSCF and the logarithm octanol/water partition coefficient (log K_{ow}) have been reported (e.g. [9,11–13]). The characteristic bell-shaped curves used to relate TSCF to the log K_{ow} suggest an optimal lipophilicity for uptake and translocation and infer that compounds that are either highly polar (log K_{ow}<0.5) or are highly lipophilic (log K_{ow}>4.5) will not be significantly taken up by plants. Based on these prediction schemes, both DIPA (log K_{ow}=−0.86) and sulfolane (−0.77) are not expected to show significant uptake. However, laboratory experiments with 1,4 dioxane [14] and MTBE [15] along with the recent field data for sulfolane and DIPA [4] suggest these predictive schemes may not be applicable for non-ionizable, highly water-soluble organics.

To help substantiate the limited field data and to improve our understanding of the uptake of water-soluble organics by plants, a series of hydroponic studies was conducted to determine the uptake of sulfolane and DIPA as a function of exposure concentration and water transpired. Common cattails (*Typha latifolia*) were selected as the test wetlands plant species because of their almost ubiquitous nature in North American wetlands and because sulfolane and DIPA had been previously found in cattails near a sour gas facility.

Table 1
Environmental fate properties of sulfolane and DIPA

Property	Sulfolane	DIPA
Aqueous solubility, S (mg/L)	1E+6[a]	8.7E+5
Vapor pressure, P_v (Pa)	0.827[b]	0.0167[c]
Henry's law constant, log H (dimensionless)	−3.67[d]	−8.51[d]
Octanol/water partition coefficient, log K_{ow}	−0.77[e]	−0.86[e]
Dissociation constant, pK_a	15.3[a]	9.1[f]

[a] [22].
[b] [23].
[c] [24].
[d] [25].
[e] [26].
[f] [27].

2. Methods and materials

2.1. Plant propagation, transplanting and aeration

Cattails were obtained as bare-root plants from Aquatic and Wetland Company (Fort Lupton, CO). Plants were grown hydroponically in a greenhouse for several weeks, selected for uniformity and transplanted into 12 individual glass reactors. The cattails were then allowed to grow under aerobic conditions for several weeks prior to the initial exposure to sulfolane and DIPA. Each of the 12 hydroponic reactors consisted of a 2-L glass jar wrapped in foil to exclude light and filled with hydroponic nutrient solution, an aeration tube to deliver air or nitrogen gas to the root zone, and a plant support constructed of both open-cell and closed-cell foam. One day prior to the initial dosing, the aeration gas was switched from atmospheric air to nitrogen gas to achieve the low dissolved oxygen conditions (1 to 3 mg/L) typically observed at the field site. Cattails were removed from 6 of the 12 containers to serve as unplanted controls, immediately prior to the initial dosing. The hydroponic solution in unplanted controls was not changed after removing the cattails.

2.2. Experimental design

A total of 12 hydroponic reactors were used. Three of the planted reactors were dosed with sulfolane and DIPA to achieve concentrations of 40 and 20 mg/L (low dose), respectively, while the other three were dosed at concentrations of 200 and 100 mg/L (high dose). The low dose exposure was designed to be representative of the field exposure levels observed previously [4], while the high dose was used to examine the impact of concentration on uptake. The six remaining bioreactors served as unplanted controls. All controls received the low dose of sulfolane and DIPA, but three were poisoned with sodium azide (8 mM) to quantify any abiotic losses. The duration of the study was 50 days from the first dose.

2.3. Plant growth conditions

The hydroponic reactors were enclosed within a greenhouse for control of environmental conditions. Air temperature within the greenhouse was maintained at 20/16 ± 3 °C day/night. Root zone temperature fluctuated diurnally and ranged from 20 to 27 °C over the course of the study. The photosynthetic photon flux during the day averaged ~500 μmol m^{-2} s^{-1}. A dilute modified Hoagland's solution [16] was used to provide vigorous growth and near optimal concentrations of the essential nutrients for *Typha*. During the experiment, bioreactors were bubbled with nitrogen gas to ensure mixing and maintain low dissolved oxygen levels similar to those observed in the field. The dissolved oxygen levels measured during the course of the experiment were generally 1 mg/L except for a few instances when the nitrogen gas ran out during the evening hours and levels near 5 mg/L were measured the following morning.

2.4. Addition of sulfolane and DIPA to the bioreactors

Sulfolane (purity 99%, Aldrich Chemical, Milwaukee, WI) and DIPA (purity 99%, Aldrich Chemical, Milwaukee, WI) were added manually to reactors via a glass syringe at two times, initially (first dose) and midway the study (second dose). One of the three high dose bioreactors received only DIPA (and no sulfolane) at the first dose, but received both sulfolane and DIPA at the second dose.

2.5. Sampling protocol

Hydroponic solutions in each of the bioreactors were sampled immediately prior to and following the addition of sulfolane and DIPA, and then again at weekly intervals. All hydroponic solution samples were taken in duplicate and were collected in 40-mL glass vials equipped with screw top lids and Teflon-lined rubber septa and stored at 4 °C until analysis.

Root and leaf (base, middle and tip) samples were collected intermittently (when sufficient plant tissue mass was available) throughout the study in order to examine the kinetics of uptake. The plant tissues were placed in wide-mouth jars after collection and the samples were stored at 4 °C until analysis (maximum holding time was 21 days). Sub-samples of each tissue type were dried at 80 °C for 48 h to determine percent dry weight.

2.6. Sulfolane analysis

The concentrations of sulfolane in the hydroponic solution samples were determined using a liquid–liquid extraction/gas chromatography procedure. Five-milliliter samples of the hydroponic solution were extracted three times with 2 mL dichloromethane. The extracts were combined and analyzed using a Shimadzu Model GC-14A equipped with a DB-5 (30 M×0.45 mm, 0.25 μm film thickness) column (J&W Scientific, Folsom, CA) flame ionization detector, AOC-1400 autosampler and Agilent GC Chemstation Rev A.08.03 [847] data acquisition and analysis software. Sulfolane eluted at 3.8 min using the following temperature program: 80 °C (2 min hold) to 160 °C at 10 °C/min, then 40 °C/min to 220 °C (2 min hold). Nitrogen (10 mL/min) was used as the carrier gas.

External standards prepared in dichloromethane (minimum of five different concentrations) were used to quantify the amount of sulfolane in the extracts. Spike recoveries for the aqueous extracts ranged from 60% to 70% and duplicates varied within 5–10%.

Plant tissue samples (5 to 10 g wet weight) were cut into small pieces with a scissors or knife and then ground further with a hand-powered food processor. A known weight (approximately 1 g fresh weight) of each tissue sample was then placed into a 20-mL vial with 10.0 mL of deionized distilled water, agitated for 1 h at 180 oscillations/min using a Eberbach Model 6010 reciprocal shaker (Ann Arbor, MI) and then vacuum filtered through a 0.20-μm syringe filter. The filtrate was then extracted with dichloromethane as described previously for the hydroponic solutions. Emulsions formed during the extraction procedure were broken up by centrifugation. Recoveries for the plant tissue spikes ranged from 50% to 60% and duplicate samples varied between 5% and 10%.

2.7. DIPA analysis

The concentrations of DIPA in the root zone solution were measured over time by reverse phase high performance liquid chromatography (HPLC) with fluorescence detection following derivitization with 9-fluorenyl methyl chloroformate (FMOC, Acros Organics USA, Morris Plains, NJ). Aqueous samples (1 mL) were buffered to pH 7.7–9.0 with 300 μL of a borate buffer solution and then derivatized by adding 500 μL of 15 mM FMOC in 1:1 acetone/acetonitrile followed by vigorous shaking. After standing at least 5 min, the excess FMOC was removed by extracting the aqueous solution twice with 2 ml of pentane. The aqueous solution was then acidified with 25 μL of glacial acetic acid and mixed well.

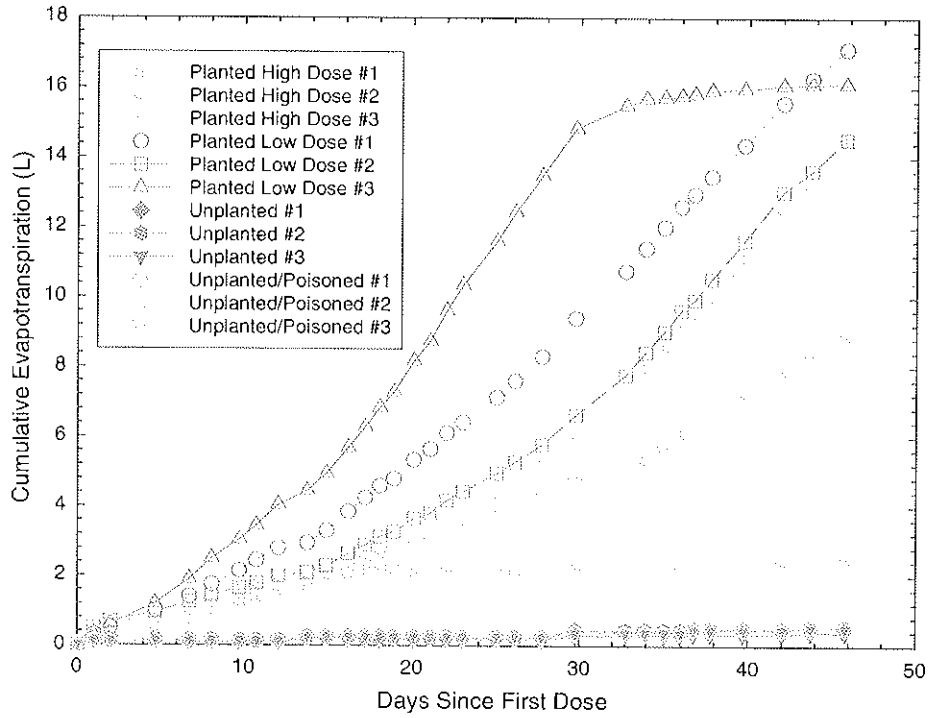

Fig. 1. Evapotranspiration from each bioreactor over the course of the study.

The HPLC system consisted of a Shimadzu Model SLC 6A system controller, LC6A pumps, SIL9B autoinjector, RF535 fluorescence detector and Class-VP, Version 4.2 chromatography software (Shimadzu Scientific Instrument, Columbia, MD). Derivatized samples (50 μL) were injected onto a Supercosil LC-8 column (25 cm×4.6 mm ID 5 μm, Supelco, Bellafonte, PA) and eluted with an acetate buffer (3 ml of acetic acid in 1-L water with pH adjusted to 4.2 with 0.25 N NaOH solution)/acetonitrile mobile phase at a flow rate of 1.5 mL/min. The following gradient elution program was used: isocratic for 2 min using 75% CH_3CN/acetate buffer (25/75%), then linear gradient elution ramped to 75% CH_3CN over 20 min, then isocratic for 10 min. The fluorescence detector was

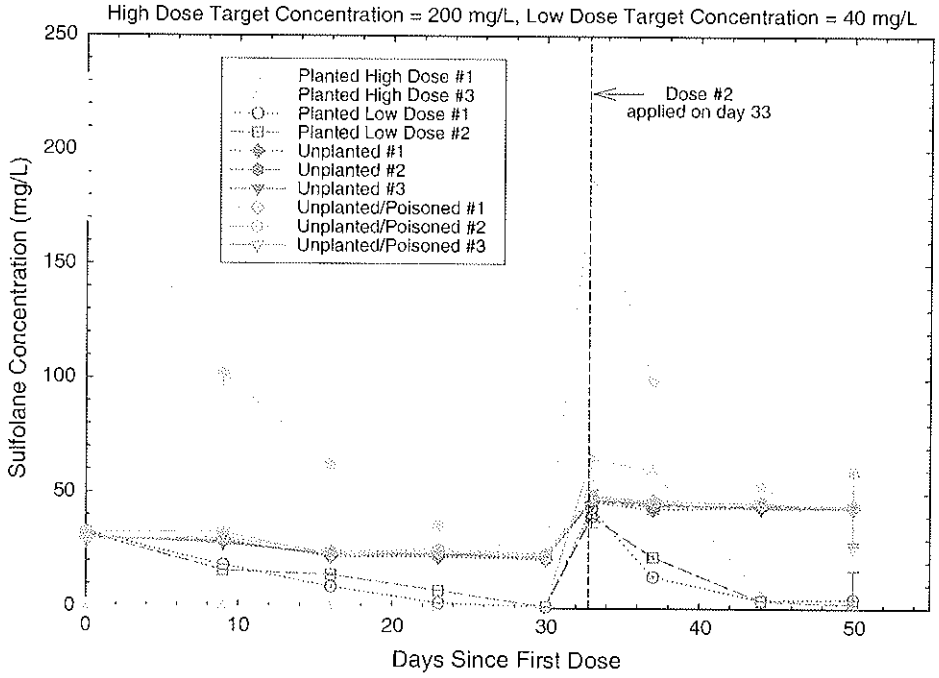

Fig. 2. Sulfolane concentration in each bioreactor over the course of the study.

Table 2
Final distribution (% of total recovered) of sulfolane in planted systems

Reactor	Shoots	Roots	Water
High dose 1	91.67	1.35	6.98
High dose 3	98.26	0.92	0.83
Low dose 1	92.94	2.40	4.66
Low dose 2	97.60	1.30	1.10

operated at an emission wavelength of 310 nm and excitation wavelength of 249 nm.

A minimum of five DIPA standards were prepared in 0.10 N HCl in 4:1 methanol/water to cover the calibration range 2.0–25 ppm. Samples more concentrated than the highest calibration standard were diluted to fall within the calibration curve. Analyses of duplicate samples were generally within 5%.

Aqueous extracts of plant samples were prepared as previously described for the sulfolane analysis and analyzed for DIPA using ion-exchange electrospray ionization liquid chromatography mass spectrometry [5].

3. Results and discussion

3.1. Cattail water use

The amount of water transpired by the cattails during the course of the study is summarized in Fig. 1. Water transpired was determined from the volume of hydroponic solution needed to replenish the planted reactors each day minus that required by the unplanted reactors. Evaporation from the reactors was negligible as illustrated by the data for the unplanted bioreactors (Fig. 1). The amount of water transpired was used to assess the relative health of each plant and to calculate approximate TSCF values for sulfolane and DIPA. As shown in Fig. 1, the high dose #2 and low dose #3 plants stopped transpiring before the completion of the experiments (on days 21 and 35, respectively). These plants were not included in the data analysis. The percent dry weight of cattail roots and leaves was determined to be 15% and 22%, respectively.

3.2. Aqueous phase sulfolane concentrations

Fig. 2 shows the aqueous phase concentrations of sulfolane in each of the 12 reactors over the course of the experiment. For the unplanted bioreactors, sulfolane concentrations did not change appreciably over time and nearly doubled with the addition of the second dose. For the planted reactors, the concentrations gradually decreased over time between doses due to root sorption, plant uptake and/or degradation. One of the three high concentration bioreactors (solid triangle symbols) did not receive sulfolane until day 33 (second dose). The concentrations of sulfolane shown in Fig. 2 were not corrected for the method extraction efficiency.

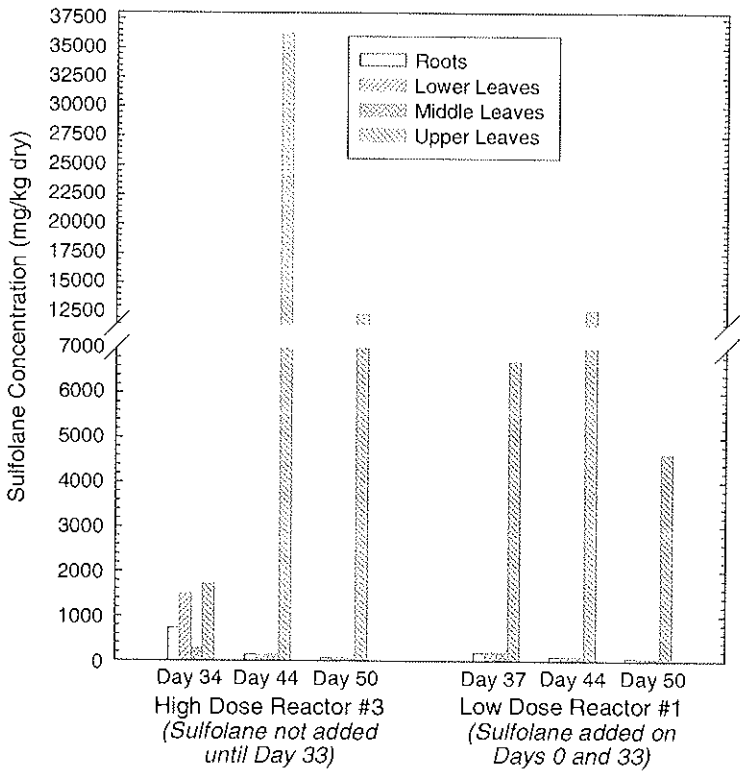

Fig. 3. Sulfolane concentration in one high dose and one low dose plant at three sampling times during the study.

Table 3
Final sulfolane concentrations (mg/L in water and mg/kg dry weight in plant tissues) in planted hydroponic reactors

Reactor	Water (n=2)	Roots (n=2)	Leaves (base, n=1)	Leaves (middle, n=1)	Leaves (tip, n=1)
High dose 1	27.59 ± 0.07	197.53 ± 2.10	485.61	2145.66	33,031.44
High dose 3	2.12 ± 0.02	62.76 ± 16.6	94.55	308.81	12,355.18
Low dose 1	4.02 ± 0.22	54.83 ± 4.61	38.74	249.80	4629.68
Low dose 2	1.84 ± 0.03	37.53 ± 16.9	57.17	36.48	5996.48

3.3. Distribution of sulfolane

At the end of the 50-day exposure period, the concentrations of sulfolane within the root zone and plant tissues were determined for each reactor. The final distribution of sulfolane within each reactor is summarized in Table 2. For the planted reactors, the largest percentage of sulfolane recovered was in the foliar or shoot tissue.

The high concentration of sulfolane in the foliar section of the plants indicates that it is readily translocated from roots to shoot. While this seems to contradict translocation models based on hydrophobicity (e.g. [11]), it is not surprising given the recent literature reports of significant plant uptake of highly water-soluble or miscible organics like MTBE [15,17,18] and 1,4-dioxane [14]. The appearance of the highest plant tissue concentrations in the foliar portion of the plant also matches the trends observed in the field data reported by Headley et al. [4,5].

3.4. Kinetics of plant uptake of sulfolane

A qualitative examination of the kinetics of sulfolane uptake by cattails was conducted by collecting plant tissue samples at several times within the 50-day study and by dosing one of the triplicate plants 33 days later than the other two. In addition, the leaves were divided into base, middle and tip components, and analyzed separately to look at the kinetics of sulfolane movement within the foliar section of the plant. The division was based upon the length of each leaf (i.e. each leaf was divided into thirds).

The plant tissue data summarized in Fig. 3 show that the leaf tips were consistently higher in sulfolane concentrations. This is likely the result of greater amounts of water being transpired by the tips due to their older age and the additional sunlight received relative to the lower leaf sections [19]. In reactor H3, where the sulfolane was not added until day 33, Fig. 3 shows that measurable levels of sulfolane moved into the leaves within only 1 day of dosing but the concentrations in the different leaf fractions were similar. However, 11 days later, almost all the sulfolane was found in the leaf tips.

The final concentrations of sulfolane in the planted reactors are shown in Table 3. Concentrations are reported on a dry weight basis. Percent dry weight for cattail leaves and roots was determined to be 15% and 22%, respectively. For the plants exposed to the higher dose, the concentrations of sulfolane at the end of the experiment were much higher

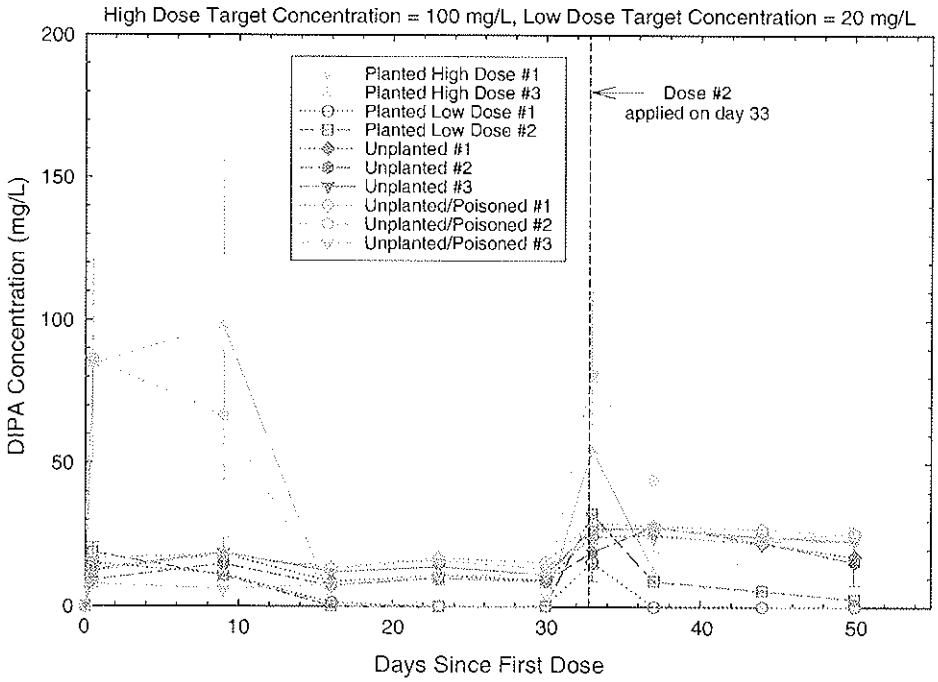

Fig. 4. DIPA concentration in each bioreactor over the course of the study.

Table 4
Final distribution (% of total recovered) of DIPA in planted systems

Reactor	Shoots	Roots	Water
High dose 1	14.81	83.08	2.11
High dose 3	39.01	60.99	0.00
Low dose 1	16.89	83.11	0.00
Low dose 2	11.78	25.75	62.47

in the leaf tips than the other plant tissue types. This trend was also observed in the low dose reactors although the differences in leaf concentrations from the leaf base to the tip were not as great. In general, the foliar tissue concentrations of sulfolane in the high dose plants were about a factor of 5 greater than the low dose plants. This was essentially the same as the ratio of exposure concentrations supporting the assumption that sulfolane is taken up passively along with the water transpired.

3.5. Aqueous phase DIPA concentrations

Fig. 4 shows the aqueous phase concentrations of DIPA in each of the 12 bioreactors over the course of the experiment. As previously observed for sulfolane, the DIPA concentrations in the unplanted bioreactors did not change appreciably over time and were almost doubled with the addition of the second dose. For the planted reactors, the concentrations gradually decreased over time between doses due to root sorption, plant uptake and/or degradation.

3.6. Distribution of DIPA

For the planted reactors, the largest percentage of DIPA recovered was in the root tissue whereas for sulfolane the largest percentage was associated with the foliar portion of the plant. This is not unexpected based on the differences in physical–chemical properties between the two compounds. In most environmental situations, DIPA will be in its cationic form, while sulfolane is a water miscible neutral compound. The appearance of the highest plant tissue concentrations of DIPA in the roots also matches the trends observed in the field data reported by Headley et al. [4] (Table 4).

3.7. Plant uptake of DIPA

Because of problems associated with the co-eluting peaks, plant tissue samples were collected for DIPA analysis only at the end of the study. The final DIPA tissue concentrations for the plants grown in the three high dose and three low dose reactors are shown in Table 5. For the plants exposed to the higher dose of DIPA, the concentrations of DIPA at the end of the experiment were a factor of four higher, roughly proportional to the exposure dose.

3.8. Transpiration stream concentration factors (TSCF) for sulfolane and DIPA

TSCF values for sulfolane and DIPA were determined by normalizing the foliar tissue concentrations to the volume of water transpired and dividing the value by the average exposure concentration. Table 6 shows the TSCF values for sulfolane and DIPA calculated using average leaf concentrations and the values calculated for sulfolane using the leaf tip concentrations. The TSCF values for sulfolane approach one when the leaf tip concentrations are used. The extent of DIPA translocation is much less than for sulfolane as indicated by the TSCF values in Table 6.

3.9. Using TSCF values to estimate the plant uptake of sulfolane and DIPA on a field scale

Because of the relatively high concentrations of sulfolane observed in the foliar tissue samples, an attempt was made to evaluate the potential impact of plant uptake on a field scale. The following simplified expression (Eq. (1), [20]) illustrates the critical variables needed to estimate sulfolane and DIPA uptake by wetland plants in the field (per unit area per year) using the TSCF values generated in this study.

Mass of sulfolane and DIPA taken up into plants

$$= (\mathrm{TSCF})(C_{\text{sulfolane or DIPA}})(T)(f) \quad (1)$$

where TSCF is assumed to be constant, $C_{\text{sulfolane or DIPA}}$ is the average water concentration in the wetlands of sulfolane or DIPA (mg/L), T is the cumulative volume of water transpired per unit area per year (L/m^2 year) and f is the fraction of the plant water needs met by contaminated water. T can be estimated by pairing site-specific climatological data with typical cattail transpiration rates. For wetland plants, f is assumed to be one. This expression also assumes that $C_{\text{sulfolane or DIPA}}$ is constant. A more realistic calculation would incorporate the reduction in $C_{\text{sulfolane or DIPA}}$ that would occur over time as a function of the physical, chemical or biological processes that may be occurring.

Table 5
Final DIPA concentrations (mg/L in water and mg/kg dry weight in plant tissues) in planted hydroponic reactors

Reactor	Water (n=2)	Roots (n=2)	Leaves (base, n=1)	Leaves (middle, n=1)	Leaves (tip, n=1)
High dose 1	0.45 ± 0.21	695.14 ± 301	273.58	176.17	189.09
High dose 3	0 ± 0	97.57 ± 12.6	107.73	39.65	103.71
Low dose 1	0 ± 0	14.82 ± 11.3	7.87	4.78	8.58
Low dose 2	2.7 ± 0.28	19.38 ± 7.53	27.89	10.28	14.62

Table 6
TSCF values for sulfolane and DIPA

Reactor	Sulfolane TSCF (average)	Sulfolane TSCF (tips)	DIPA TSCF (average)
High dose 1	0.151	0.857	0.016
High dose 3	0.149	0.924	0.007
Low dose 1	0.110	0.481	0.002
Low dose 2	0.197	0.885	0.005

For sulfolane, TSCFs were calculated using both average leaf concentrations and leaf tip concentrations. The high dose 2 and low dose 3 plants died during the study, resulting in much lower sulfolane TSCFs.

Transpiration rates in the field vary widely depending on evaporative demand and the soil water availability. For cattails, Pauliukonis and Schneider [21] report transpiration rates ranging from 3 to 10 L/m^2 day for a site in northern Utah. Using water concentrations representative of those observed in the field (40 mg/L for sulfolane, 20 mg/L for DIPA), TSCF values determined in this study (averaging 0.153 and 0.683 for sulfolane in whole leaves and leaf tips, respectively, and 0.004 in whole leaves for DIPA), and maximum and minimum estimates for the transpiration rate of cattails obtained from Pauliukonis and Schneider [21], high and low yearly plant uptake estimates can be calculated. Assuming a 120-day growing season, uptake of sulfolane ranges from about 2200 to 32,800 mg/m^2 year, while DIPA ranges from 30 to 100 mg/m^2 year. Calculations of this type can be used to determine the potential impact of plant uptake at a particular site and compare the relative uptake of two different compounds. The use of site-specific values for transpiration, growing season, and length of day would improve the accuracy of the uptake estimations.

The estimated uptake values for sulfolane suggest that wetland plants could play a significant role in its natural attenuation, provided the sulfolane is not released by the plants during winter dormancy.

4. Conclusions

The main objective of this study was to determine the extent to which sulfolane and DIPA are taken up and translocated into the above-ground portion of wetland plants. Both sulfolane and DIPA were taken up by cattails and translocated into the foliar portion of the plants as a function of exposure concentration and water transpired. However, sulfolane was translocated into the foliar portion of the cattails to a significantly greater extent than DIPA. The difference in plant uptake between sulfolane and DIPA is most likely due to the differences in their physical–chemical properties. Sulfolane is a highly soluble, neutral organic compound that apparently readily passes through the root membrane and into the foliar portion of the cattail via the xylem flow. DIPA is protonated at most environmentally relevant pHs which restricts it movement through the lipophilic root membrane.

Sulfolane tissue concentrations at the end of the study ranged from 12,000 to 32,000 mg/kg dry weight for the 200 ppm exposure concentration and 4000 to 6000 mg/kg dry weight for the 40 ppm exposure concentration. DIPA concentrations in the foliar tissue ranged from 100 to 250 mg/kg dry weight for the 100 ppm exposure and 6 to 20 mg/kg dry weight for the 20 ppm exposure. The plant tissue concentrations of sulfolane were highest in the leaf tips, while for DIPA the concentrations were highest in the roots. This followed the general trend observed at several field sites [6].

TSCF values for sulfolane ranged from 0.1 to 0.9, depending on the leaf concentration used (leaf tip or leaf average), while the TSCF values for DIPA were only <0.01 to 0.02 for all plants. The sulfolane TSCF values are much higher than would be predicted from previously published models based on hydrophobicity as expressed by log K_{ow}. The sulfolane TSCF values measured in this study along with recent values reported for 1,4-dioxane and MTBE suggest that the relationship between TSCF and log K_{ow} should be reevaluated for highly water-soluble, non-ionized organic compounds.

The laboratory derived TSCF values generated in this study could be used along with site-specific transpiration values to estimate plant uptake on a field scale. These estimates could be used to determine if plants have a significant impact on the natural attenuation of sulfolane.

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• 2nd MENDT Proceedings

Corrosion Problem in Sulfolane Extraction Unit (U 7300)

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Description of Process:

Sulfolane Extraction Unit uses as a separation process an extractive solvent (sulfolane) to separate aromatics from non-aromatics.

Aromatics and non-aromatics mixture is coming from platformer Unit 7200, where aromatics are generated.

In sulfolane Extraction RDC, aromatics are dissolved in sulfolane and this mixture is the extract phase (bottom), while the remaining non-aromatics counter-currently contacted and efficiency of stage is improved by mixing with rotating baffles.

Sulfolane is recovered from raffinate first in a coalescer and then in a water wash column. The final raffinate is pumped to Naphtha Blending as gasline components.

Extract is stripped and enriched in aromatics after recontacting with additional sulfolane. Solvent is recovered under vacuum distillation form extract; extract is separated from water by cooling and clay treated to eliminate olefins and diolefins, sent to Aromatics Fractionation Unit 7400 to separate benzene, toluene and xylenes.

Summary

This unit has a history of severe erosion/corrosion and especially after shutdown March-96; it has been observed an increase in corrosion rate in the SEU (sulfolane extraction unit) especially the fat solvent line to stripper C-7303 (after upgrading the bottom section of C7302 , March 99) . This loop contents of extractive stripper column(C-7302), reboilers (E7306 A/B), transfer lines (P73214/P73006) and solvent recovery column (C-7303).

The Extraction Stripper Column (C7302) has been lined with Carbon Steel plated at the bottom section in Dec-1989. In Nov-1991 the lining plates started to corrode. The bottom section has been lined with 410 SS in Mar-1996. In Aug-1997 a leak developed on the bottom dome. In Mar-1999 the bottom section 7m from the bottom has been replaced with duplex SS.

The reboilers (E-7306 A/B) have been retubed six times since day one 1985. The last retubing was by Duplex SS at Mar-01.

After those modifications the erosion/corrosion problem has shifted to transfer lines (P73214/P93006) and solvent recovery column. The corrosion rate became higher than before and three pinholes were developed in the transfer lines after that modification.

At the last shutdown the solvent recovery column was opened for inspection and found the inlet and bottom sections have corrosion more than was expected.

The root cause is mostly the accumulation of acidic material in the circulating solvent.

The accumulation of acidic material in the circulating solvent (i.e. chlorine ex feed and suffocate degradation products due to reactions with oxygen) has the combined effect:

1. Oxygen ingress
2. Solvent filter not always in operation
3. Solvent regenerator operated below max. capacity.
4. Reduction in water bleed ex C-7307 after shutdown in Mar-01

SEU Corrosion / Erosion Problem

In general the following four items are seen as the main causes for SEU corrosion/erosion problems in the SEU

- Oxygen in the plant (ingress or via incoming flows)
- Chlorine in circulating solvent.
- Accumulation of degradation and corrosion products in the plant.
- High temperature in reboilers.

Oxygen

Oxygen in contact with suffocate at the condition in the SEU plant leads to rapid degradation of the solvent. The most likely places for oxygen entering the system are the vacuum parts of the unit, dissolved oxygen in the feed and in fresh or wet solvent supply. To check where oxygen ingress takes place it will be required to check all flanges in the vacuum system. This can be done during normal operation (very difficult) or at least this should be checked before the plant is started up after a shutdown or having opened equipment in the vacuum section. After a shutdown it is recommended to do both a vacuum test as well as a pressure test to find leaks.

Chlorine

Chlorine can form HCL in the hotter parts of the unit and will therefore be very corrosive Chlorine can enter the unit with the platformate feed (usually 1 ppmwt or less) or via cooling (sea) water leaks.

Accumulation of degradation and corrosion products

Over the years, degradation and corrosion products will have accumulated in the plant. Experience from other sites that once in a while a very through cleaning of the plant is required. Dirt accumulated in the plant is usually corrosive material and/or act as a kind of catalyst to make more degradation products. It is therefore advised to plan for the next major shutdown to do a though cleaning. In the Stanlow SEU about 10-15 m3 dirt was taken out of the unit.

High steam and reboiler temperature

The temperature has a large effect on the degradation of sulfolane by oxidation. To

minimize the temperature effect it is advised to operate always at temperature lower than 175° C on the process side and at a (condensation) temperature of max. 205° C on the steam side of a reboiler. The operating data from the SEU show that most of the time these criteria are met.

RECOMMENDATION

- Check tightness of vacuum system
- At start up do pressure test as well as vacuum
- Check chlorine content a regular basis
- Check water of V-7301/V-7304 on Na (if there sea water leak)
- Operate regenerator at max. throughput and drain every 2-3 months
- Clean SEU equipment and lines in shutdown
- Max temperature on process-side reboilers is 175° C
- Steam condensation temperature in reboiler max 250° C

 |Top|

Section 15. REFINERY WASTES

BIODEGRADATION OF SULFOLANE IN REFINERY WASTEWATER

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Sulfolane (thiocyclopentane-1,1-dioxide) is an important process chemical for the petroleum and chemical industries. It has outstanding solvent properties for most classes of organic compounds and many common polymers and is chemically and thermally stable. At ambient temperatures, sulfolane is a colorless solid and is miscible with aromatic hydrocarbons and water. It does not dissociate or polymerize under normal acidic or basic conditions.

Sulfolane is synthesized through the hydrogenation of 3-sulfolane, an addition product of sulfur dioxide and butadiene. The main commercial outlets for sulfolane are its use in a sulfolane extraction process for the production of aromatics, and the Sulfinol® process for purifying acid gas streams. Further applications are in the separation of low-boiling alcohols, fractionation of wood tars, tallow oil and fatty acids, concentration of SO_2, and dehydration.

Sulfolane is usually present in wastewaters from petroelum refining and gas treating plants at levels of about 10 mg/l or less. Spills occur occasionally. Usually such streams are diverted to a storage facility to reduce instantaneous organic shock loading. The stored concentrate waste is normally treated in an existing biotreater.

In this study, the biodegradability of sulfolane in two bench-scale suspended growth systems was assessed. Spill simulation tests were also conducted to provide empirical guidance as to the handling and treatment of possible sulfolane spills. Efforts were also made to identify the metabolic intermediates and products to determine the fate of sulfolane in aerobic biotreaters.

METHODS AND MATERIALS

Analysis

Sulfolane was analyzed with a Varian 3700 GC and Vista 401 integrator. A 4-ft column with 5% Carbowax 20M on 60–80 mesh Chromosorb T was employed. Temperature programming was set at 165°C for 9 min and then increased to 185°C at 10°C/min. Both the injector and the detector temperature was maintained at 225°C.

All the oxygen uptake tests were done with a 250-ml BOD bottle and an Orbisphere oxygen probe equipped with an adapter. Endogenous rates were taken after 30-min aeration without feed. When substrate was included, the sludge was washed twice with 10 or 20 m*M* pH 7 phosphate buffer.

BOD_5 and COD (dichromate) analyses were done according to *Standard Methods* [1]. TOC was analyzed with a Beckman Tocamaster Model 915-B. Sulfate was determined by ion exchange chromatography (Dionex).

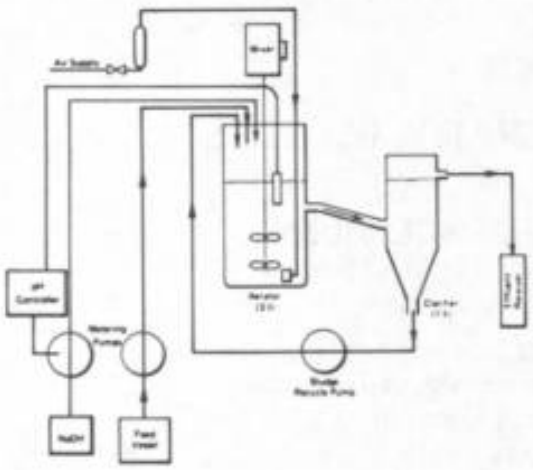


Figure 1. Schematic of CMAS reactor.

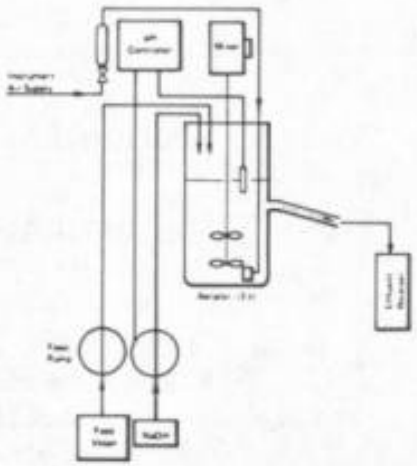


Figure 2. Schematic of CSTR reactor.

Bench-Scale Completely Mixed Activated Sludge System (CMAS)

The bench CMAS system was employed to simulate wastewater treatment operations. The schematic of the laboratory unit is shown in Figure 1 and consisted of a 3-liter cylindrical aerator, a 1-liter clarifier, and a variable-speed sludge recycle pump. Aeration and mixing were provided with a bottom air diffuser and an impeller. Dissolved oxygen was maintained at 3–6 mg/l and the temperature at 75 ± 5°F. Feed and effluent were refrigerated and the feed flowrate adjusted to 2–4 liter/day. Daily effluent composite samples were used for routine BOD, COD, sulfolane and sulfate analyses.

The pH was maintained at 7.0 ± 0.2 with a pH controller, and sodium hydroxide was used to neutralize the acid generated from sulfolane oxidation. Mixed liquor suspended solids were not wasted, but samples were taken for solids analysis, oxygen uptake, and batch degradation studies.

Bench-Scale Continuously Stirred Tank Reactor (CSTR)

This unit was used for the simulation of sulfolane degradation in an aerated lagoon facility with approximately a 2-day hydraulic detention time operated at 75 ± 5°F. As shown in Figure 2, the reactor is similar to the CMAS less the clarifier and sludge recycle line. Feed and effluent storage, pH control were conducted as for the CMAS unit.

Batch Die-Away Biodegradation Tests

Degradation of sulfolane by activated sludge was performed in a 1-liter cylinder with bottom diffusers. The activated sludge was taken from the CMAS reactor, settled, decanted, washed with 20 m*M* pH 7.2 phosphate buffer, and resuspended in the same buffer solution. Sulfolane was added at 100 mg/l and the removal of the compound was analyzed over several days.

Sludge Settling Tests

The sludge volume index (SVI) was done according to *Standard Methods* [1]. The interfacial settling velocity (ISV) of the activated sludge was measured in a 1-liter volumetric cylinder using a scraper rotating at 1 rpm. The linear portion of the settling curve was used for calculating sludge settling velocities [2].

RESULTS AND DISCUSSION

Acclimation

The CMAS reactor was seeded with fresh activated sludge taken from a refinery biotreater and continuously fed with primary effluent from the same plant. The feed rate was maintained initially at 2 liter/day. The feed was supplemented with 20 mg/l sulfolane during the acclimation period. Oxygen uptake rates (OUR) of the MLSS were monitored with sulfolane addition. OUR was neither inhibited nor increased during the first few days of acclimation with 20 mg/l sulfolane. The activated sludge in the CMAS unit became acclimated to 20 mg/l sulfolane and showed more than 80% sulfolane removal after a week of sulfolane feeding. At this time, the bench CSTR unit was seeded with somewhat acclimated activated sludge from the CMAS reactor. Although the CSTR was started with about 10% of the VSS concentration of CMAS, it was effective in sulfolane removal capacity at less than 2-day hydraulic retention time. The performance data of both units will be discussed in later sections.

Oxygen Uptake Rate

Although sulfolane did not affect the OUR of the nonacclimated activated sludge, it did enhance the uptake rate after a short-term acclimation. As shown in Table I, the OUR doubled in the presence of only 1–2 mg/l sulfolane; however, the rate was not higher with 2–40 mg/l. This suggested that sulfolane was oxidized by zero-order kinetics when sulfolane concentration is 1 mg/l or higher.

After a few months of acclimation, several suspected intermediates of sulfolane degradation were also included in the oxygen uptake test. They are butane sulfonic acid, *n*-butanol and butyric acid—all considered structurally analogous to sulfolane. Although the sulfolane adapted sludge failed to show any increased OUR in the presence of butane sulfonic acid, it did oxidize *n*-butanol and butyrate. The uptake rate was increased from 35 to 220% when 2–100 mg/l of these four-carbon straight-chain compounds were added to washed MLSS (Table I).

Table I. OUR of Activated Sludge Adapted to Sulfolane

Test No.	Substrate	S (mg/l)	Oxygen Uptake Rate ($mgO_2/gVSS/hr$)
A	Endogenous	0	4.3
	Sulfolane	1	7.1
	Sulfolane	2	6.9
	Sulfolane	4	7.1
	Sulfolane	8	6.8
	Sulfolane	40	6.9
	Glucose	8	6.5
	Glucose	2	5.4
B	Endogenous	0	4.0
	Sulfolane	2	8.6
	Sulfolane	10	8.4
	Butane sulfonic acid	2	4.0
	Butane sulfonic acid	10	4.3
	Butyric acid	2	5.6
	Butyric acid	10	6.5
	n-butanol	2	10.2
	n-butanol	10	12.9
C	Endogenous	0	7.4
	n-butanol	10	10.6
	n-butanol	100	10.7
	Butyric acid	10	11.4
	Butyric acid	100	13.8

Sulfate Formation

During some batch degradation and oxygen uptake tests, it was observed that there was a rather significant decrease of pH accompanying sulfolane disappearance. For the two continuous-flow reactors, supplemental alkalinity was always required to maintain a neutral pH when sulfolane was included in the feed. Since inorganic sulfate seemed to be the most probable end product, sulfate and sulfolane analyses and balances were made. The data shown in Tables II and III clearly indicate that the sulfur in sulfolane is stoichiometrically converted to inorganic sulfate through biological oxidation. In most of the batch and continuous flow studies, 95–102% of the sulfur was recovered. No sulfite was observed in effluents from the continuous-flow reactors or in batch die-away tests. It is possible, however, that sulfite may have been oxidized spontaneously and/or intracellularly to sulfate.

Since the acclimated culture showed a substantial increase in OUR with *n*-butanol or butyric acid, it is conceivable that sulfolane may be converted to a four-carbon intermediate and sulfate (or sulfite) after initial ring cleavage.

CMAS Reactor

The CMAS reactor was continuously operated for about four months. The test program was divided into five test periods according to various F/M ratios and sulfolane loadings. The performance data are summarized in Figure 3 and Table IV.

The first period lasted for two weeks and no sulfolane was added. The reactor performed very well and consistently produced an effluent with average 2 mg/l soluble BOD. The second period started when 20 mg/l sulfolane was included in the feed (Figure 3). After only a few days acclimation, sulfolane was almost totally removed. The highly efficient BOD removal (effluent soluble BOD = 1 mg/l) also indicates that the CMAS has acquired its sulfolane degrading capability at no expense of its normal organic removing capacity.

Similar performance results were also obtained in periods III, IV and V, when sulfolane was step-increased to 40 and 80 mg/l. The F/M ratio was kept at 0.05–0.15 lb BOD removed/lb VSS-day for the entire CMAS test program to simulate field operating conditions. Most of the daily effluent composites had no detectable sulfolane (less than 1 mg/l),

Table II. Degradation of Sulfolane: Batch Die-away Test

Reaction Time (hr)	pH	Sulfolane (mg/l)	TOC (mg/l)	SO_4^{2-} (mg/l)	Sulfur Recovery as SO_4^{2-} (%)
0	7.2	100	48	58	
24	7.0	<1	9	137	98.8[a]
48	7.0	<1	6	140	102[a]

[a]Total degradation of sulfolane is assumed.

Table III. Distribution of Organic and Inorganic Sulfur in the Activated Sludge Reactor

	Influent Sulfur (mg/l)			Effluent Sulfur (mg/l)			
Test No.	Organic-S	SO_4^{2-}-S	Total[a]	Organic-S	SO_4^{2-}-S	Total[a]	Sulfur Recovery (%)
1	12.1	88	100.1	ND[b]	114	114	88
2	12.1	95	107.1	ND	113	113	95
3	24.2	80	104.2	ND	107	107	97
4	24.2	81	105.2	ND	109	109	97

[a]Assuming any other influent sulfur source is negligible.
[b]ND: Nondetectable or less than 1 mg/l.

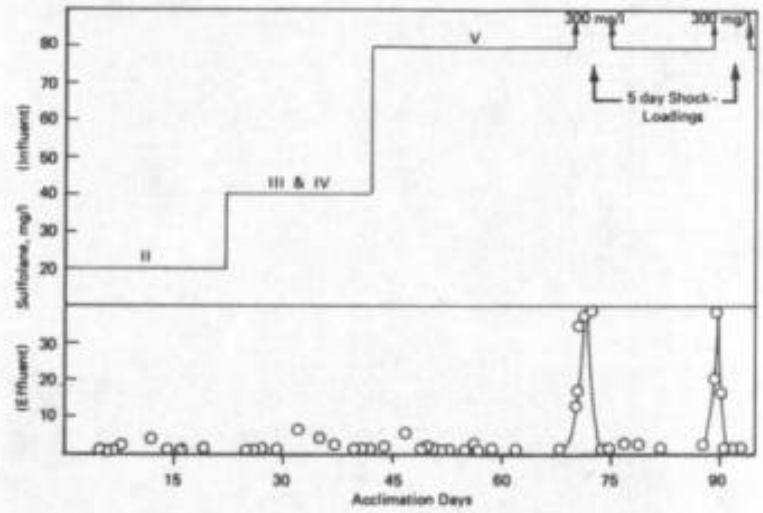


Figure 3. Chronological performance data of the CMAS reactor.

Table IV. Removal of Sulfolane in Bench CMAS

	Test Period				
	I	II	III	IV	V
MLSS/MLVSS	3020/2380	1684/1424	1600/1352	1190/1014	1180/1010
Hydraulic Detention Time (hr)	28	26	19	23	28
F/M (lb BOD/lb VSS-day)	0.06	0.08	0.12	0.13	0.12
Influent (mg/l)					
BOD5	155	118	124	124	150
COD	337	262	233	233	329
Sulfolane	0	20	40	40	80
Effluent (mg/l)					
$SBOD_5$	2	1	1	2	3
SCOD	38	36	35	42	48
Sulfolane	0	1	1	2	1

Table V. Effluent Characteristics of CMAS During Sulfolane Shock Loadings

Time After Shock-Loading Started (hr)	Sulfolane (mg/l)			$TBOD_5$ (mg/l)		
	A	B	C	A	B	C
0–12	13.9	16.2	47.0	38		128
12–24	34.7	39.2	130	52	47[d]	158
24–48	37.6	4.3	210	64	7	237
48–72	3	<1	200	28	2	182
72–96	<1	<1	42.5			31
96–120	<1	<1	10.0			3

[a] A = first 300 mg/l sulfolane shock loading–acclimated CMAS.
[b] B = second 300 mg/l sulfolane shock loading–acclimated CMAS.
[c] C = 325 mg/l shock loading–nonacclimated CMAS, initial VSS = 1780 mg/l, final VSS = 2276 mg/l.
[d] 0–24 hr composite.

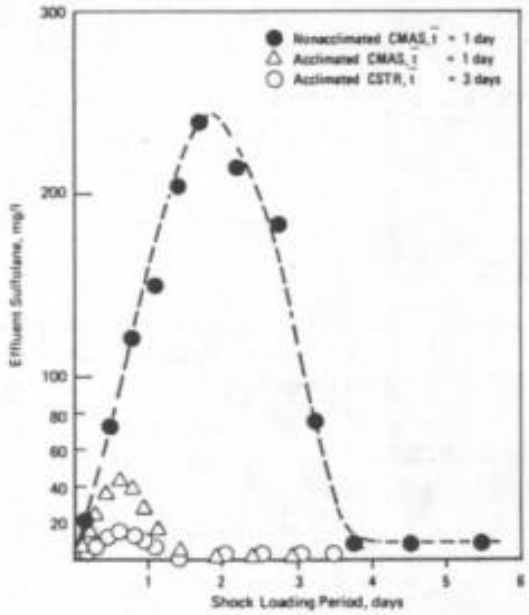


Figure 4. Responses of the CMAS and CSTR reactors to sulfolane shock loadings.

although a few samples contained more than 5 mg/l sulfolane (Figure 3). During period V, two concentration shock loadings were administered at a flowrate of 3 liter/day. In each case, sulfolane was dosed at 300 mg/l for a 5-day period. This caused the influent BOD to increase to 447 mg/l. As shown in Figures 3 and 4, the response patterns of the two shock loadings were similar, although the effluent sulfolane peaked and then subsided earlier during the second shock loading. In both cases, the effluent sulfolane reached a peak of about 40 mg/l and then decreased to less than 1 ppm after 2-3 days. BOD data also indicated (Table V) that a sudden increase occurred within the first two days. The system could adjust to the threefold increase in organic loading and produced effluent low in BOD. Therefore an acclimated completely mixed activated sludge system could significantly dampen the impact of a sulfolane surge in refinery wastewater, as indicated by the responses of the CMAS reactor to the step increases and the rather severe shock loadings of sulfolane.

Another shock loading test was conducted with a nonacclimated CMAS. The reactor was replaced with fresh activated sludge from a refinery. Sulfolane and TBOD of the feed were 325 and 536 mg/l, respectively (feed rate of 3 liter/day). The sulfolane was not removed in the first 40 hr, as shown in Figure 4, but the biomass seemed gradually to develop sulfolane-degrading capability at day 3 and could remove over 95% of sulfolane on day 5 (Table V, Case C).

Our studies demonstrated the biodegradability of sulfolane in a CMAS reactor and the rapid adaptability of activated sludge to sulfolane. The short period of acclimation indicates that facilities providing spill diversion, storage and subsequent introduction of a diverted concentrate sulfolane stream could minimize a sudden buildup of sulfolane in a biotreater. A slow release of sulfolane could increase the treatment efficiency.

The settleability of the activated sludge was monitored during various test periods and shock-loading conditions. Both the sludge volume index (SVI) and the interfacial settling velocity (ISV) were measured and the results are summarized in Table VI. The SVI ranged from 70 to 117 ml/g TSS. The ISV increased from an initial 9.0 ft/hr without sulfolane, to 16-20 ft/hr after sulfolane addition. This improvement in settleability may have been due to a higher F/M ratio from periods II to V. For nonacclimated activated sludge sulfolane shock loading had no effect on its settleability since both ISV and SVI were almost unchanged.

CSTR Unit

The bench-scale CSTR was seeded with preacclimated biomass from the CMAS reactor. The unit had been operated continuously for three months. The test results are summarized in Table VII and Figure 5. In the first two periods in which sulfolane was present in the feed at 20 mg/l, removals of sulfolane and soluble BOD were about 90 and 97%, respectively, at

Table VI. Settleability of the Activated Sludge During Various Test Periods

Test Period	Sulfolane (mg/l)	SVI (ml/g TSS)	ISV[a] (ft/hr)
I[b]	0	70	9.0
II	20	117	20.0
III	40	104	15.8
V	80	75	19.2
During Shock-Loading[b]	325	91	12.4
Post Shock-Loading[b]	0	87	9.7

[a]Interfacial settling velocity, measured with approximately 2000 mg/l MLSS.
[b]Nonacclimated activated sludge.

Table VII. Removal of Sulfolane in Bench Aerated Lagoon Reactor (CSTR)

Test Period	Hydraulic Retention Time (days)	VSS (mg/l)	Influent (mg/l)			Effluent (mg/l)		
			BOD_5	COD	Sulfolane	BOD_5	COD	Sulfolane
I	1.4	205	118	262	20	4	47	2
II	2.1	146	124	233	20	2	44	2
III	2.4	86	157	245	40	2	48	2
IV	2.0	80	150	329	80	4	56	1

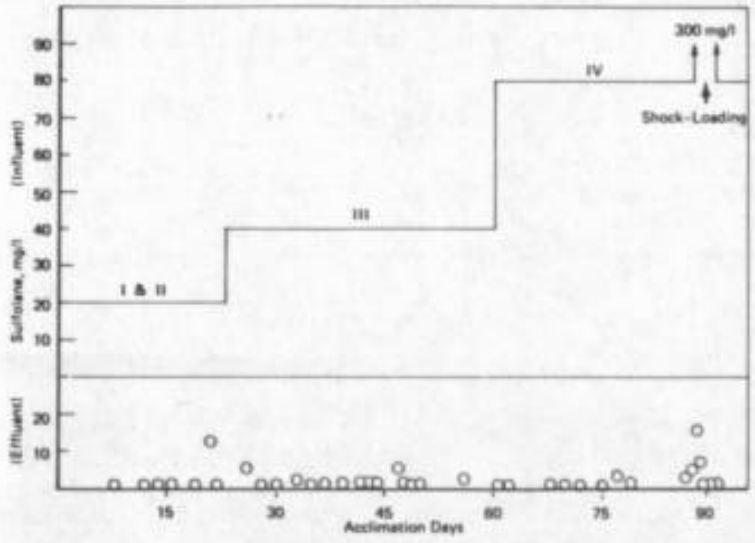


Figure 5. Chronological performance data of the CSTR reactor.

hydraulic loadings of 1.42–2.1 days. During these two transient periods, there was a gradual reduction in VSS from an initial level of 205 to 146 mg/l. The VSS concentration decreased further to less than 100 mg/l after the first month operation.

For test periods III and IV, influent sulfolane was increased to 40 and 80 mg/l, and the hydraulic detention time was maintained at 2.4 and 2.0 days, respectively. The step increase did not reduce sulfolane removal efficiency. The effluent sulfolane never exceeded 6 mg/l and averaged 1–2 mg/l for these two test periods. The average soluble BOD was less than 5 mg/l.

A 3-day 300-mg/l sulfolane shock loading was administered to the acclimated culture in the CSTR at the end of test period IV (hydraulic retention time of 3 days). The response is depicted in Figures 4 and 5. Sulfolane reached a maximum of 16 mg/l in the effluent at 15 hr and then gradually diminished to less than 1 mg/l at 30 hr. The effluent sulfolane averaged 10 mg/l for the first day and decreased to less than or equal to 2 mg/l for the second and third days. The effluent total BOD (settled 24-hr composite) of the three consecutive days during which shock loadings were 23, 10 and 21 mg/l, respectively.

These data indicate that a CSTR with relatively low concentration of acclimated biomass could effectively absorb a major sulfolane shock. It must be emphasized that the removal may not have been as effective with unacclimated sludge or with a simultaneous increase in hydraulic loading. In addition, a considerable amount of alkalinity would be required to compensate for the sulfuric acid generated from sulfolane decomposition during the shock loading period.

CONCLUSIONS

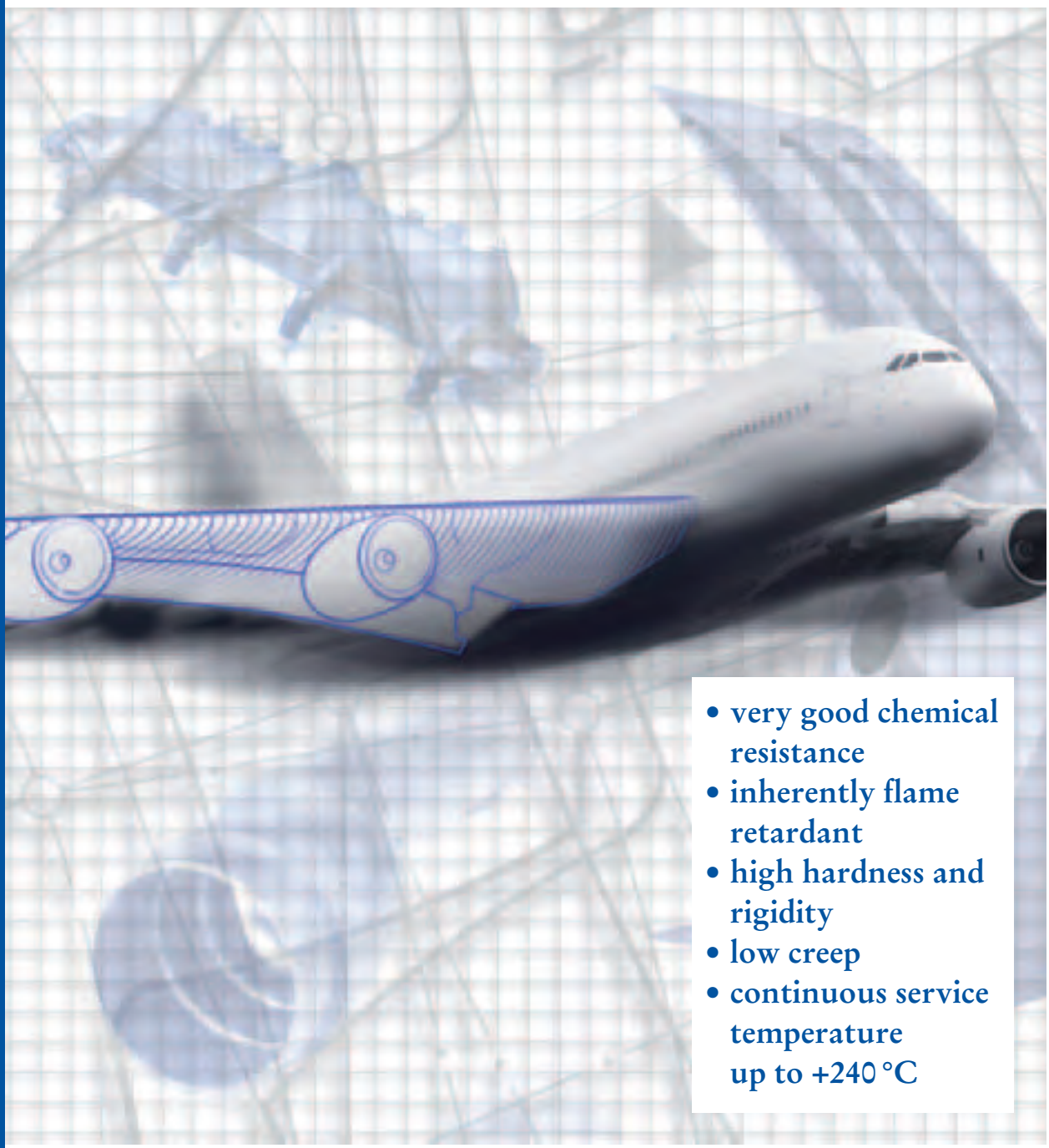
Sulfolane can be biodegraded by activated sludge cultures from refinery biotreaters. A short-term acclimation period is required in an activated sludge system or an aerated lagoon system for effective removal of 80 mg/l sulfolane. Inorganic sulfate has been identified as a degradation product of sulfolane metabolism. Supplemental alkalinity may be required to maintain the pH of a bioreactor due to acid formation. Acclimated activated sludge has a greater capacity to dampen a 300 mg/l sulfolane and threefold organic shock loading than a nonacclimated refinery activated sludge. Nonacclimated activated sludge is not inhibited by at least 200 mg/l sulfolane and can develop high degradative capacity after a few days exposure to sulfolane. An aerated lagoon reactor that has been acclimated to 80 mg/l sulfolane could absorb a 5-day 300-mg/l sulfolane discharge and still produce good quality effluent. The addition of sulfolane (up to 80 mg/l) to refinery wastewater does not affect the general performance of the two biological treatment processes studied.

REFERENCES

1. *Standard Methods for the Examination of Water and Wastewater,* 14th ed. (Washington, DC: American Public Health Association, 1975).
2. *Wastewater Engineering–Treatment, Disposal, Reuse,* 2nd ed. (Metcalf & Eddy, Inc., 1979).

Fortron®

Polyphenylene sulphide (PPS)



- very good chemical resistance
- inherently flame retardant
- high hardness and rigidity
- low creep
- continuous service temperature up to +240 °C

Ticona

Fortron® *Polyphenylene sulphide (PPS)*

Contents

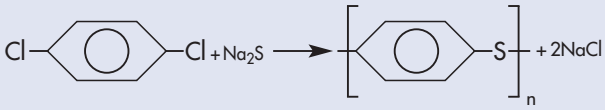
1. Introduction

Fortron® polyphenylene sulfide (PPS) is a high-performance thermoplastic with an excellent balance of properties. It is stiff, strong, hard and tough and has outstanding chemical and oxidative resistance. It retains these properties at temperatures well above 200 °C, i.e., its continuous use temperature extends to 240 °C.

It absorbs little moisture and is both dimensionally stable and inherently flame retardant. It also has excellent electrical properties, is highly impermeable to most liquids and gases, has minimal creep, even at elevated temperatures, and flows well in molding to fill long, thin and complex parts.

Fortron PPS is a linear, partially aromatic plastic containing a phenylene ring and a sulfur atom, which are linked alternating in para-postition (Fig. 1.1). It is made from the relatively complex reaction of para-dichlorobenzene and sodium sulfide in a special solvent. It is semicrystalline (Fig. 1.2), with the linear structure providing relatively more toughness compared to branched PPS.

Fig. 1.1 · Chemical Structure of Fortron PPS



Polyphenylene sulfide

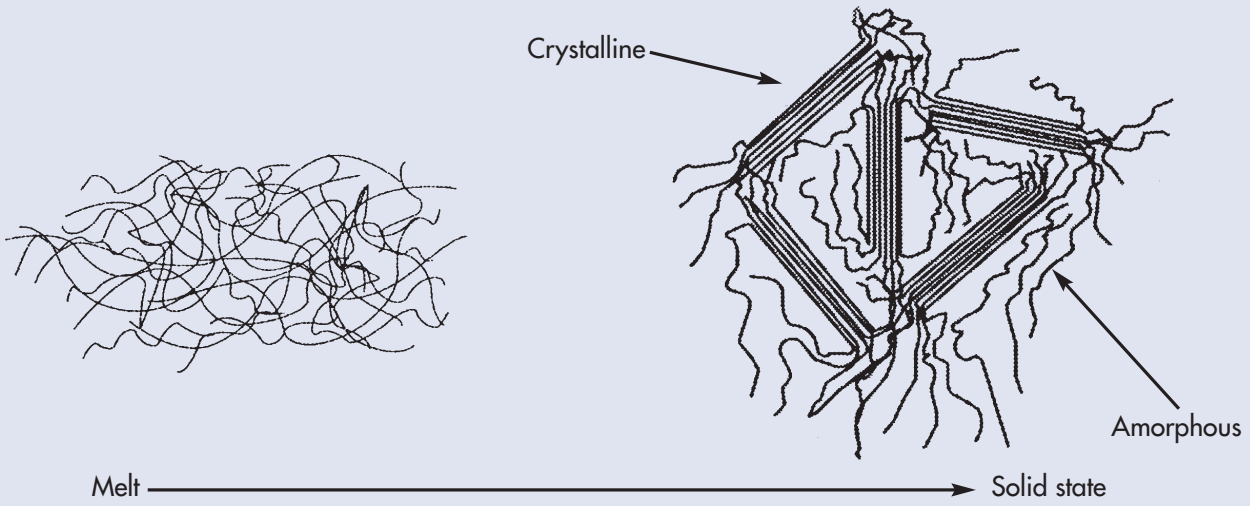
1.1 Typical applications

Fortron PPS is often the material of choice for hot, corrosive environments in the automotive, chemical, pharmaceutical, food and most other industries (Table 1.1). It is often selected to replace metals , thermosets and other thermoplastics when superior chemical resistance, mechanical integrity and creep resistance is needed.

It is increasingly used in the automotive sector where resistance to fuel, antifreeze, and transmission and brake fluids at elevated underhood temperatures is paramount. Specific auto applications include air intake systems, seals, fuel rails, valve covers, manifolds, connectors, light sockets and reflectors.

It is commonly injection molded to form industrial components, such as pump housings, valves, chemical tower packing, oil field parts, motor end bells, con-

Fig. 1.2 · Representation of Semicrystalline Polymer



Fortron PPS is a semicrystalline polymer having an optimal crystallinity of about 30 %.
Its amorphous phase density is 1.32 g/cm³ and crystalline phase density is 1.43 g/cm³.

veyor belt links, sensors and heater housings. Its electrical and electronic applications include complex connectors, plug boards, coil formers, relay elements and switches, as well the encapsulation of capacitors and transistors.

Fortron PPS can be blow-molded and extruded as films and fibers for specialty filtration media, mesh conveyer belts and flame resistant clothing. As a filter media and support material, it is a good choice for bag-house and flue-gas filters in coal-fired boilers, cogeneration units and cement kilns. It is also used to filter aggressive fluids, including hot water, amine, glycol, sulfolane, methylene chloride, naphtha and potassium hydroxide.

It can be extruded into profiles such as rod, tube, pipe, and slab. As a fine powder, it is used as a binder material in composite applications ranging from golf club shafts to commercial aircraft wings.

Table 1.1 · Major Markets for Fortron® PPS

Market area	Application Benefits
Automotive	Solvent resistance, temperature resistance, dimensional stability
Technical Fabrics	Temperature resistance, chemical resistance, flame retardancy
Pipe	Chemical resistance, temperature resistance, flexibility, impact resistance, stiffness, strength
Film	Good processability, stiffness, strength, chemical resistance
Industrial	Friction and wear properties, stiffness, strength, dimensional stability, temperature resistance, chemical resistance
Electrical/Electronic	Dimensional stability, heat deflection temperature, ionic purity, flame retardant, flowability
Healthcare	Chemical resistance, withstand sterilization, stiffness, strength
Audio/Video	Stiffness, strength, dimensional stability, temperature resistance
Telecommunications	Dimensional stability, stiffness, strength
Fiber optics	Dimensional precision, excellent barrier properties
Cryogenics	Excellent barrier, good flow at low temperature, stiffness, strength
Business machines	Dimensional stability, chemical resistance
Aircraft	Chemical resistance, temperature resistance, stiffness, strength

References

1. Cebe, P, Polymer and Polymeric Materials, 1995.

2. Product line

2.1 Grades

The Fortron PPS product line encompasses a broad array of standard and specialty grades for use in injection molding, extrusion, fiber spinning and blow molding (Table 2.1 – 2.3). Unreinforced grades are available as both pellets and free-flowing granules for easy feeding, while reinforced and filled grades are sold in pellet form.

Ticona continues to expand the breadth of Fortron PPS grades it provides. Beyond the products shown in Table 2.1 – 2.2, specialty grades provide enhanced strength, electrical properties, surface properties, dimensional stability and other properties. These grades include those for electrostatic dissipation, reflective surfaces such as headlamp reflectors, and thermal conduction, as well as those extra-long glass, carbon and other fibers. The long fiber reinforced PPS grades are available as Celstran® PPS grades.

Table 2.1 · Unreinforced Fortron PPS grades

Unreinforced grades	Supply form	Description
0203B6, 0203P6, 0203C6	Granules, pellets and crystallized pellets	Very low melt viscosity
0205B4, 0205P4, 0295C4	Granules, pellets and crystallized pellets	Low melt viscosity
0205B4/20 μm	Fine powder	Low melt viscosity for use in powder-based technologies
0214B1, 0214P1, 0214C1	Granules, pellets and crystallized pellets	Medium melt viscosity
0309B4, 0309P4, 0309C4	Granules, pellets and crystallized pellets	Low melt viscosity
0317B1, 0317P1, 0317C1	Granules, pellets and crystallized pellets	High melt viscosity
0320B0,0320P0, 0320C0	Granules, pellets and crystallized pellets	High melt viscosity

Table 2.2 · Reinforced Fortron PPS grades

Reinforced grades	Fillers Glass	Process	Description
1115E7	15 %	Injection molding	Very easy flow, low flash
1130L4	30 %	Injection molding	Medium flow
1140L4	40 %	Injection molding	Medium flow
1140L6	40 %	Injection molding	Easier flow

Given its affinity for fillers, Fortron PPS can carry as much as 70% in fillers and/or reinforcements. Glass filled grades and glass fiber-mineral blends are optimized to the best blend of stiffness, strength, toughness and heat deflection temperature. The Fortron line offers a wide range of melt viscosities and flowabilities in both neat and reinforced grades.

Unreinforced pellet grades are primarily used in extrusion for fibers, monofilaments and multifilaments, as well as for rods, slabs, pipes, films, fibers and other extruded items. Powder grades are used with many powder technologies such as composites, coatings and binders.

(For more information contact your local Ticona representative.)

In addition special grades for medical technology are available. Fortron® PPS MT grades are optimized for applications in medical technology and are certified to conform to specific property and quality standards, and to comply with applicable regulatory requirements. All medical technology grades have passed a variety of biocompatibility testing by independent bodies. Fortron® MT grades have the necessary certifications (Food and Drug Administration, European Union, BgVV). In addition, Drug and Device Master Files have been listed with the US FDA.

Table 2.2 · Reinforced Fortron PPS grades (continued)			
Reinforced grades	**Fillers Glass/mineral**	**Process**	**Description**
6850L6	50 %	Injection molding	Low warp
4184L4	53 %	Injection molding	Medium flow
4184L6	53 %	Injection molding	Easier flow
6160B4	60 %	Injection molding	Very easy flow
4332L6	65 %	Injection molding	Very easy flow
6165A4	65 %	Injection molding	Medium flow
6165A6	65 %	Injection molding	Easier flow
4665B6	65 %	Injection molding	Medium flow

Table 2.3 · Fortron PPS Specialty grades			
Reinforced grades	**Fillers Glass/mineral**	**Process**	**Description**
1115L0	15 %	Blow molding and extrusion	High melt viscosity
1120L0	20 %	Extrusion	High melt viscosity
1131L4 ITT	30 %	Injection molding	Lower flash
1140L0	40%	Extrusion	High melt viscosity
1141L4	40 %	Injection molding	Lower flash
1342L4	40 % low wear modified	Injection molding	Medium melt viscosity
6341L4	40 % low wear modified	Injection molding	Medium melt viscosity
6345L4	30 % low wear modified	Injection molding	Medium melt viscosity
6450A6	65 % low wear modified	Injection molding	Medium melt viscosity
1200L1	not modified	Extrusion and injection molding	Higher toughness
SKX-390	Electrically modified	Injection molding	Electrically conducting

Further information can be found in Product Info Medical technology (B 245 PR E), which can be sent to you on request.

2.2 Colorability

Reinforced Fortron PPS grades are available in natural and black, while most unreinforced grades black and brown, while most unreinforced grades are available only in natural. Color concentrates (or masterbatches) formulated in other colors can meet set color requirements (Table 2.4). All color concentrates used are cadmium-free. FDA compliant colors are available.

As is the case with most polymers, the addition of colorants can slightly alter flowability and mechanical properties such as tensile strength and elongation at break. Also, oxidative reactions due to light and heat can alter color in layers having thin edges. Processors who use their own colorants should ensure they do not decompose or change color at the processing temperature of Fortron PPS (upto 350 °C). End users should test colored components to ensure they meet specifications. Fortron PPS products are suitable for color coding, but not specific color match.

Table 2.4
Available color concentrates for Fortron PPS

Color No.	Standard Letdown.	Color
SD3002 K40	40:1	Black
SD3039 K40	40:1	FDA Black
SJ3013 K20	20:1	Green
SY3004 K40	40:1	Brown
SN3012 K20	20:1	Orange
SC3010 K20	20:1	Dark Grey
SC3011 K20	20:1	Pale Grey
SL3017 K20	20:1	Yellow
SS3006 K20	20:1	Red
SG3005 K20	20:1	Blue

2.3 Packaging

Fortron products are available in 15, 20 and 25 kg bags, 500 kg supersacks, 500 kg and 750kg gaylord boxes. Certain products are available only in specific packaging sizes.

2.4 Quality assurance

Meeting the quality requirements of our customers is a critical activity for Ticona. We constantly pursue and update the certifications needed for this purpose. Our quality management system has been certified to ISO 9000 standards since the early 1990s. In 2003, we built on this foundation by implementing the Global Ticona Integrated Management System (TIMS) for quality, environmental and risk management.

Important certifications include the following standards:

- ISO 9001
- ISO 14001
- ISO/TS 16949
- ISO/IEC 17025

Quality Management System Certifications under ISO 9001:2000 and ISO/TS 16949:2002 have now been achieved for all production sites and supporting remote locations of Ticona worldwide. The ISO/TS 16949:2002 standard combines the automotive regulations in Europe of VDA 6.1, EAQF and AVSQ with the requirements of QS-9000 in North America and supersedes all of these. Ticona received the certification for this standard in 2003.

The Ticona Oberhausen site in Germany gained registration under ISO 14001, the Environmental Management System Standard, in 1999. All Ticona facilities in the Americas achieved certifi cation under ISO 14001 in 2002. At Kelsterbach, Germany, registration has been completed 2005.

The appropriate Ticona laboratories are accredited to meet general requirements according to ISO/IEC 17025:2000 for testing and calibration laboratories.

Our www.ticona.com website provides further information under “Company” > “Quality and Certifications”. This information includes the details of business lines and facilities covered and PDF files of all certificates of registration.

3. Properties

Fortron PPS is an advanced polymer that performs well in challenging environments. It provides high hardness, rigidity and dimensional stability, excellent thermal resistance, inherent flame-retardance, and low creep and moisture absorption, among many other benefits. Furthermore Fortron PPS shows an excellent media resistance.

The data in Table 3.1, which derive from standard test methods, form a basis for comparing different Fortron grades. While the data in the table is representative of typical values, components should be tested in use to ensure they meet the specifications.

The data listed in Table 3.1 shows an extract of the product portfolio. Further data is listed in the Short Term Property Guide.

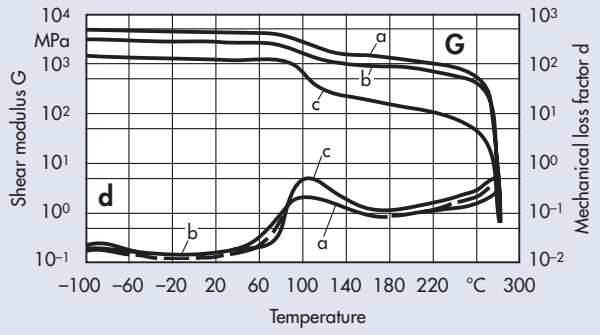
3.1. Physical properties

Grades in the Fortron PPS family have a density of from 1.35 to over 2.0 gm/cm3. Fortron PPS has minimal water absorption: just 0.01 to 0.02% after 24 hours of immersion at 23 °C. It also provides excellent dimensional stability in molding.

3.2 Mechanical properties

All plastic's mechanical properties change with temperature. Figure 3.1 illustrates how the shear modulus and mechanical loss factor of Fortron PPS vary at temperatures from – 100 to 300 °C. The inflections on the curves are indicative of the glass transition region at about 90 °C and the melting region at about 280 °C.

Fig. 3.1 · Shear modulus and mechanical loss factor as a function of temperature (ISO 6721-1,2)



a Fortron 6165A4
b Fortron 1140L4
c Fortron 0214C1

3.2.1 Properties under short-term stress

The behavior of materials under dynamic short-term stress, as measured by ISO 527-1, 2, determines tensile strength and strain at break. Figs. 3.2 and 3.3 show the stress-strain properties of Fortron 1140L4 and 6165A4 at five temperatures from -30 to 200 °C. Both the 40% glass reinforced Fortron 1140L4 and the 65% glass reinforced/mineral filled Fortron 6165A4 grades have similar responses below and above the glass transition region.

Other short-term stress properties include tensile modulus and flexural modulus as determined by ISO 527-1, 2 and ISO 178. These moduli indicate rigidity and so help in characterizing plastics and in calculating strength when designing molded parts. Tensile and flexural moduli in Fortron PPS decrease as temperature rises to about 80 °C and drop sharply between about 80 to 120 °C. Reinforced Fortron PPS has high tensile and flexural moduli (Fig. 3.4 and 3.5). Both moduli are higher for Fortron 6165A4, a 65% mineral filled blend, than for grades with 40% glass fibers.

3.2.2 Properties under long-term stress

Long-term testing provides design data for components that must withstand prolonged stress. Such testing involves two basic methods: the creep rupture test (ISO 899-1), which measures how deformation increases in a specimen under constant stress, and the stress relaxation test (DIN 53 441), which measures how stress decays in a specimen at constant strain.

The creep rupture test gives creep strength, or the time it takes a test specimen to rupture at a set tensile stress under defined environmental conditions, either in air or in another medium. The strain values and creep moduli it defines are good approximations for the values expected under flexural and compressive stress in actual use. This test involves a uniaxial stress and has limited applicability when multiaxial stresses are present.

Table 3.1 · Short-term properties for selected Fortron PPS products*

Physical	Test Method	1140L4	6165A4	0320	0214
Density, g/cm^3	ISO 1183	1650	1950	1350	1350
Mold shrinkage – parallel, %	ISO 294-4	0.2 – 0.6	0.2 – 0.6	1.2 to 1.5	1.2 to 1.5
Mold shrinkage – normal, %	ISO 294-4	0.4 – 0.6	0.3 – 0.7	1.5 to 1.8	1.5 to 1.8
Water absorption (23 °C-sat), %	ISO 62	<0.02	<0.02	<0.02	<0.02
Mechanical Properties					
Tensile modulus (1mm/min), MPa	ISO 527-2/1A	14700	19000		3800
Tensile stress at break (5mm/min), MPa	ISO 527-2/1A	195	130	90	90
Tensile strain at break (5mm/min), %	ISO 527-2/1A	1.9	1.2	8	3
Flexural modulus (23 °C), MPa	ISO 178	14500	18800	4200	3750
Flexural stress @ break, MPa	ISO 178	285	210	145	125
Charpy impact strength @ 23 °C, KJ/m^2	ISO 179/1eU	53	20		
Charpy impact strength @ 30 °C, KJ/m^2	ISO 179/1eU	53	20		
Charpy notched impact strength @ 23 °C,KJ/m^2	ISO 179/1eA	10	7		
Charpy notched impact strength @-30 °C, KJ/m^2	ISO 179/1eA	10	7		
Unnotched impact strength (Izod) @ 23 °C, KJ/m^2	ISO 180/1U	34	20	82	45
Notched impact strength (Izod) @ 23 °C, KJ/m^2	ISO 180/1A	10	6	2.6	3.5
Notched impact strength (Izod) @ 30 °C, KJ/m^2	ISO 180/1A	10	6	2.5	
Rockwell hardness, M-Scale	ISO 2039-2	100	100	90	95
Thermal Properties					
Melting temperature (10 C/min), °C	ISO 11357-1,-2,-3	280	280	280	280
Glass transition temperature (10 C/min), °C	ISO 11357-1,-2,-3	90	90	90	90
DTUL @ 1.8 MPa, °C	ISO 75-1, -2	270	270	115	110
DTUL @ 8.0 MPa, °C	ISO 75-1, -2	215	215	95	95
Coeff. of linear therm expansion (parallel), 10^{-4}/°C	ISO 11359-2	0.26	0.19	0.52	0.52
Coeff. of linear therm expansion (normal), 10^{-4}/°C	ISO 11359-2	0.62	0.24	0.53	0.53
Limiting oxygen index (LOI), %	ISO 4589	47	53		
Flammability / thickness tested (h), mm	UL94	V-0 / 0.38	V-0 / 0.75	V-0 / 3	
Electrical Properties					
Relative permittivity – 10KHz	IEC 60250	4	5.4	2.7	3.2
Dissipation factor – 10KHz, 10^{-4}	IEC 60250	2	10		
Dissipation factor – 1MHz, 10^{-4}	IEC 60250	62	20	11	
Volume resistivity, Ω · m	IEC 60093	>10^{13}	>10^{15}	10^9	10^9
Surface resistivity, Ω	IEC 60093	>10^{15}	>10^{15}		
Electric strength, KV/mm	IEC 60243-1	28	25	18	18
Comparative tracking index CTI	IEC 60112	125	175	125	125

* For more detailed information on the properties of Fortron PPS, see either the Ticona website, www.ticona.com, the Fortron PPS Short Term Properties brochure.

Fig. 3.2 · Stress/strain curves for Fortron 1140L4 at five temperatures

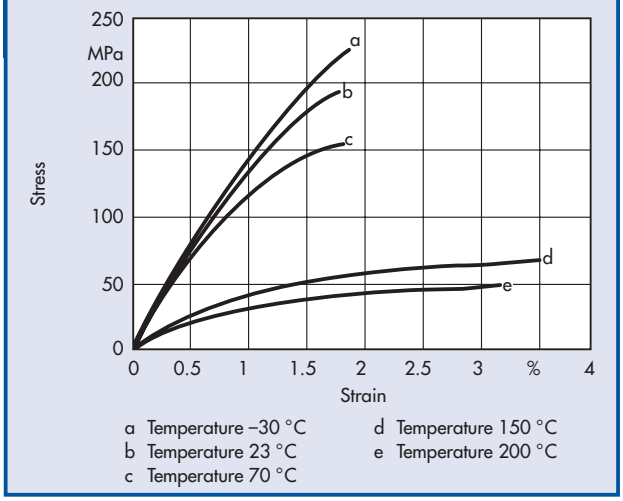


Fig. 3.3 · Stress/strain curves for Fortron 6165A4 at five temperatures

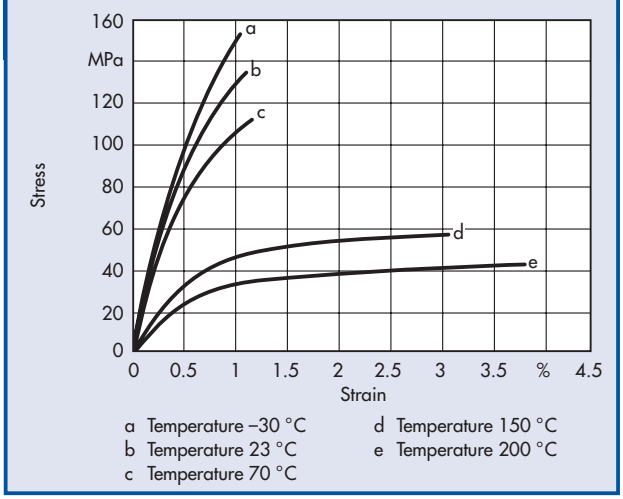


Fig. 3.4 · Tensile modulus for selected Fortron PPS grades

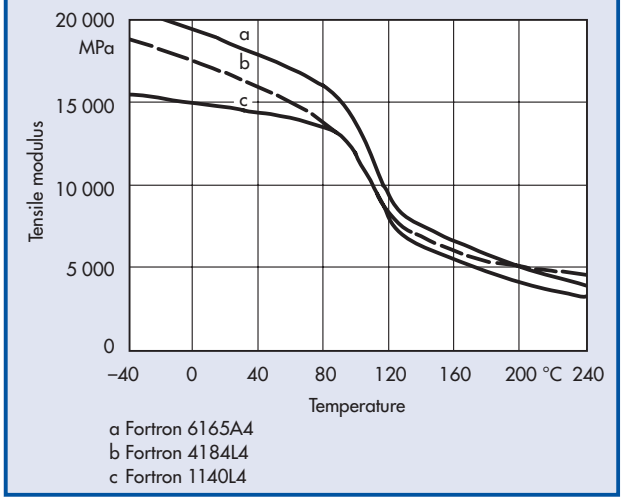
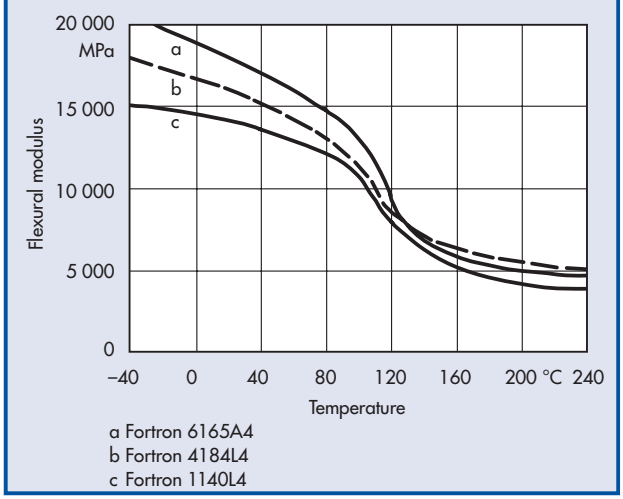


Fig. 3.5 · Flexural modulus for selected Fortron PPS grades

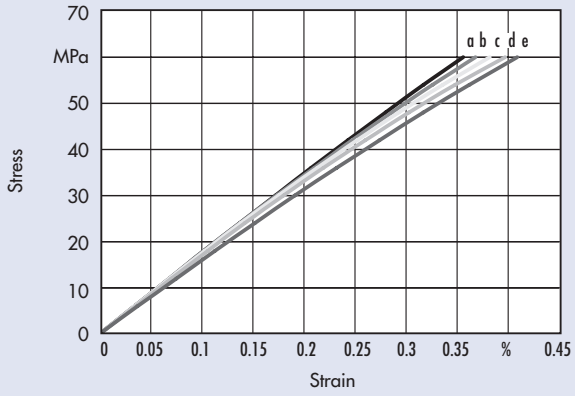


The deformation of a plastic component depends on time, temperature and type of stress. When deformation is relatively small, the variation between the characteristic values is negligible so a part's time-dependent compression under compressive stress can be calculated with sufficient accuracy using the flexural creep modulus (determined under flexural stress).

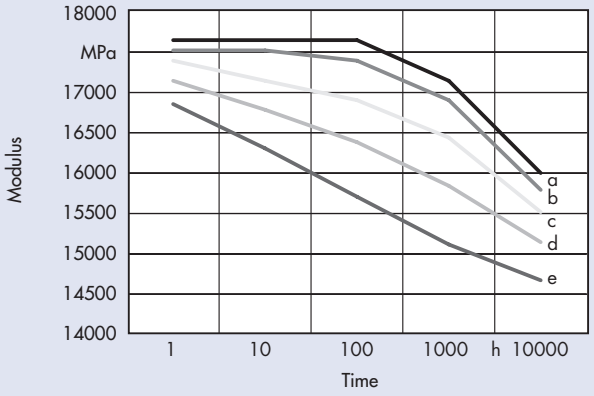
Creep rupture testing shows that reinforced Fortron PPS has little tendency to creep, as can be seen in Figures 3.6 to 3.8 for Fortron 1140L4. The tests were done under load for up to 1,000 hours and extrapolated to 10,000 hours. For a full set of creep-related curves for Fortron 1140L4 and 6165A6 at other temperatures, see the Ticona web site.

In addition to creep under tensile stress, a polymer's behavior under flexural stress is important when designing many structural components. Figs. 3.9 and 3.10 show the flexural creep modulus curves for Fortron 1140L4 and 6165A4 at 80, 120 and 200 °C. At temperatures above and below the glass transition temperature (T_g) of 80 °C and 120 °C respectively, the rates of decay of flexural creep modulus are similar, indicating that the material does not change in behavior appreciably above and below the T_g. Figure 3.10

Fig. 3.6 · Fortron 1140L4 (standard climatic conditions 23/50)

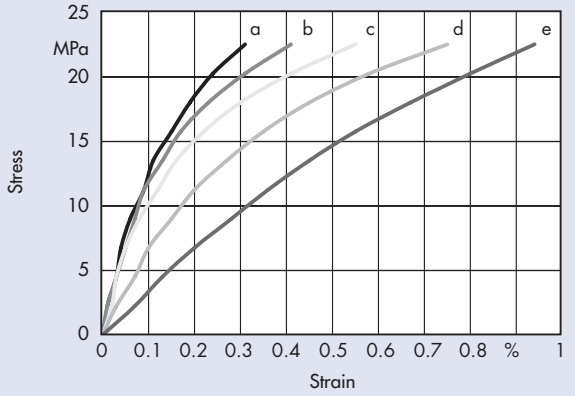


a = Time 1 h c = Time 100 h e = Time 10000 h
b = Time 10 h d = Time 1000 h

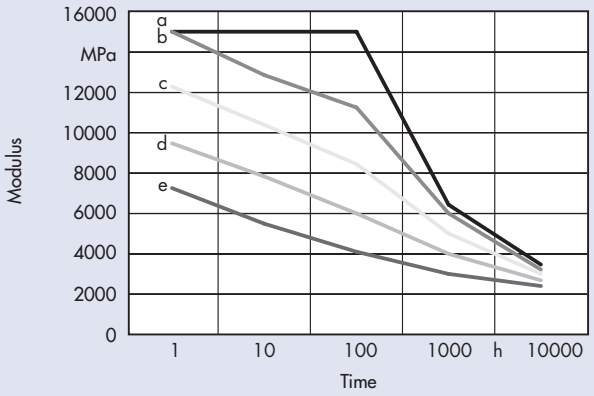


a = 12 b = 24 c = 36 d = 48 e = 60

Fig. 3.7 · Fortron 1140L4 (temperature of 120 °C)

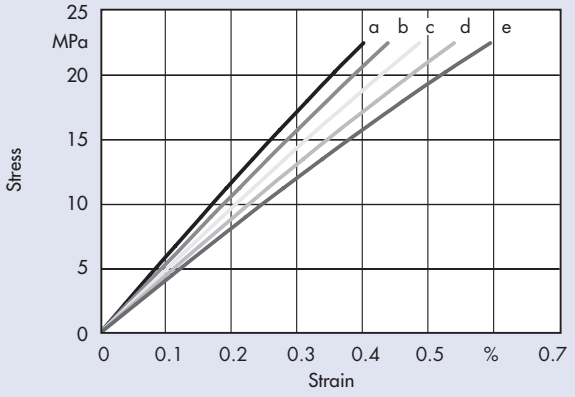


a = Time 1 h c = Time 100 h e = Time 10000 h
b = Time 10 h d = Time 1000 h

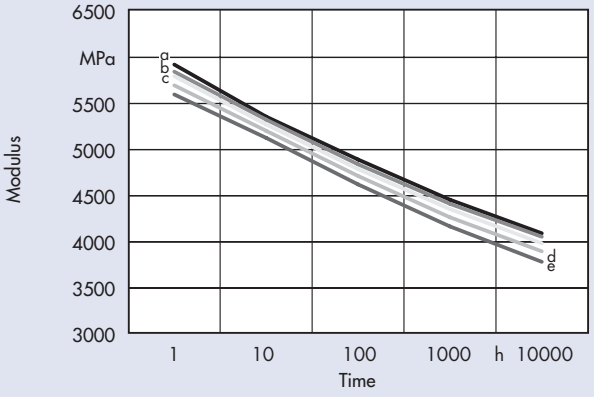


a = 4.5 b = 9 c = 13.5 d = 18 e = 22.5

Fig. 3.8 · Fortron 1140L4 (temperature of 200 °C)



a = Time 1 h c = Time 100 h e = Time 10000 h
b = Time 10 h d = Time 1000 h



a = 4.5 b = 9 c = 13.5 d = 18 e = 22.5

Fig. 3.9 · Flexural creep modulus for Fortron 1140L4 and 6165A4 at 80 and 120 °C (measured with an outer-fiber stress σ_b = 50 MPa)

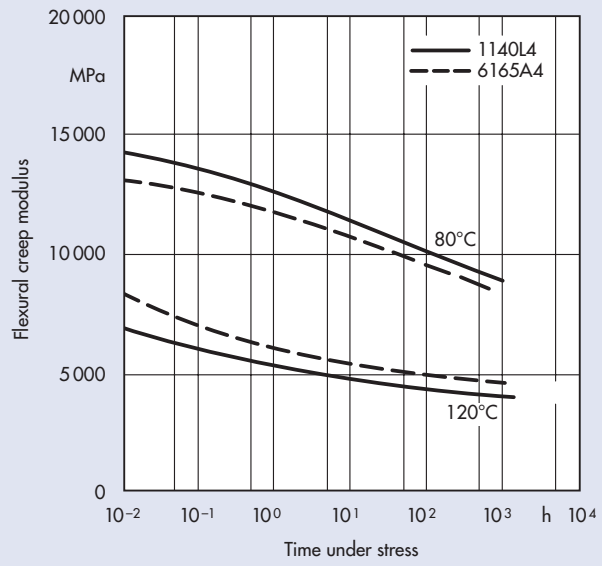
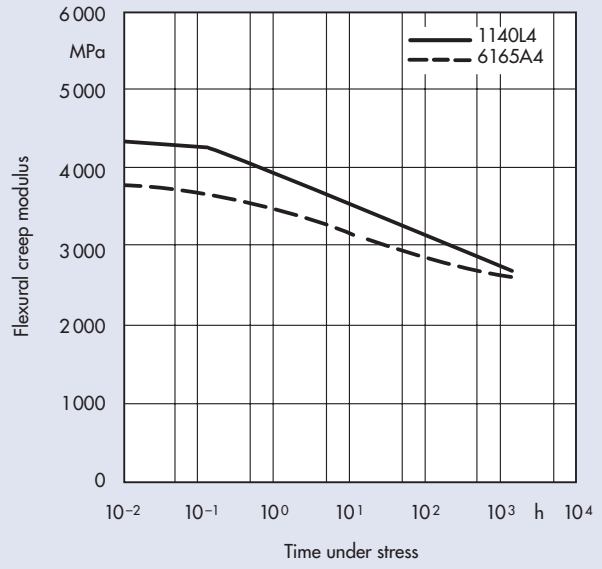


Fig. 3.10 · Flexural creep modulus for Fortron 1140L4 and 6165A4 at 200 °C (measured with an outer-fiber stress σ_b = 30 MPa)



shows a similar behavior even at a significantly higher temperature of 200 °C.

3.2.3 Fatigue

Fatigue strength is an essential parameter for parts subjected to periodic loading. It is defined as the stress amplitude, σ_a, that a specimen can withstand without failure for a set number of load cycles at a specified average stress, σ_m. The various stress ranges for such tests are shown in Fig. 3.11 as "Wöhler curves".

Fatigue strength for Fortron PPS at 10^7 load cycles is about 15% to 30% of its tensile strength. Fig. 3.12 and 3.13 show how Fortron 1140L4 and 6165A4 PPS behave in the fluctuating tensile stress range at 23 °C and 90 °C. Fatigue strength falls as temperature and load cycle frequency increase. Wöhler curves for fluctuating flexural stress for four Fortron grades are shown in Fig. 3.14.

Fig. 3.11 · Stress ranges in fatigue tests

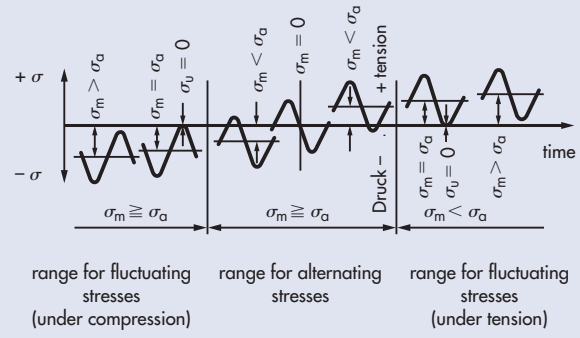


Fig. 3.12 · Wöhler curve for Fortron 1140L4 and 6165A4, determined in the fluctuating tensile stress range at 23 °C

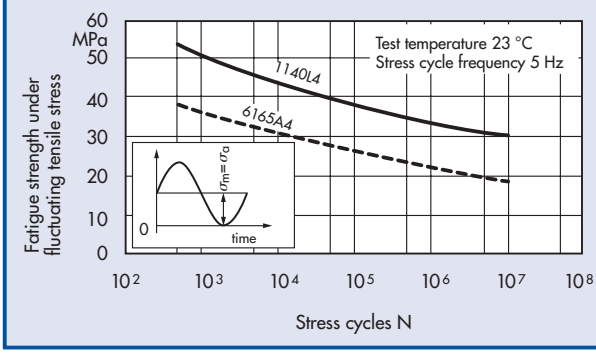


Fig. 3.13 · Wöhler curve for Fortron 1140L4 and 6165A4, determined in the fluctuating tensile stress range at 90 °C

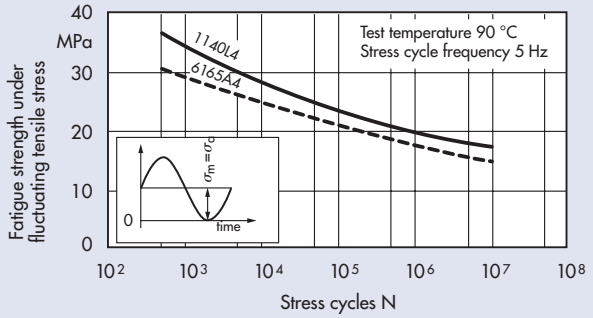
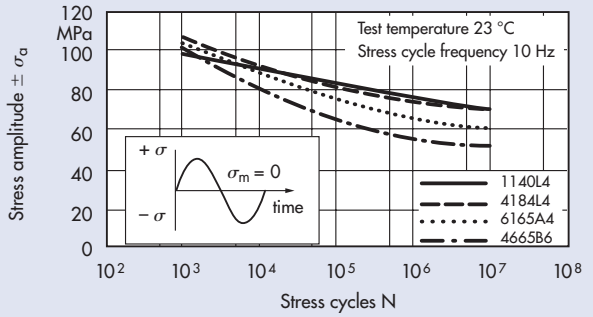


Fig. 3.14 · Wöhler curve for four Fortron grades in the fluctuation tensile stress range at 23 °C.



3.3 Thermal

Fortron PPS is used in high-temperature environments because of its exceptional thermal properties. The service temperature of Fortron PPS is up to 240°C. These grades have pronounced thermal transition ranges:

- Glass temperature, T_g : 85 – 95 °C
- Precrystallization temperature, T_{cc} : 120 – 130 °C
- Recrystallization temperature, T_{ch} : 220 – 255 °C
- Crystalline melting range, T_m : 275 – 285 °C
- Heat of Fusion About 112 J/g[1]

Such transitions are important in processing. For instance, in injection molding it is important to set mold wall temperature above T_{cc}.

3.3.1 Deflection temperature under load

Deflection temperature under load (DTUL), determined by ISO 75-1, 2 at test stresses A, B and C (A = 1.8 MPa, B = 0.45 MPa, C = 8.0 MPa), provides initial guidance as to the continuous service temperature a plastic can withstand. Figure 3.15 compares the DTUL for five Fortron PPS grades (at stress level A and C) with that of liquid crystal polymer, polyester and acetal copolymer.

Figure 3.15 · Deflection temperature under load for Fortron PPS and other resins

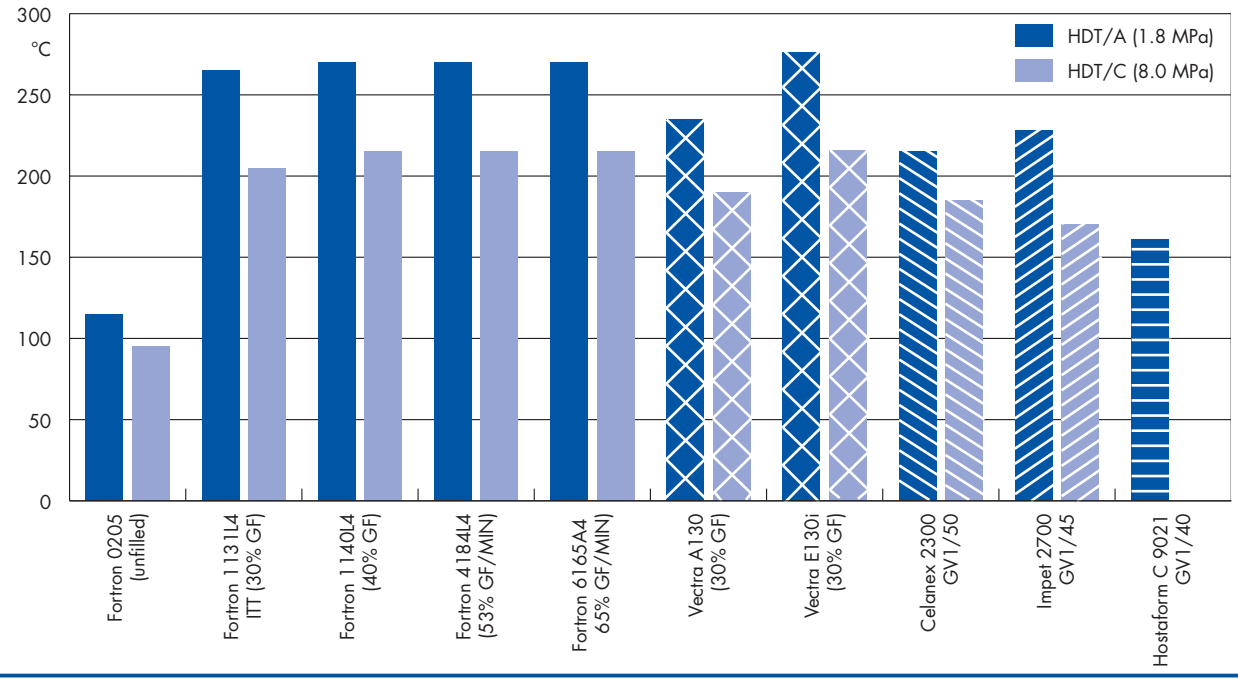
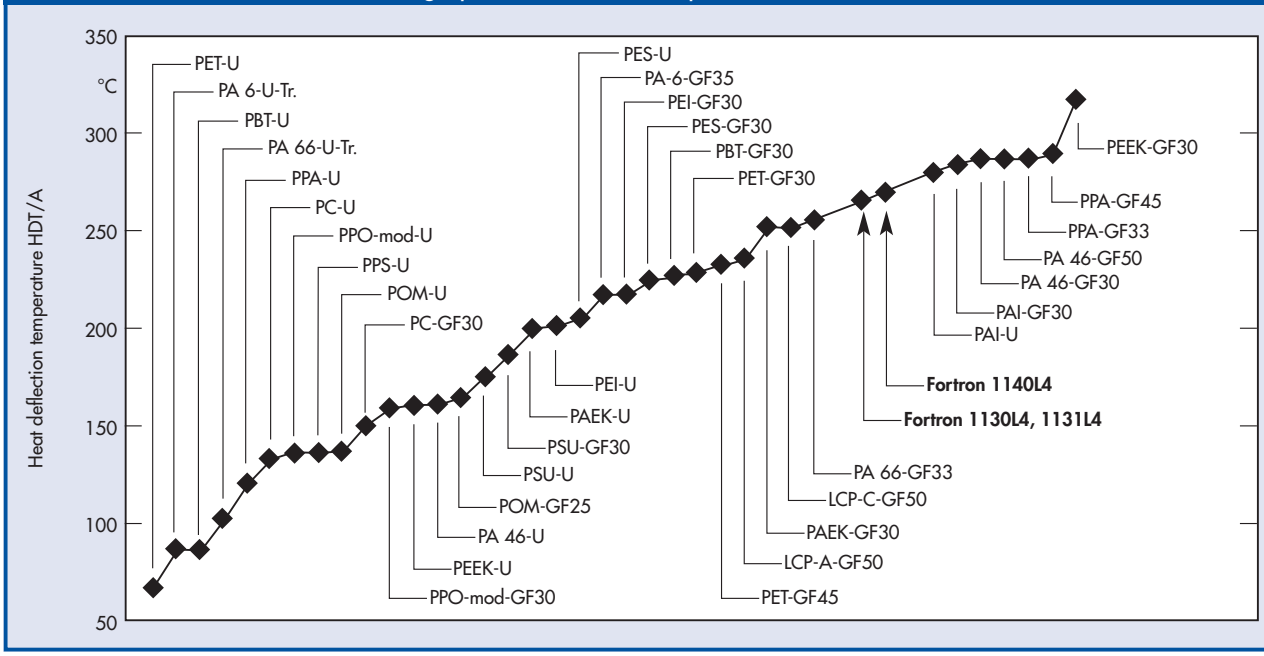


Fig. 3.16 · Comparison of deflection temperatures under load DTUL (1.8 MPa) of engineering and high-performance thermoplastics (ISO 75-1,2)[2]



Reinforcing Fortron PPS increases its DTUL into the region of its crystalline melting point. The DTULs of reinforced Fortron grades are 270 °C at 1.8 MPa and up to 220 °C at 8 MPa. These are some of the highest values attained by thermoplastics (Fig. 3.16).

3.3.2 Coefficient of linear thermal expansion

The coefficient of linear thermal expansion (ISO 11359) is different in the longitudinal and transverse directions. In the longitudinal direction, CLTE for different Fortron grades varies from about $12x10^{-6}$ 1/K to $17x10^{-6}$ 1/K between –50 and 90 °C and from $7x10^{-6}$ 1/K to $25x10^{-6}$ 1/K between 90 and 250 °C. In the transverse direction, CLTE for these grades varies from about $25x10^{-6}$ 1/K to $40x10^{-6}$ 1/K between 90 and 250°C. These values for the coefficient of linear thermal expansion are comparable with those of some metals.

3.3.3 Thermal conductivity

The thermal conductivity of Fortron PPS matches that of other partially crystalline polymers and remains nearly constant with temperature (Table 3.2).

Table 3.2 · Thermal conductivity [W/m · K]

Temperature [°C]	Fortron 1140L4	Fortron 6165A4
25	0.20	0.30
125	0.20	0.35
230	0.25	0.35
300	0.25	0.35

Fortron SKX-390 PPS, a special grade with a thermally conductivity of about 2.3 W/m · K. It can be used alone in injection molding applications or masterbatched with other Fortron grades to create intermediate thermal conductivities, e.g., a mixture of 50% Fortron SKX390 and 50% Fortron 1140L4, for instance, has a conductivity of about 1.3 W/m · K. The thermal conductivity is associated with an electrical conductivity, see also section 3.4.

3.3.4 Soldering resistance

Reinforced Fortron PPS grades are often used in surface mounted devices (SMD) attached to circuit boards and other components by vapor phase, infrared- or wave soldering. Fortron has excellent dimensional stability and a very low and predictable shrinkage at high soldering temperatures. Bowing or warping is minimized in an optimally molded part. Withstanding these higher temperatures can make lead-free soldering possible (RoHS and WEEE).

3.3.5 Flammability and combustion

Fortron PPS is inherently flame-retardant (it is rated at UL 94: V-0, with some grades rated at 5 VA) and needs no flame-retardant addition to pass UL-type flammability tests.

The limiting oxygen index (LOI) is the minimum percent of oxygen in air needed for a polymer to continue to burn after ignition without an additional source of energy. The LOI of Fortron ranges at about 50 %. Since the atmosphere contains about 21% oxygen, PPS does not sustain burning under normal conditions.

The hot wire test in IEC 60695 part 2-1 (for 1, 2 and 4 mm thicknesses) yielded a value of 960 °C in each case for five Fortron grades (1140L4, 4184L4, 4665B6, 6160B4 and 6165A4). In addition, Fortron 1140L4, 6165A4 and 4665B6 PPS were evaluated under the IEC 60335 glow wire test at 1, 2 and 3 mm thicknesses. In passing this test, flame duration lasted 24 seconds or less after heating ceased (at temperatures to 850 °C). In most cases, burning extended less than 3 mm into the samples.

The five grades used in the hot wire test above were also tested under the US Vehicle Safety Standard FMVSS 302. None of the grades flamed after a flame was applied for 15 seconds, so burning rate could not be specified. This indicated excellent resistance. In addition, Fortron 1140L4 natural meets the requirements of the building class B2 under DIN 4102, part 1 at wall thicknesses of 3 and 6 mm (testing followed DIN 50 050 part 1 (1/88) at application of flame to the edge).

Flammability testing following procedures defined in National Bureau of Standards, NFPA 258, found that smoke from smoldering Fortron would not obscure a typical room (Table 3.3).

Different Fortron PPS grades were tested according to the standards of the aircraft and rail vehicle construction industries.

Fortron 0214C1 and 1140L4 meet all the requirements of FAR 25.853 and ABD0031. FAR 25.853 is the legal specification for the aircraft industry. ABD0031 (Airbus standard) includes FAR 25.853 but, in addition to flammability and smoke density tests, also contains toxicity tests.

Table 3.3 · Fortron PPS Smoke Density*

	Fortron 1140L4		Fortron 6165A4	
Specimen – 1/8″ (3.2 mm)	Smoldering	Flaming	Smoldering	Flaming
Max. Value of Specific Optical Density** (DS)	12	95	10	44
DS, corrected	11	91	9	42
Spec. Opt. Density @ 1.5 minimum	0	1	0	0
Spec. Opt. Density @ 4.0 minimum	0	18	1	4
Obscuration Time*** (min) (Time to DS-16)	—	4.1	—	7.1

* Following procedures proposed by the National Bureau of Standards, NFPA 258. Tests conducted in an Aminco-NBS Smoke Density Chamber.
** Optical density measures the attenuation of a light beam by smoke that accumulates in a closed chamber as a material decomposes and/or combusts.
*** Obscuration time is the time it takes a typical room to reach a critical smoke density. At this density, an occupant's vision would be impaired by smoke and hinder his or her escape. The critical level of smoke density or specific optical density is 16.

Fire resistance for the rail vehicle construction industry was tested on Fortron 0214C1 according to DIN 5510. The test was passed. The smoke density and toxicity requirements according to DIN 5659 were also fulfilled.

3.4 Electrical

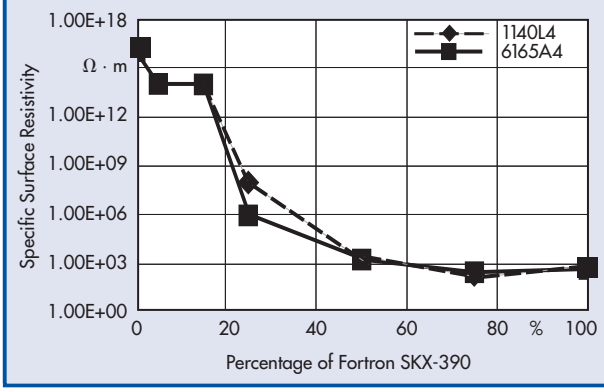
Fortron PPS is a high-purity material with very low levels of ionic impurities. It has good electrical insulating properties and a low dissipation factor, so it is a valued insulating material, especially at high temperatures.

3.4.1 Volume and surface resistivity

The volume resistivity of unfilled Fortron grades at 23 °C is > 10^9 Ω · m, and of reinforced Fortron grades is >10^{13} Ω · m (IEC 60093). These values diminish with increasing temperature. Surface resistivity, which indicates insulation resistance across a surface, depends on humidity and surface contamination. The surface resistivity of Forton is normally > 10^{15} Ω (IEC 60093).

Fortron SKX-390 is a special electrically conductive grade having a volume resistivity of 400 and a surface resistivity of 500 Ohm. This grade also has improved thermal conductivity. The volume- and surface resistivity is measured in accordance to IEC 60093. This grade can be blended with other Fortron resins to tailor volume resistivity to a specific range (Fig. 3.17).

Fig. 3.17 · Surface Resistivity of Fortron SKX-390 PPS Blends



3.4.2 Relative permittivity and dissipation factor

Fortron PPS has a relative permittivity of 4.0 to 5.4 at 10 kHz and 4.1 to 5.6 at 1 MHz (Fig. 3.18). This factor increases slightly with increasing temperature.

Fig. 3.18 · Relative Permittivity of Selected Fortron Grades

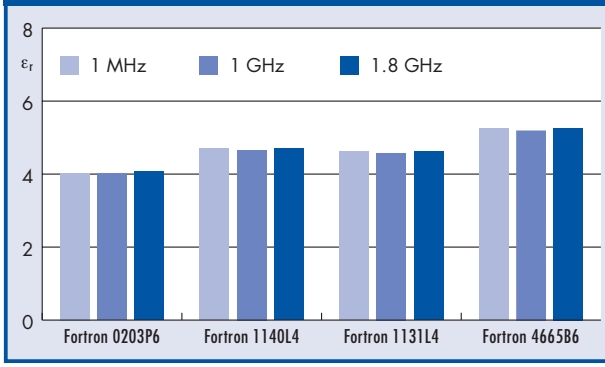
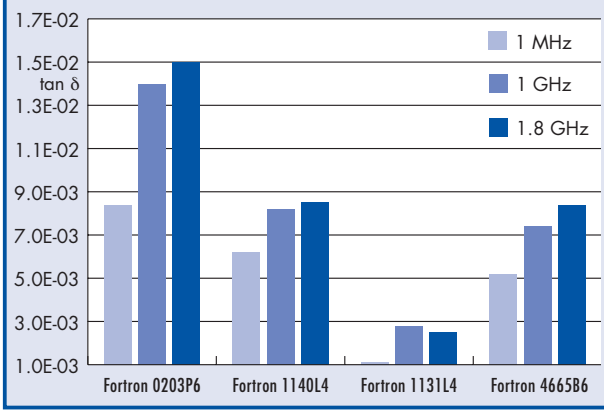


Fig. 3.19 · Dissipation Factors for Selected Fortron Grades



Dissipation factor, tan δ, is a measure of the energy loss in a dielectric material by conversion into heat. The values for Fortron PPS range from 0.2 to 1.0 · 10^{-3} at 10 kHz and from 1.0 to 2.0 · 10^{-3} at 1 MHz (Fig. 3.19). This factor depends on frequency and temperature.

3.4.3 Electric strength

Electric strength describes behavior under short-term, high-voltage stress and should not be used for continuous stress conditions. In electric strength tests, the voltage (at a frequency of 50 Hz) is steadily increased at a rate of 1 kV/s until insulation breakdown occurs (IEC 60243-1). Fortron PPS has electric strength values of 25 to 28 kV/mm.

3.5 Surface properties

3.5.1 Hardness

Fortron PPS is a hard material that has ball indentation hardness values (ISO 2039 Part 1) of 190 for unreinforced grades and from about 320 to 460 for filled and reinforced grades. Its Rockwell hardness (ASTM D 785) is 93 for unreinforced pellet grades and 100 for both Fortron 1140L4 and 6165A4.

3.5.2 Sliding and abrasion properties

UTI tests (see fig. 3.20) of the coefficient of dynamic friction between various Fortron grades and steel at 23 °C and a fairly high surface pressure gave an average value of 0.4. Sliding properties must be considered in the context of tribological systems, so coefficient of friction depends on the sliding partner, surface pressure, sliding speed and the measuring equipment.

Testing under simulated service conditions should be done when designing any part subject to abrasion. Fortron grades with improved sliding and abrasion properties are 6341L4, 1324L4, 6345L4 and 6450A6.

Method: UTI-Test (dynamic frication and wear test)

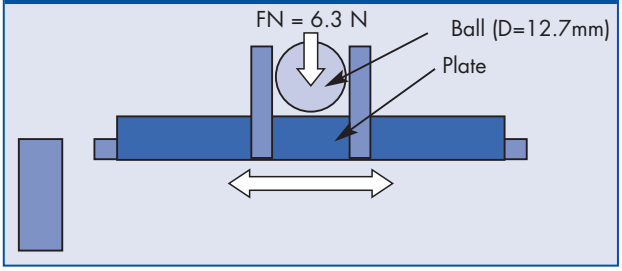
Speed:	10 mm/s
Distance:	5 mm
Frequency:	1 Hz
Test-Cycle:	8 hours per test sample
Number of samples:	5 per material

Table 3.4 · Friction and Wear for Fortron PPS on Steel

Steel Ball	Fortron PPS Plate	Coef. of Friction	Ball Wear*	Plate Wear*
100 Cr6	6165A6	0.5	(1)**	10
100 Cr6	1140L4	0.6	41***	90***
100 Cr6	1342L4	0.3	0.2	4
100 Cr6	4184L4	0.5	(1)**	6
Fortron PPS Ball	**Fortron PPS Plate**			
6165A6	6165A4	0.3	22	71
1140L4	6165A4	0.4***	133***	59***
1342L4	6165A4	0.3***	41	15
4184L4	6165A4	0.4	4	79***

* Measured as mm^2 · 10^{-3}
** Grinding not measurable
*** These values had a higher variation

Fig. 3.20 · UTI Testing Method



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1. Cebe, P, Polymer and Polymeric Materials, 1995.
2. Modern Plastsics Encyclopedia '95, Mid-November 1994 Issue (71) 12, New York, p. B-150.

4. Environmental resistance

4.1 Thermal resistance

Fortron PPS has great resistance to thermal oxidation, so parts made from it withstand high thermal stress. The service environment affects the course of heat aging, so terms such as heat resistance and continuous use temperature should be considered in the context of particular requirements. Experience shows that Fortron PPS generally withstands service temperatures as much as 240 °C for periods of years.

Figures 4.1 and 4.2 show the change in tensile strength and elongation of Fortron 1140L4 in hot air as a function of time[1]. The specimens were not subject to mechanical load during the evaluation.

Fig. 4.1 · Heat Aging Test – tensile strength of Fortron 1140L4 black

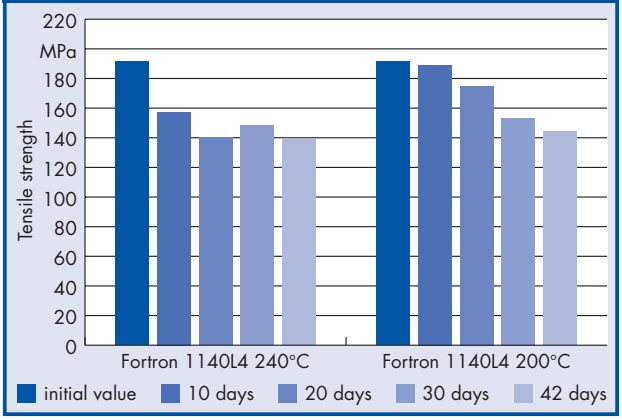
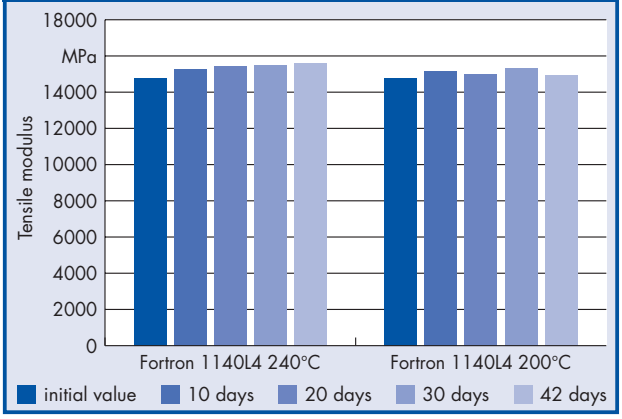


Fig. 4.2 · Heat Aging Test – tensile modulus of Fortron 1140L4 black



4.2 Moisture resistance

Fortron PPS is not hygroscopic. It absorbs just 0.02% water after immersion in water at 23 °C for 24 hours (ASTM Method D-570). This is far less than occurs in many other polymers. Opposite to e.g. polyamides it does not expand when exposed to water. It releases the absorbed moisture when stored in dry air. Absorbed atmospheric moisture causes no molecular degradation.

Fortron PPS has excellent resistance to hydrolysis. It undergoes little or no change in tensile strength and elongation when exposed to 95°C water for over 1,000 hours at 15 psi. Glass-fiber-reinforced grades lose some mechanical properties after immersion in 95 °C water after several months. As with many glass-fiber-reinforced plastics, this occurs through chemical attack on the glass fibers and by capillary action at the glass fiber-polymer interfaces[2].

4.3 Chemical resistance

Fortron PPS has superb chemical resistance. It does not dissolve in any known organic solvent below 200 °C and is virtually unaffected by acids, bases, alcohols, oxidizing bleaches and many other chemicals at elevated temperatures for extended times[2]. Its mechanical properties do decline, however, when exposed to concentrated nitric and other oxidizing acids.

It has excellent resistance to all liquid and gaseous fuels, including methanol and ethanol, and withstands hot engine oils, greases, antifreeze and other automotive fluids. It is especially useful in fuel applications because of its stability during prolonged contact with gasoline formulations having various octane, sulfur, oxygenate and contaminant levels.

A 5000 hour/121 °C fuel immersion study comparing how commonly used fuel system plastics age when exposed to various gasoline blends (as defined in the SAE1681 protocol) confirmed that Fortron 1140L4 had the least weight and dimensional change and the highest tensile strength retention compared to nylon 6/6, high temperature nylon (HTN) and polyphthalamide (PPA). This was especially true with the more aggressive fuels.

In fuel CAP*, for example, nylon 6/6 had the greatest initial weight gain and then dropped to 3.5% by 5,000 hr. (Fig. 4.3). Both PPA and HTN had a similar pattern and ended the study with a 3% and 5% loss, respectively. Only Fortron PPS held steady at between a 3.0% and 3.5% increase after an initial weight gain.

In fuel CM15A*, nylon 6/6 again had the greatest weight gain (Fig. 4.4). Other resins rose initially and held steady, with PPS showing the least gain. HTN and nylon 6/6 had the greatest dimensional change at first, but fell off late in the study. PPA and Fortron PPS remained steady after an initial rise. Fortron PPS

Fig. 4.3 · Weight Change – Fuel CAP* (121 °C)

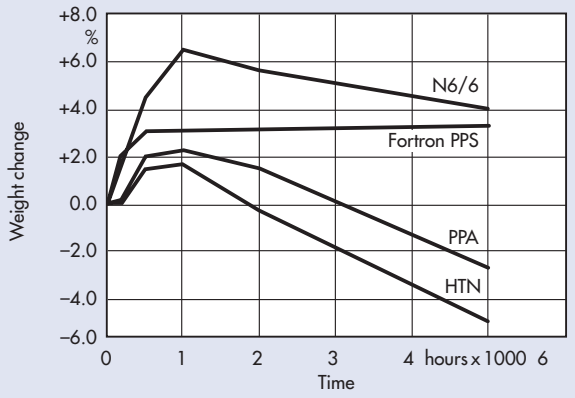
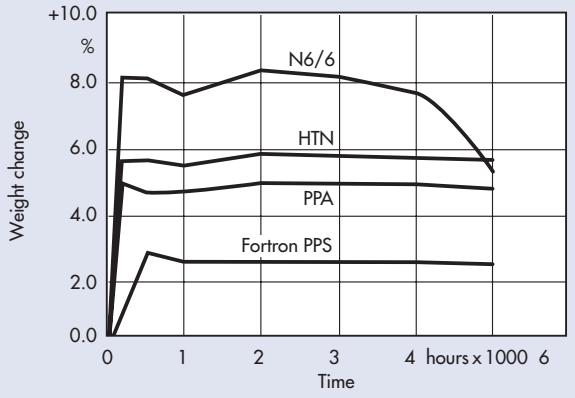


Fig. 4.4 · Weight Change – Fuel CM15A* (121 °C)



* Fuel CAP contains Fuel C (50% isooctane and toluene), aggressive water and peroxide (sour gas). Fuel CM15A contains 85% Fuel C, 15% methanol and aggressive water.

Table 4.1 · Change in the mechanical properties of Fortron PPS after UV exposure in an Atlas Weather-O-meter*

	Tensile test according to ASTM D 638				ASTM D 256
Fortron Grade	**Exposure time [hours]**	**Tensile strength [MPa]**	**Strain at break [%]**	**Tensile modulus [MPa]**	**Notched impact strength (Izod) [J/m]**
1140L4 natural	0	181	1.7	15200	85
	200	181	1.7	15200	85
	500	179	1.6	15200	85
	1000	177	1.7	14500	85
	2000	176	1.6	14500	85
1140L4 black	0	176	1.7	13800	80
	200	176	1.7	14500	75
	500	178	1.6	15200	80
	1000	176	1.7	14500	80
	2000	175	1.6	15200	80

* The tests used injection molded specimens according to ASTM G 23, Method 3, without water spray. It also involved a black standard temperature of 60 °C and a radiation intensity of 0.35 $W/m^2 \cdot nm$ at a 30% relative humidity under a xenon arc lamp according to ASTM G 26. Mechanical properties were tested according to ASTM standards. None of the test specimen showed signs of erosion.

retained 80% of its initial tensile strength by the end of the study, while the other materials had fallen to between 30% and 40% of their original values.

4.4 UV resistance

Fortron PPS has good resistance to ultraviolet radiation. Laboratory Weather-O-meter trials on unpigmented and pigmented injection molded specimens show little change in tensile strength, notched impact strength and other mechanical properties after 2,000 hours of exposure (Table 4.1).

4.5 Permeability

Fortron PPS is relatively impermeable to gases and to fuels and other liquids compared to other materials (Fig. 4.5 and 4.6). Permeation is lowest with unfilled Fortron PPS grades. The combination of low permeability and high chemical resistance makes Fortron PPS an excellent candidate for many automotive, industrial, chemical, petroleum and aircraft applications, and where a high gas barrier is needed for medical and packaging uses.

Fig. 4.5 · Comparative permeability coefficients

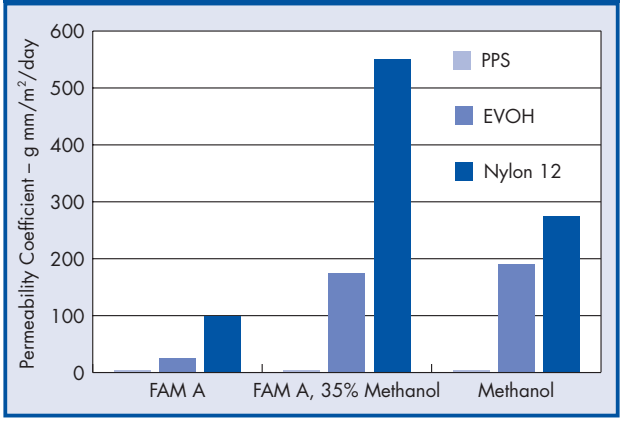
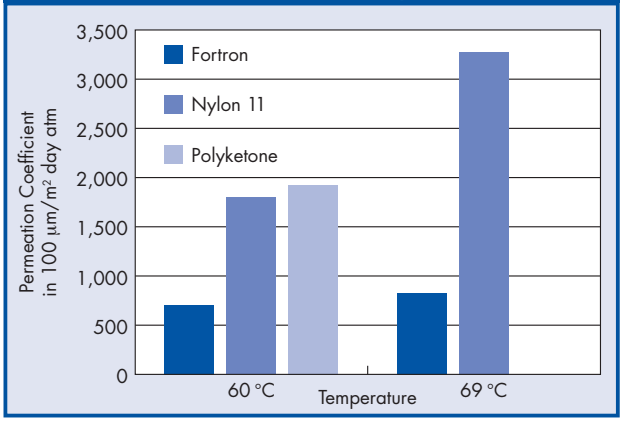


Fig. 4.6
CO_2-Permeability



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1. Kohlhepp, K., "High-Performance Plastic for Difficult Components," Kunststoffe plast Europe, vol. 85, no 8 (German version: Kunststoffe 85 (1995) 8, p. 1095 – 1100)
2. Fortron Chemical Resistance Guide Version 3.0, www.ticona.com

5. Specifications and standards

Fortron PPS has become a proven material in many industries that have specialized requirements, from potable water and automotive to healthcare and food. Over the years, it has been certified under a great many specifications and standards that apply to these applications.

5.1 Automotive specifications

Fortron PPS is marketed internationally and must therefore comply with all the relevant automotive industry specifications applying to mechanical, electrical, thermal and other properties as well as flammability. Typical examples of automotive industry specifications that Fortron PPS meets include:

- The globally applicable Ford ISO specifications:
  - WSL-M4D 807-A for Fortron 1140L4 and 1140L6
  - WSF-M4D 803-A2 for Fortron 6165A4 and 6165A6

- Chrysler: MS-DB 570 CPN No. 3502 for Fortron 1140L4, 4184L4 and 6165A4

- General Motors:
  - GMP.PPS.001 for Fortron 1140L4 and 1140L6
  - GMP.PPS.002 for Fortron 6165A4 and 6165A6
  - GMP.PPS.004 for Fortron 4184L4 and 4184L6

Fortron products are contained in the IMDS (International Material Data System), the materials database set up by the automotive industry. This internet-based system (www.mdsystem.com) provides the automotive industry and its partners with information on the constituents of the materials used in order to facilitate recycling of end-of-life vehicles.

In addition, our products comply with the GADSL (Global Automotive Declarable Substance List), which replaces the individual standards of automotive manufacturers. It can be accessed via the following link: http://www.gadsl.org.

5.2 Drinking water approvals

Fortron® PPS grades and color masterbatches based on Fortron are generally suitable for use in the drinking water sector. Each country has its own approval procedure but they are all based on the same principle: the end customer sends his product to the testing institute, which then – on request – obtains the relevant formulation from the material manufacturer (e.g. Ticona) and conducts the test. Finally, the end customer is informed about the successful result of the test and receives a corresponding test certificate from the testing institute.

In some countries, Ticona has successfully conducted the relevant tests for standard grades on test specimens to give end customers the best possible assurance that their products will also pass the official approval test. However, the possession of such a "material test certificate" does not exempt end customers from having their end products tested by a testing institute.

The most important approval application procedures in EU countries (UK, F, D, NL) and the USA differ in some details, which need to be taken into account in the material approval tests.

UK – WRAS (Water Regulations Advisory Scheme)

Under the UK WRAS regulations, all materials must be listed before an end product approval test can be carried out: various Fortron® PPS grades are listed and "pretested" for contact with drinking water up to a temperature of 85°C – these can be viewed on the WRAS website: http://www.wras.co.uk/.

D – KTW (Kunststoffe im Trinkwasserbereich) Regulations on Plastics in the Drinking Water Sector

In Germany, the Fortron grade 1140L4 black successfully passed the KTW tests, which were carried out on test plaques. The plaques were tested in cold water and in hot water at 90°C. The KTW certificate we received for these tests is available on request.

F – ACS (Attestation Conformité Sanitaire) Sanitary Conformity Certificate

The Fortron® PPS grades 1140L4 and 1140L6 PPS are currently being tested in the form of plaques for compliance with the French ACS requirements.

In the case of glass-fiber-reinforced plastics, the relevant glass fibers must be on the French positive list for glass fibers before the end product can be tested; the fiber used in glass-fiber-reinforced Fortron® PPS grades is listed.

USA – NSF (National Sanitary Foundation)

In the USA, the Fortron® PPS grades 1140L4 and 1140L6 PPS have been successfully tested in accordance with the requirements of NSF Standard 61 and are therefore suitable for applications involving contact with drinking water.

Important: the drinking water regulations cover products used in the drinking water supply system, which extends from the public reservoir, through the pipeline system and domestic installations to the end of the faucet. Once the water has left this system, products that come into contact with it as consumer articles are exclusively subject to the FDA food-contact regulations (see section 5.3).

5.3 Products for food-contact applications/ consumer articles

In the EU, the requirement for using plastics in contact with food is that the material components must be registered on a positive list in the German Regulations on Food-contact Articles (Bedarfsgegenständeverordnung) or corresponding national regulations, such as the recommendations by the BfR (Bundesinstitut für Risikobewertung = Federal Institute for Risk Assessment, previously known as the BgVV and BGA).

The monomers and other starting components used in the manufacture of the Fortron grade 1140L4 are listed in EU Directive 2002/72/EC and its 3 amendments 2004/1/EC, 2004/19/EC, 2005/79/EC. These EU lists are transposed into German national law in the German Regulations on Food-contact Articles (Bedarfsgegenständeverordnung) of December 23, 1997 (most recently amended on July 13, 2005).

If individual substances registered on the positive list are subject to specific restrictions, then the finished part must be tested for compliance with such specific restrictions by the manufacturer or vendor. If the plastic consists of listed substances that are not subject to any specific restrictions, then the finished part must be test for compliance with global migration limits in accordance with the EU Migration Directive (82/711/EEC).

In the case of Fortron® PPS polymers, a restriction applies to 1,4-dichlorobenzene: SML = 12 mg/kg food product.

In the USA, the requirement for “repeated use” in contact with food is met through Food Contact Substance Notification (FCN) No. 40 “Polyphenylene sulfide polymers (CAS Reg. No. 25212-74-2 or 26125-40-6)” submitted to the US Food and Drug Administration (FDA) (see also: http://www.cfsan.fda.gov).

5.4 Products for medical and pharmaceutical applications

The Fortron PPS MT 9000 series is the first PPS line certified for medical, pharmaceutical and repeated-use food contact applications. The grades in this line comply with US Pharmacopeia Class VI, International Standards Organization 10993, and U.S. Food and Drug Administration (FDA) Food Contact Substance Notification No. 40. FDA Drug and Device Master Files are also available for specific requirements. The series contains unreinforced grades for extruding tubing, profiles and filaments, as well as reinforced grades for injection molding.

6. General processing considerations

Although Fortron PPS is traditionally seen as an injection molding material, many other processes are commonly used to convert it into useful products. These processes include extrusion for film, profile, pipe, filaments and fibers, as well as blow molding, thermoforming and composites. Sections 7, 8, 9 and 10 look in some detail at specific processing areas. This section considers general topics that apply to all processing methods.

6.1 Safety

Fortron PPS is a relatively inert material that poses relatively few safety issues in the processing environment so long as a few simple steps are taken regarding the maximum melt temperature and ventilation.

6.1.1 Thermal stress

Fortron PPS melts should not exceed 370 °C (taking into account permissible extruder barrel residence times). Excessive thermal stress will degrade it and generate gases, including various sulfide compounds. If thermal degradation in the barrel is suspected or established, pump the charge out and quench in water to minimize unpleasant odors. Refer to the Material Safety Data Sheet for additional detail regarding safe handling and processing.

6.1.2 Odors in processing

Although odors may occur when processing PPS, these odor species do not pose a health hazard. Odors can occur in processing PPS under certain conditions due to the presence of residual, low-molecular-weight organic species, including various sulfide compounds. When off-gassing by Fortron PPS during processing was measured by personal industrial hygiene monitors, the levels of the organic gases found were consistently below the detectable limits of the analytical methods used and significantly below the regulatory and/or recommended exposure limit.

Even so, when using PPS in injection molding, extrusion and other processes, adequate local ventilation is recommended. See the Material Safety Data Sheet for additional safety and health information.

6.1.3 Fire precautions

Even though Fortron PPS is inherently flame-retardant, processors should take necessary fire prevention measures when storing, processing or fabricating the material, especially those defined by regulations in specific countries. Some end products and fields of application may be subject to special fire prevention requirements. It is the responsibility of the raw material processor to ascertain and observe such requirements. Again, Material Safety Data Sheets for the individual Fortron grades are available.

6.2 Start up and shut down

During start-up, processing equipment should stabilize for 30 minutes at the temperatures recommended. In injection molding, for instance, a machine should be purged with an appropriate material (see section 6.4) and then PPS should be fed until it is the only material exiting the die or nozzle. Check the melt temperature with a pyrometer to ensure that the melt is within the recommended temperature range. When a machine that had used Fortron PPS is shut down, hold it at operating temperature until it is purged with an appropriate material.

6.3 Drying considerations

Although Fortron PPS is not hygroscopic and degradation due to moisture is unlikely, dry resin should be used in molding because high moisture levels can create voids and intrusive streaks near the gate that can affect part performance and aesthetics. Unfilled grades (see Table 2.1) should be dried at 120 °C for 1-2 hours, reinforced grades (Table 2.2) at 140 °C > 4 hours. Some specialty grades may need milder conditions. Fortron PPS should be dried in dehumidifying hopper dryers.

6.4 Purging

6.4.1 Changing from another thermoplastic to Fortron PPS

Many plastics are unstable at PPS processing temperatures and should be removed from the machine before molding with Fortron PPS. Suitable purging materials include high density polyethylene (HDPE), polyamide (PA) and cross-linked polymethyl methacrylate (PMMA). Such materials are ejected at the appropriate melt temperatures in rapid shot sequence with the cylinder disconnected from the mold.

As soon as the previous material is expelled completely, cylinder temperatures are brought to the settings recommended for Fortron PPS. Fortron is then fed into the molding machine until the purging material is expelled. Molding can begin when the purging material is fully removed.

6.4.2 Changing from Fortron to another thermoplastic

As soon as the melt is free of all traces of the PPS, cylinder temperatures should be reduced to a level suitable for the purging material as the melt continues to flow out of the nozzle into the open ('air-shot'). Purging is complete when the required temperatures are reached.

7. Injection molding

Fortron PPS is injection molded in conventional screw injection molding machines. Although it absorbs little moisture, it should be predried before being fed to the machine (see Section 6.3).

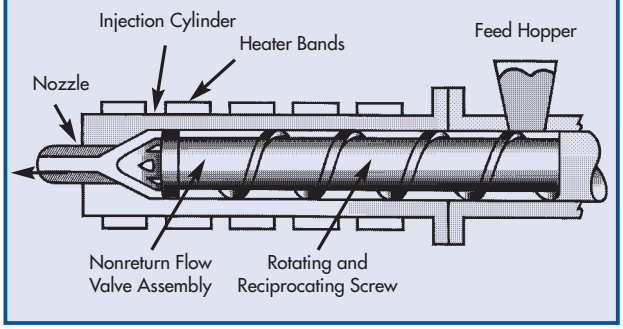
Mold temperature should be controlled precisely to create parts that remain dimensionally stable at high heat. A measured mold temperature of min. 140 °C is needed so the PPS crystallizes. When a part that was not fully crystallized during processing is placed in service above the original mold temperature, it will crystallize and shrunk (see section 11.1). Molds processed with mold temperatures < 140°C may create rough surfaces. In cold-molded parts, filler can appear on the surface and be attacked by chemicals.

7.1 Equipment considerations

The process is crucial in producing high-quality parts, so it is essential to understand the molding process and equipment used. Figure 7.1 shows the basic parts of a single-stage, reciprocating screw injection molding machine.

Clamping force keeps the mold closed and is developed by either a toggle mechanism or a hydraulic cylinder. With Fortron PPS, this force in a typical molding machine should be between 5 and 6 kN/cm² of projected area (including the runner).

Figure 7.1 · Molding machine schematic



7.2 Mold design

7.2.1 Tool, screw, and barrel materials

Given the abrasive nature of glass and mineral fillers, molds, screws and barrel liners used with filled Fortron grades must be made of the appropriate steels. For experimental molds or those for production short-runs (less than 50,000 molding cycles), the steels listed in Table 7.1 are sufficient. Molds for higher production volumes need steels having a having a hardness > 56 HRc (Table 7.2) to ensure long cavity life and tight tolerances. Screws made of PM steels or hard metal steels and cylinders made of Bimetals are common. Improper combinations of screw and barrel materials can lead to premature wear, so molding machine

Table 7.1 · Tool Steels for Use with Fortron PPS (less than 50,000 injection molding cycles)

Type of Steel	Designation in accord with DIN 17 006	Material Nr.	Surface hardness (HRc)	Comments
Case-Hardening Steels	X 6CrMo4	1.2341	55	Not corrosion resistant
	21 MnCr5	1.2162	55	low dimensional stability
Through-Hardening Steels	X 210Cr 12	1.2080*	54	Not corrosion resistant
	X 38CrMoV 51	1.2343*	53	very good dimensional stability
	X 40CrMoV 51	1.2344*	55	high compressive strength
	X 45NiCrMo4	1.2767*	42	
	90 MnCrV 8	1.2842	43	
Corrosion-Resistance Steels	X 42CrMO 13	1.2083	51	Still inadequate corrosion
	X 36CrMo 17	1.2316	46	resistance and hardness

* Steel also available as electroslag remelting process grades with a more homogeneous structure and higher corrosion and wear resistance.

Table 7.2 · Tool Steels for Use with Fortron PPS (greater than 50,000 injection molding cycles)

Type of Steel	Designation in accord with DIN 17 006 or trade name	Material Nr.	Surface hardness (HRc)	Comments
Through-Hardening Steels	X 155CrVMo 121	1.2379	58	Polishable, not corrosion resistant
	Böhler "M 340"	—	>56	Additional corrosion resistance
Maraging Steels (PM steels group)	Uddeholm "Elmax"	—	57	Highly wear and corrosion resistant
	Böhler "K 190"	—	60-63	Highly wear and corrosion resistant
	Böhler "M 390"	—	56-62	Highly wear and corrosion resistant
	Zapp CPM T420V	—	57	Very easily polishable
	Zapp CPM 3 V	—	57-63	Additional toughness, not corrosion resistant
	Zapp CPM 9 V	—	57-67	Additional toughness, not corrosion resistant
Hard Metal Alloys	Ferro-Titanit S	—	66-70	Extremely high wear and corrosion resistance
	WST "G25"	—	64-66	Extremely high wear and corrosion resistance

suppliers should be consulted on which materials to use together. Molds containing surface steels at or below 56 HRc-hardness can be further protected against wear through hard-facing methods. In such methods, treatment temperature should never reach the annealing temperature of the steel. Facing materials can also be used. Chromium-containing facing materials (e.g., chromium nitride) offer better wear protection than titanium nitride. Highly wear-resistant, corrosion-resistant refractory hard metal alloys such as "Ferro-Titanit S" can be used for inserts in the gate region where shear is high and greater wear occurs.

7.2.2 Draft

Fortron PPS has relatively high rigidity and low elongation, so draft is needed to aid part removal. Guidelines for proper draft include:

– Consider drafts of ≥ 1° in part areas perpendicular to the parting line.

– Drafts of less than 1° are possible for narrow parts having short ejection paths and mold surfaces have a high-gloss brushed finish in the ejection direction. Use of small draft angles in other situations may require ejection pins to aid ejection.

– On grained mold surfaces, add a draft of 1° or more for each 0.01 mm of grain depth.

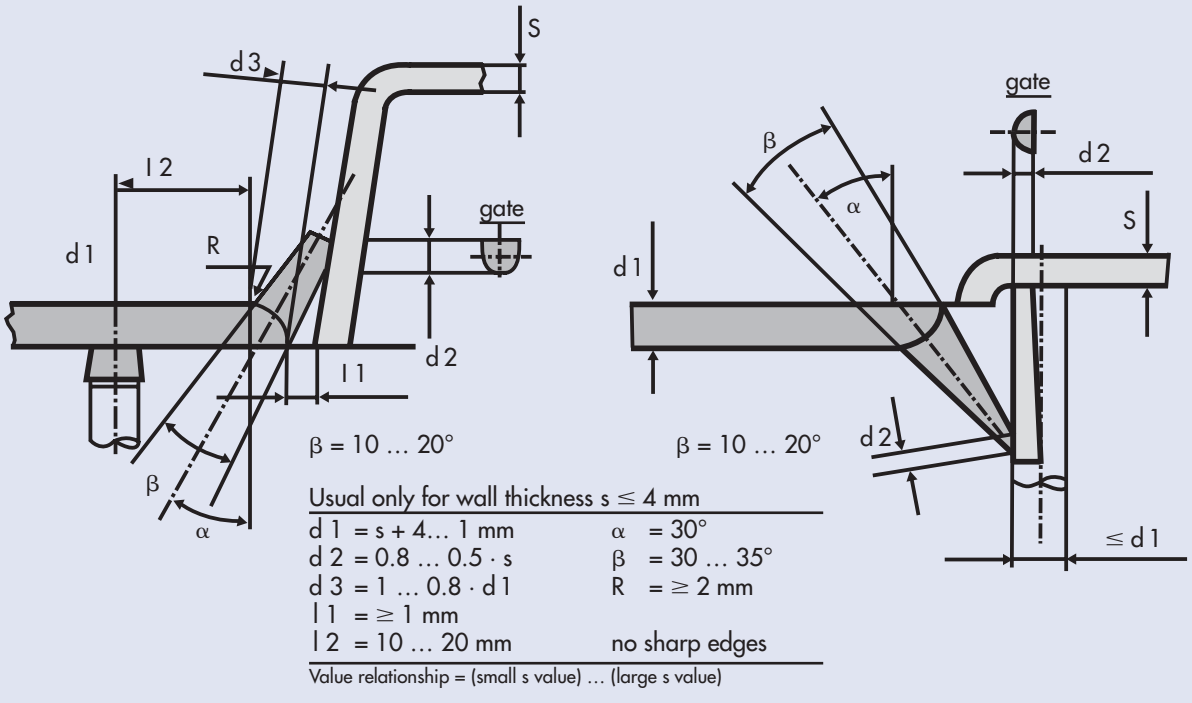
7.2.3 Undercuts

Undercuts are indentations or protuberances in the molded part perpendicular to the ejection direction. They are either essential from the design viewpoint or may be required for a component function.

Because of the high rigidity and low elongation of Fortron, undercuts that could prevent removal of the molding should be avoided. Such undercuts are only possible if suitable mold parts such as splits or collapsible cores are used.

Provided certain mold design and part ejection requirements are met, undercuts with low undercut depths are possible without using special mold parts. The following recommendations should be observed:

Fig. 7.3 · Examples of a submarine gate



Usual only for wall thickness s ≤ 4 mm

d 1 = s + 4… 1 mm	α = 30°
d 2 = 0.8 … 0.5 · s	β = 30 … 35°
d 3 = 1 … 0.8 · d 1	R = ≥ 2 mm
l 1 = ≥ 1 mm	
l 2 = 10 … 20 mm	no sharp edges

Value relationship = (small s value) … (large s value)

– Maximum undercut depth, depending on molding design and content of reinforcing material in the PPS:
  – h = 0.05 – 0.1 mm for 65% glass-fiber/mineral-reinforced Fortron and
  – h = 0.1 – 0.2 mm for 40% glass-fiber-reinforced Fortron
  – Provide the ejection surface in the mold with a brushed finish in the ejection direction
  – Ensure an ejection angle of < 30° at wall thickness transitions, radius corners and edges.

7.2.4 Sprues and runners

Sprues and runners should be designed to ensure a balanced filling behaviour. Sprues and runners should have a 2 to 3° taper. A sprue diameter of 4 mm is often adequate. Sprue bushings, runners and gate channels should be polished.

Use full-round runners having diameters as small as 3.2 mm (dependent on wall thickness), or equivalent trapezoidal runners. Balance the runner system in multicavity molds so all cavities finish filling at the same time and no cavity is overpacked.

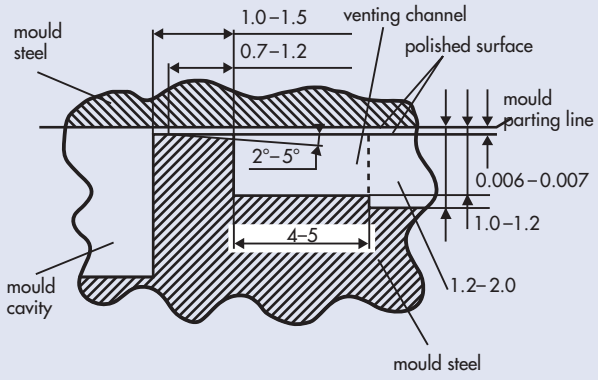
7.2.5 Gates

Multiple gates are often used for parts having long flow lengths and/or thin-walls to minimize pressure and flash. Locate gates so resin flow into the mold cavity is uniform and uninterrupted, while holding the number of gates present to a minimum. Place gates so weld lines occur in areas having minimal load-bearing requirements. The addition of venting at weld lines promotes stronger welds.

Gates should be rectangular and sized as large as possible to minimize wear.

All types of gates can be used with Fortron PPS[1]. Submarine or pinpoint gates typically measure > 1 mm (Fig 7.3). Tunnel gates should have an ejector pin at the gate to assist ejection. Generally the gate diameter depends on the wall thickness in the gate area. Data suggests gate diameters should be 0.5 to 0.8 times the wall thickness.

Fig. 7.4 · Mold venting for Fortron PPS parts



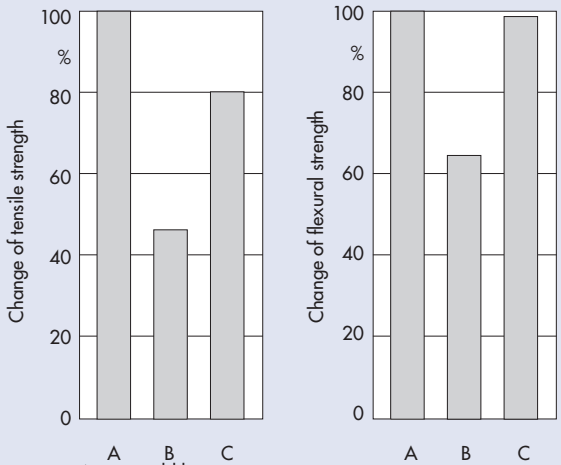
width of channel: dependent on shape of part
depth of channel: at junction of venting channels and at length of channel > 150–200 mm: 0.8–1.2 mm

The usage of rectangular sprue is very common, as is the diaphragm sprue for single cavity concentric moldings of ring shape with medium or small internal diameter.

7.2.6 Venting

Insufficient mold venting can cause burn marks on parts due to the high compression of trapped air and cause corrosive wear of the mold. Locate vents where air is likely to be trapped in a mold cavity by the molten Fortron PPS, especially in the last areas to fill.

Fig. 7.5 · Weld line strength comparisons for Fortron 4184L4



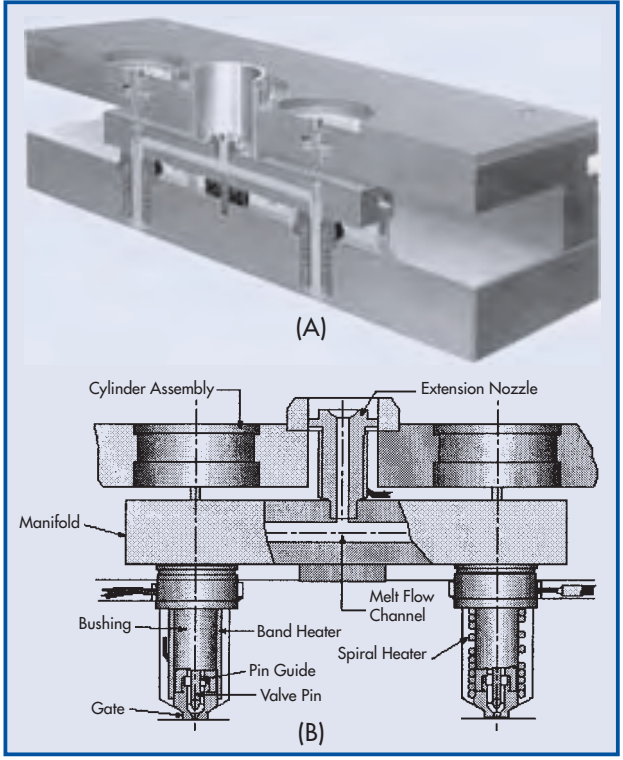
A = no weld line
B = with normal weld line area
C = with "optimized" weld line area

Effective venting often involves channels in the parting line. Vent channel depth of the land zone should not exceed 0.006 to 0.007 mm to prevent flashing. Channel width depends on molding size. It is best to polish the surface of the land zone and the surface opposite (Fig. 7.4). Venting may be achieved or improved with suitably machined ejector pins. Venting of runners has also proven successful.

7.2.7 Weld lines

Reinforcing fibers near a weld line tends to orient parallel to the weld line, weakening the part. Place weld lines in low-stress areas by positioning the gate properly. Weld strength can be increased through proper design, e.g., increasing wall thickness near weld lines or by using effective venting and others steps. Figure 7.5 compares tensile and flexural strength of Fortron 4184L4 (50% glass fiber reinforced) for different weld line strengths.

Fig. 7.6 · Schematic of a hot runner system



7.2.8 Ribs and radii

Ribs should have the same thickness as the adjacent wall section, if possible. If sink marks occur in a wall opposite a rib, then restrict rib thickness to 0.5 to 0.7 times the adjacent wall thickness. Use radii at the junctions between ribs and adjacent walls. The radius is usually 0.1 to 0.2 times the thickness of the adjacent wall. To avoid notch stresses in parts subject to high mechanical stress, use radii of at least 0.5 mm. Also, provide generous radii for changes in section, corners and edges.

7.2.9 Tolerances

Fortron PPS can hold fine tolerances. Glass- and mineral-reinforced grades allow for tolerances below 0.3%, although such extremely tight tolerances call for proper design and careful attention to mold construction and the molding process.

7.3 Hot runners

Fortron PPS uses hot-runner molds (Fig. 7.6) having comparable specifications, construction and operation as those for other engineering plastics. The design of hot-runner systems (geometry, steel selection and component selection) is usually done by the runner manufacturer. The information below on the use of hot runners with Fortron PPS should be applied in collaboration with runner manufacturers.

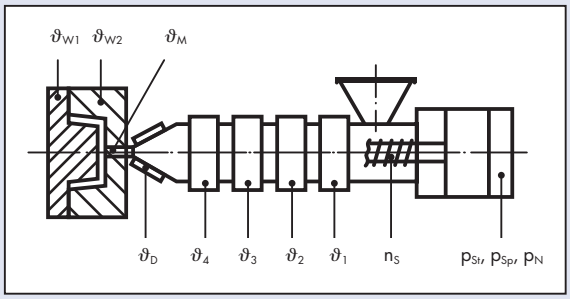
Use wear-resistant steels having a surface and working hardness >56 HRc for long-life hot runner systems. The steel used in hot runner components (manifold blocks, runners, nozzle tips, needles and needle guide parts and associated parts) can be coated or surface treated. (See 7.3.1 for further information on wear protection.)

7.3.1 Hot runner nozzles

Fortron PPS can be processed by various nozzle systems (Fig. 7.7). Use externally heated nozzles with Fortron PPS. Internally heated systems and indirectly heated nozzles do not heat the melt uniformly enough. They also can allow degraded material in the insulating layer to cause molding defects and the insulating layer to cause high pressure drops with highly filled Fortron PPS grades. Hot runner systems can be used when set up involves direct gating or a connecting cold sub-runner. Standard interchangeable or screw-in gate bushings, nozzle tips, shut-off needles and needle guide parts are generally recommended for reinforced Fortron PPS grades.

- Free-flow nozzles
  - Not recommended for direct gating because of material drooling and cold slugs
  - Nozzle drooling and cold slugs can be influenced by changing the temperature in the hot runner region and land zone L (contact length with the mold plate)
  - Limited suitability for use with a cold sub-runner (indirect gating); cold slugs should be retained in a slug well in the cold runner
- Nozzles with tips
  - Suitable for direct gating
  - Good temperature control of the nozzle can avoid or keep cold slugs small
- Needle shut-off nozzles
  - Can be used with direct gating for standard reinforced Fortron PPS
  - Melt isolation by the needle eliminates cold slugs, assuming ideal thermal design of the gate region
- Side-gating nozzles
  - Suitable for direct gating perpendicular to the parting line
  - Cold slugs can be kept small or avoided by good temperature control of the nozzle and the providing a tip that extends to the gating surface.

Fig. 7.7 · Processing conditions for reinforced and unreinforced Fortron PPS



Cylinder temperatures:	ϑ_1: 300–320 °C ϑ_2: 310–330 °C ϑ_3: 320–340 °C ϑ_4: 320–340 °C ϑ_M: 320–340 °C ϑ_m: 310–340 °C
Max. res. time in cylinder	≤ 60 min (at 320–340 °C)
Injection pressure p_I:	500–1000 bar (spec.)
Holding pressure p_H:	300– 700 bar (spec.)
Back pressure p_A:	low
Screw speed n_S:	low, e. g. 40–100 min^{-1}
Injection rate:	medium to high
Mould wall temperatures ϑ_{C1}, ϑ_{C2}:	140–145 °C
Nozzle:	free-flow nozzle, preferably shut-off nozzle

Note:
Tool steel, hardened and corrosion-resistant.
Bimetallic cylinder and screw corrosion-resistant.

7.4 Processing conditions

Fortron PPS can be processed on standard molding machines. Standard Fortron PPS grades at 135 °C for 3 to 4 hours before using them (see section 6.3). Some specialty grades may need milder conditions.

When starting processing, ensure that mold and injection molding machine are thermally balanced. During start-up, stabilize the machine for 30 minutes at the recommended zone temperatures (Fig. 7.7) before rotating the screw. If purging is needed, use high-density polyethylene (HDPE), polypropylene (PP) or a special purging compound.

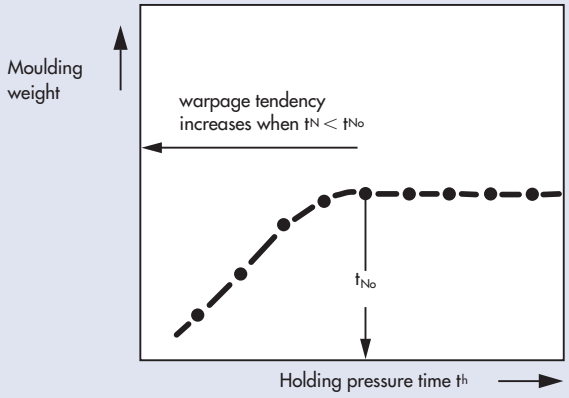
Check the melt temperature with a pyrometer to ensure the melt is in the recommended temperature range. Be sure that the melt temperature does not exceed 370 °C. The minimum mold temperature should be 140 °C so the resin can crystallize.

When shutting down a machine that had used Fortron PPS, hold the nozzle and barrel heaters at the molding temperature as they are purged with HDPE or PP. In case special purging material is used, it is strongly recommended to refer and adhere to the manufacturer's MSDS.The machine can be turned off when the purging resin fills the barrel. Place the ram in the forward position for shut down.

Fortron PPS is an easy-to-mold material. Considerations to keep in mind when processing Fortron PPS include:

- Melt temperatures of 320 to 340 °C are recommended. If molding geometry requires it, e.g., a small wall thickness, melt temperatures to about 340 °C are possible.
- Mold wall temperatures should be at least 140 °C to allow a sufficient crystallization rate and degree of crystallinity to create high-quality parts. It is best to use circulating-oil heating systems. Electric heating can be used in experimental molds and should have a power density of 40 to 50 W/kg.
- In practice, medium to fast injection speeds have proven to work best, depending on part and mold design. Mold venting is key to success.
- Screw speed should fall between 40 and 100 min^{-1}, depending on screw diameter.
- For plasticization a back pressure less than 30 bar is sufficient. A higher back pressure accelerates screw wear.
- Specific injection pressure should be between 500 and 1000 bar.
- Specific holding pressure is normally between 300 and 700 bar (as specific pressure, to be converted to hydraulic pressure).
- Holding pressure time depends mainly on the design of the runner and the gate and the wall thickness of the molded part. The required hold time can be optimized at the point of gate freeze. Lower holdong times may lead to warpage (fig. 7.8).
- Barrel residence times longer than 20 minutes may cause a modest decrease in viscosity and color darkening, although mechanical properties are virtually unchanged.
- Cycle time depends on the part molded. Theoretical cooling times are 20 to 30 seconds for 4 mm-thick parts, 10 to 15 seconds for 2.5 mm-thick parts, and 5 to 10 seconds for 1.5 mm-thick parts.
- Recommended is a shot weight of 50 to 70% of a machine's capacity.

Fig. 7.8 · Optimum holding pressure time

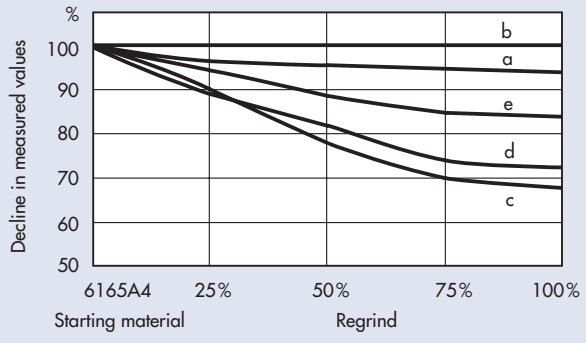


7.5 Use of regrind

Fortron PPS can be recycled by remelting and repelletizing. Sprues, rejects and post-consumer parts that are clean and not thermally degraded can be reprocessed as regrind in blends with virgin material. Parts to be recycled must be clean, dry and properly sorted. To minimize damage to fillers and fibers in Fortron PPS compounds during granulation, grind parts under the gentlest possible conditions.

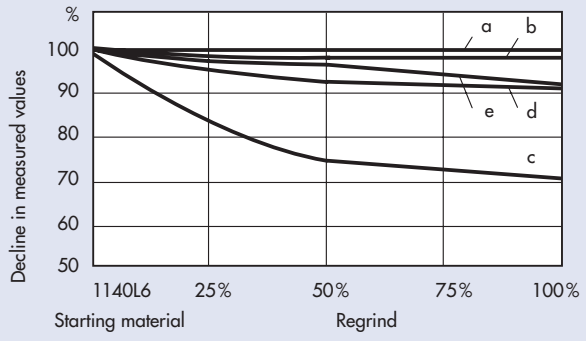
Regrind can impair feed behavior, so it is best to match regrind particle size to the pellet size of the virgin material. Regrind content of 25 to 30% should not be exceeded (Fig.7.9 and 7.10). If too much regrind is used, molded parts properties are likely to deteriorate. If a resin has been recycled several times, some decline in physical properties will occur (Fig. 7.11).

Fig. 7.9 · Mechanical properties for regrind addition for Fortron 6165A4



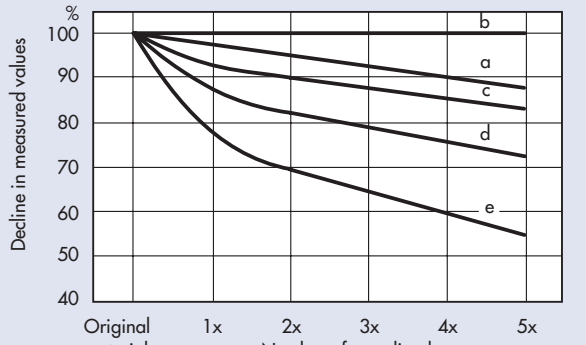
a tensile modulus
b strain at break
c notched impact strength (Charpy)
d impact strength (Charpy)
e tensile strength

Fig. 7.10 · Mechanical properties for regrind addition for Fortron 6165A4 regrind addition for Fortron 1140L6



a tensile modulus
b strain at break
c notched impact strength (Charpy)
d impact strength (Charpy)
e tensile strength

Fig. 7.11 · Mechanical properties as a function multiple processing



a tensile modulus
b strain at break
c tensile strength
d damage force
e damage energy

7.6 Troubleshooting guidelines

Many processing problems are caused by easily corrected conditions, such as inadequate drying, incorrect temperatures and/or pressures, etc. Solutions can often be found by following the recommendations given below. Try them in the order in which they are listed in each problem category.

Burn Marks
- Check for adequate ventilation
- Decrease the injection speed
- Decrease the booster time
- Alter the position of the gate
- Increase the gate size.

Discoloration in Fortron PPS may be caused by excessive temperatures. It is more of a surface phenomenon and is not necessarily indicative of degradation.

- Purge the heating cylinder
- Reduce the material temperature by:
  - Lowering the cylinder temperature settings
  - Decreasing the screw rotational speed
  - Lowering the back pressure
- Lower the nozzle temperature
- Shorten the overall cycle time
- Check the hopper and feed zone for contamination
- Check the ram and feed zone for proper cooling
- Move the mold to a press with a smaller shot size
- Provide additional vents in the mold.

Dull Surface Appearance is generally caused by too cold a mold (less than 135 °C).

- Increase the mold temperature
- Increase the injection speed
- Increase the packing/hold pressure.

Flash Reduction
- Check to see that the mold is closing properly
- Check for material caught on the parting surface
- Reduce the material temperature by:
  - Lowering cylinder temperature settings
  - Decreasing screw rotational speed
  - Lowering back pressure
- Decrease injection pressure/speed
- Decrease injection hold time/booster time
- Check parting line of mold for wear
- Move the mold to a larger (clamp) press if injection pressure is too high
- Reduce pressure by using lower viscosity grade of resin
- Refinish mold surfaces.

Nozzle Problems

Nozzle Drool
- Lower the nozzle temperature
- Increase the decompression time
- Lower the material temperature by:
  - Lowering the cylinder temperature settings
  - Decreasing the screw rotational speed
  - Lowering the back pressure
- Decrease the mold open time
- Dry the material
- Use a nozzle with a smaller orifice
- Use a nozzle with a reverse taper
- Use a nozzle with a positive shutoff.

Nozzle Freeze-off
- Increase the nozzle temperature
- Decrease the cycle time
- Increase the mold temperature
- Use a nozzle with a larger orifice
- Insulate nozzle from mold if using a cold mold (appr. 80 °C).

Poor Dimensional Control
- Maintain a uniform feed/cushion from cycle to cycle
- Fill the mold as rapidly as possible.
- Increase the gate size
- Balance the layout of the runners, gates, and cavity
- Use closed-loop controllers
- Add vents
- Check the machine's hydraulic and electrical systems for erratic performance
- Reduce the number of cavities in the mold.

Short Shots, Pit Marks, and Surface Ripples indicate the part is not being packed out or that there is leaking through the check ring.

- Check the hopper to see that the resin supply is adequate. If not, add resin
- Check to ensure a proper cushion exists and increase/decrease feed if necessary
- Increase the injection pressure
- Increase the injection speed
- Increase the booster time
- Increase the melt temperature by:
  - Raising the cylinder temperature(s)
  - Increasing the screw speed (with unfilled grades only)
- Raise the mold temperature
- Check cavity vents for blockage (trapped gas prevents the part from filling)
- Increase the size of the sprue/runners/gates.

Sinks and Voids
- Increase the injection pressure
- Increase the hold time
- Use a booster and maximum injection speed
- Raise the mold temperature (do this only with voids)
- Lower the mold temperature (do this only with sinks)
- Decrease the cushion/pad
- Increase the size of the sprue/runners/gates
- Relocate the gates into a heavier cross sections.

Sticking Problems

Sticking in the Cavity
- Check the mold temperature for overheating
- Decrease the injection/hold temperature
- Decrease the injection speed
- Decrease the booster time
- Decrease the injection hold time
- Increase the mold close time
- Lower the mold temperature
- Decrease the cylinder and nozzle temperature
- Check the mold for undercuts and/or insufficient draft.

Sticking on the Core
- Increase the injection pressure
- Increase the booster time
- Increase the injection speed
- Decrease the mold close time
- Decrease the core temperature
- Check the mold for undercuts and/or insufficient draft.

Sticking in the Sprue Bushing
- Check the sizes and alignment of the holes in the nozzle/sprue bushing
- Decrease the injection pressure
- Decrease the injection hold time
- Increase the mold close time
- Increase the nozzle temperature
- Provide a more effective sprue puller.

Unmelted Pellets
- Increase the melt temperature
- Increase the back pressure
- Dry/preheat the resin
- Use the proper screw design
- Ensure that check valve is working properly to prevent back flow. (Does machine hold cushion?)
- Move the mold to a press with a larger shot capacity.

Warpage and Part Distortion
- Equalize the temperature in both halves of the mold (eliminate hot spots)
- Observe the mold for uniformity (or lack thereof) of part ejection
- Check for proper handling of parts after ejection
- Increase the injection hold time
- Increase or decrease the pressure as appropriate
- Check for contamination
- Check the mold temperature
- Increase the mold close time
- Lower the material temperature by:
  - Lowering the cylinder temperature settings
  - Decreasing screw rotational speed
  - Lowering the back pressure
- Try differential mold temperatures to counter act warp
- Fixture the part and cool uniformly.

Weld Line Integrity
- Increase the injection pressure
- Increase the injection hold time
- Increase the injection speed
- Increase the mold temperature
- Increase the material temperature by:
  - Raising the cylinder temperature settings
  - Increasing the screw rotational speed
  - Increasing the back pressure
- Vent the cavity in the weld area
- Provide an overflow well adjacent to the weld area
- Change the gate location to improve the flow pattern.

In a runnerless mold system, the following guidelines often can solve typical problems that arise. Consult the manufacturer of the hot runner system for further information.

Gate Freezes Off
- Raise temperature of gate bushing.
- Raise temperature of hot runner manifold.
- Raise temperature of hot runner drop.
- Check all heater circuits to ensure that all heaters are functioning.
- Put heater band on machine if none is present.
- Decrease cycle time.
- Raise temperature of mold cavity detail.
- Optimize gate type
- Inject into a short secondary cold runner.

Some Gates in Multicavity Mold Freeze Off While Others Remain Open
- Raise temperature of gate bushings at frozen gate only
- Try above solutions for “Gate Freezes Off”.

Drooling at Gate
- Ensure that suck back control is operating
- Reduce temperature of gate bushing
- Reduce temperature of hot runner manifold
- Reduce temperature of hot runner drop
- Increase cycle time
- Decrease mold open time
- Alter the mold to reduce the gate size or to increase the gate land length.

Bubbles in Molded Part
- Ensure that the material is dry
- Optimize mold venting.

References

1. Further information can be found in the Fortron Poyphenylene Sulfide Process and Troubleshooting Guid (FN-6) and on Ticona’s website, www.ticona.com.

8. Extrusion processing

Fortron PPS is commonly extruded as sheet, pipe, rod, slab, film and fiber.

8.1 Processing conditions

Fortron PPS should be dried before processing (see section 6.3)

Certain specialty extrusion grades might require slightly milder drying conditions, typically around 90°C for 3 to 4 hours. Table 8.1 shows temperature guidelines for extrusion of Fortron PPS.

8.1.1 Screw design

For the best results, use a metering-type screw with a uniform "square" pitch having a compression ratio (depth of feed zone/depth of metering zone) of 3:1 to 4:1. This ratio range provides for an optimum combination of high output, low melt temperature and pressure variation. Screw L/D ratio may range from 16:1 to 24:1. As with injection molding, zone distribution should 1/3 metering zone, 1/3 transition zone, and 1/3 feed zone.

8.1.2 Screen pack

Different mesh sizes can be placed in the screen pack to adjust filtering. While most Fortron resins can be extruded without the use of a screen pack, some special grades/applications may require the use of screens to remove non-melts and ensure a controlled flow. In such cases, screen packs with mesh widths of 40 – 90 µm are recommended.

8.1.3 Head and die

Film and sheet extrusion usually involve coat-hanger-type dies that can be fed via crossheads designed for monolayer or multilayer films and sheets.

Table 8.1 · Extrusion temperature guidelines for Fortron PPS*

Extrusion Parameters	Unfilled	Filled
Feed Zone	285 – 290 °C	290 – 300 °C
Transition Zone	290 – 295 °C	290 – 310 °C
Metering Zone	290 – 300 °C	300 – 320 °C
Adapter	300 – 310 °C	300 – 320 °C
Die	300 – 310 °C	300 – 320 °C
Melt Temperature	295 – 330 °C	305 – 340 °C
Typical Draw-down	2:1	2:1

* Safety note: do not exceed 698°F (370 °C) melt temperature, otherwise the PPS may decompose and produce gases that can irritate the eyes and respiratory tract. See the Fortron PPS MSDS for more information.

It is important to control die gaps so as to regulate flow and the surface appearance of the final product. The head and die should have as few points of stagnation as possible, because stagnant flow areas can allow Fortron PPS to hang up and degrade. The degraded resin can end up in the final product and cause surface defects.

8.2 Profiles

8.2.1 Films and sheet

Fortron PPS can be extruded as monolayer and multilayer films and sheets. For monolayer film, pay special attention to roll temperature and draw down. Film surface appearance depends strongly on roll temperature, especially with steel casting rolls. Film thickness can range from 30 to 250 µm. Thicker sections can be extruded as sheets of up to 800 µm.

In a multilayer construction, Fortron PPS can be extruded as either the outer or inner layer. A tie layer is typically used between the PPS and a secondary substrate.

A standard extrusion screw can usually be used. Some cases may require a barrier screw. Most Fortron PPS grades can be extruded to form film and sheet at the extrusion temperatures in Table 8.1.

8.2.2 Pipe and tube extrusion

Fortron PPS is readily extrudable into tubing and piping. For example, pipes having diameters of 6 to 300 mm and wall thicknesses of 0.5 to 30 mm are used in the oil and gas industry and where combinations of water, gases such as hydrogen sulfide, and hydrocarbons create a harsh environment. Monolayer Fortron PPS tubes can be extruded as a flexible liner for stainless steel pipes.

In three-layer piping, a Fortron PPS interior layer and a thermoplastic exterior layer are held together by a tie layer. During production, these components should come in contact at their optimum melt states.
If melt temperature is too high or too low for any one element, delamination can occur.

Key process variables for Fortron PPS pipe include extruder barrel temperature, quenching bath temperature and take-up rate (see Table 8.2). Bath temperature is important for crystallinity and flexibility. A bath temperature below 30 °C will ensure the flexibility for easy take-up and spoolabilty. Use a vacuum sizing system to maintain a clear internal diameter in the pipe. This consists of a sizing sleeve that can be adjusted to the desired wall thickness. Take-up rate should be set so the pipe or tubing is spooled without breaking.

8.2.3 Rods and slabs

Fortron PPS can be extruded as rods, slabs and other stock shapes and solid profiles (Fig. 8.2). Rods typically have diameters of 6 mm to 80 mm, and plates typically have thicknesses of 6 mm to 50 mm.

Rods and slabs are machined into products for the aerospace, medical, electrical, electronic, food, packaging and other industries. Their applications include: handles for surgical scissors; electrical and electronic insulators; housings and connectors; polishing rings and etching heads for semiconductor fabrication; and chain guides, pump parts and other industrial components.

The extruder used for these profiles usually has standard three-zone screw geometry with a 2:1 compression ratio. Rod is extruded through a die into a cooling sleeve that has sufficient length for the walls of the profile to cool substantially. Insufficient cooling allows the walls to fracture under the internal pressure of the molten PPS.

In addition, the cooling bath temperature must be adjusted so as to prevent a large temperature gradient, which could lead to warpage of the part. To obtain a straight, warpage-free profile, the cooling bath temperature must be at least 140 °C.

In extruding thick-walled solid rods or sheets, a downstream annealing process must be incorporated. In this process, the extrudate must be heated to a minimum of 140 °C (preferably 150 to 170 °C) at a rate of 0.5 °C/min. When the final temperature is reached, this must be maintained for 10 min per 1 mm wall thickness. After that, the cooling process can begin at a recommended cooling rate of 0.2 °C/min.

Fig. 8.2 · Rods and plates extruded from 40% glass fiber reinforced Fotron PPS

Table 8.2 · Key extrusion parameters for monolayer and multilayer Fortron PPS tube and pipe

Parameters	Value
Extruder temperatures	290 – 315 °C
Melt temperature	310 – 320 °C
Die temperature	310 – 320 °C
Line speed	3 – 6 m/min
Puller speed	3 – 6 m/min
Cooling bath temperature	25 – 40 °C

The heating and cooling operation should not be carried out in steps but continuously. Slow heating and even slower cooling are important to prevent internal stresses, especially with thick-walled extrudates.

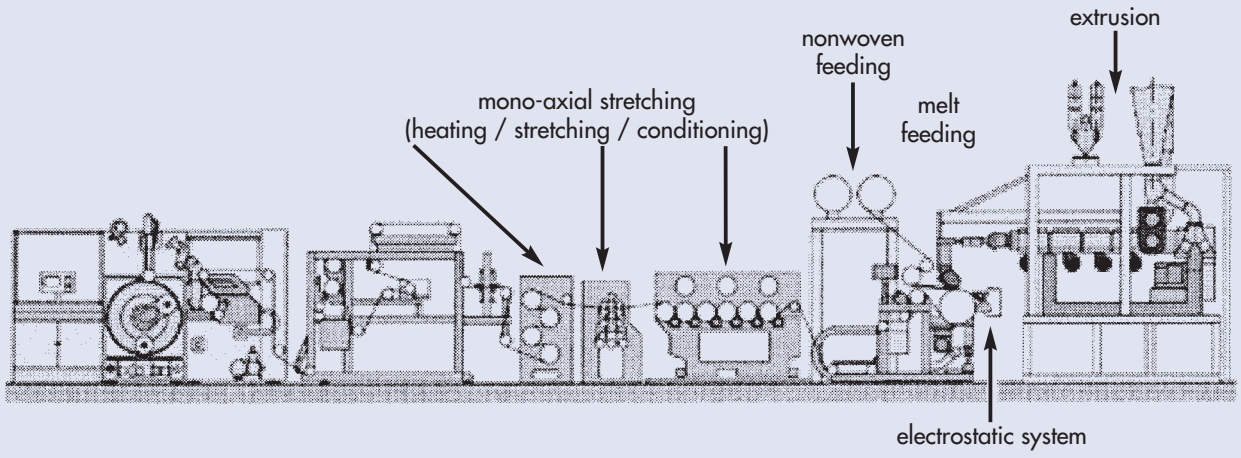
8.3 Extrusion coating and wire coating

Extrusion coating and wire coating processes melt-coat a paper, cardboard, fabric or wire substrate in a single process (Fig. 8.3). This process is similar to laminating, except that Fortron PPS is extruded as a melt web onto the substrate to form an extrusion-coated composite. The composite may undergo secondary conditioning, e.g., heating and/or stretching, before is wound on a take-up system for sale as a roll-good.

In wire coating, Fortron PPS is usually extruded as a sheath over a round, square or rectangular copper or aluminum magnet wire. Coating thickness varies from 0.1 to 0.5 mm. Specially designed tooling maintains a consistent thickness.

Fortron PPS coated wires are used in transformers because the PPS has very low moisture retention (< 0.02% when submerged in water for 24 hours). The coating also has high thermal stability and a higher dielectric strength than many alternate materials.

Fig. 8.3 · Extrusion coating setup

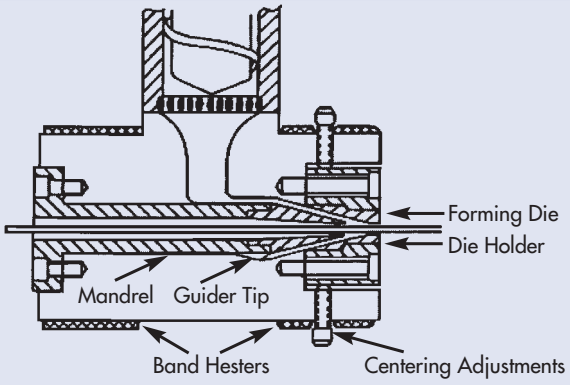


In the crosshead die of a typical wire coating operation (Fig. 8.4), the forming die controls the thickness of the annular coating on a wire fed through the center. A centering adjustment ensures the wire is uniformly coated all around.

References:

1. Principles of Polymer Engineering, McCrum, N.G., Buckley, C.P. and C.B. Bucknall., Oxford science publications, 1988.

Fig. 8.4 · Wire coating crosshead die



9. Other processing methods

Ticona has developed several grades of Fortron PPS with the viscosity ranges and other properties needed for extrusion, blow molding and other processes. The material's ability to work across many fabrication methods rests on its linear structure.

Fortron PPS has excellent processability which reduces crosslinking and the variations this causes. Fortron PPS has excellent processability based on its high melt strength, purity, thermal stability and narrow viscosity range. As a result, it yields high-quality blow-molded parts and semi-finished products. It also can be used in composites for demanding components from sporting equipment to airplane wings, as well as for blown films, powder coating, compression molding (using long glass, carbon, steel and other fibers), and rotational molding.

Table 9.1 · Blow molding conditions for Fortron PPS 1115L0

Drying conditions for Fortron 1115 L0	
TDr = 80 – 100 °C/3-4 hours	
Temperatures	
Barrel:	300 – 330 °C
Die:	310 – 330 °C
Residence time in the barrel ≤ 60 min	
Mould cavity temperature:	
140 – 150 °C	

9.1 Blow molding

Blow molding can generate parts in a single step production operation. Fortron PPS 1115L0 works well in this blow molding because it has a good melt strength and creates a well-formed parison.

In addition to melt strength, this 15% glass-filled grade has the viscosity range, purity and thermal stability needed for processing on conventional and 3-D blow molding machine (Fig. 9.1). This material should be dried before use and processed at barrel temperatures of 300 to 330 °C (Table 9.1).

Fig. 9.1 · Suction blow molding machine (photos from SIG – Kautex)

Fortron PPS can be used to blow mold a variety of components for the automotive, chemical, appliance and other industries, including air ducts for turbo-charged diesel engine (Fig. 9.2) exposed to thermal stresses of 200 °C or more, as well as auto fuel rails and intake manifolds. They also can be used in auto cooling systems and heat-shielding piping, flue pipes in gas heating systems and components for chemical transport and cooling systems in power station.

9.2 Composites

Fortron PPS grades (especially Fortron 0214, 0205 or 0320) offer the viscosities needed for use as a thermoplastic matrix in composites for automotive, aircraft, aerospace and construction applications. They can be used in a variety of composite processing technologies.

Fig. 9.2 · Blow molded air duct for turbo-charged diesel engines with hot plate welded connecting flange (Mann & Hummel)

One method involves plying up layers of film produced from Fortron resin with reinforcement layers of woven glass, carbon, and/or aramid fibres. The film, produced separately, is typically made from high molecular weight grades of Fortron resin such as 0214 or 0320 for best processability and maximum performance in use. Once laid up, the 'sandwich' is placed in a compression mold and heated and formed to the desired shape.

Another popular technique is to make uniaxially reinforced 'pre-preg' tapes (with one or more of the above noted fibres) and overlay them at various angles to maximize properties in the desired direction(s). The plyed up tapes are then compression molded as above.

A good example of a Fortron composite application is the leading edge wing on Airbus A340 and A380 aircrafts (Fig. 9.3). Its fabrication begins by converting Fortron 0214C1 PPS into film (50 to 200 µm thick). The film is bonded to carbon-fiber fabric in a press at high pressure and temperature to form high-strength,

Fig. 9.3 · Views of the Airbus A340 and A380 leading edge wing

dimensionally stable composite plates, which are pre-heated and shaped at elevated pressure and temperature.

The result is a part that meets the wing's structural needs yet weighs 20 percent less than aluminum. It also has excellent resistance to oils, fuels, acids and anti-freeze. It is installed using inductive welding, which eliminates the need for rivets as with aluminium leading edge wings.

9.3 Powder coating

Powder coating applications have been developed using some Fortron granules and powder. Typical areas of interest are in applications requiring chemical resistant and heat resistant environments. Processes have been developed to ensure that the Fortron forms a well bonded layer with the substrate on which it is coated, including metallic surfaces.

For example, Fortron PPS is used as adhesive agent between PTFE and metal for cookware/pan coatings. Furthermore, it can be utilized as a corrosion coating for metals.

10. Technical fabrics

Fortron PPS is a versatile material that can be extruded as monofilaments and multifilaments and fabricated in spunbond or meltblown operations to bonded fabric. The manufacture of nettings is also possible.

As a technical fabric material, Fortron PPS is made into various textile constructions for filtration and industrial end uses. It is a good choice for applications that involve high temperatures (to 200 °C), chemically aggressive environments and the need for inherent flame-retardancy. This is especially true for liquid and gaseous filtration in the chemical, petrochemical, pharmaceutical, food and other markets. Fluids that have been filtered by Fortron PPS include hot water, oil, amine, glycol, sulfolane, methylene chloride, naphtha and potassium hydroxide.

Fortron PPS can be processed on standard extrusion equipment.

When extruding Fortron PPS, it is important to select the proper processing temperature and the grade having the right viscosity. For processing Fortron, corrosion-resistant steel is recommended for the metal die.

10.1 Meltblown fabrics

Fortron PPS is an easy-to-use material having a broad processing window that creates meltblown nonwovens for use as filter media in chemical and industrial applications and in power plant bag houses.

One grade, Fortron PPS 0203HS, can form fine to coarse meltblown fibers having diameters of 2 to10 µm and textures ranging from soft and flexible to stiff. A medical meltblown grade, Fortron PPS 9203HS, has USP Class VI approval, US FDA Drug and Device Master Files, and approval for repeated food contact.

Fortron PPS can be extruded with standard polypropylene screws in standard melt blowing lines. Extruder temperatures should be between 260 and 315 °C and die temperatures between 305 to 320 °C (see Table 10.1). Die to conveyor distances should be appr. 10 to 40 cm.

Fiber diameters can be tuned by adjusting the die-to-conveyor distance and the quench air flow rate. Before processing, Fortron PPS should be dried at 120°C for two hours.

10.2 Spunbond fabrics

Fortron PPS spunbond nonwovens are a direct polymer-to-nonwoven fabric in which conversion occurs on one production line. They are made by melt spinning to get a continuous-filament bundle that is laid down on a conveyor at high speeds to form a spunbond substrate. The molten polymer is typically extruded through a spinneret (Table 10.2), cooled and drawn.

Meltblown fabrics are often combined with spunbond fabrics in a composite material for the industrial and medical sectors, e.g., a meltblown PPS fabric might form the filter media that is supported by a spunbond PPS fabric backing.[1]

10.3 Staple fibers

Fortron PPS is often converted into staple fibers as a raw material for other applications. An example is production of needle-punched composites which are further processed to filter hoses.

Table 10.1 · Typical meltblown process parameters for Fortron PPS

Parameter	Recommended setting
DCD	15 – 20 cm for coarser diameters, 25 – 40 cm for finer diameters
Quench air	Off to minimal
Extruder profile:	
Zone 1	260 – 270 °C
Zone 2	280 – 290 °C
Zone 3	285 – 295 °C
Zone 4	295 – 305 °C
Zone 5	305 – 315 °C
Die melt temperature	305 – 320 °C
Process Air:	
Air temperature	300 – 330 °C
Air flow rate	500 – 1100 kg/h
Extruder outlet pressure	35 – 40 bar

Fortron PPS staple fibers in various deniers and cross sections in monocomponent and bicomponent fiber formats have been used as felt substrates, e.g., in needlepunched composites. Multifilament Fortron yarns have also been made for industrial applications needing woven textile structures.

10.4 Monofilament

Fortron PPS monofilaments, primarily made from Fortron 0214B1, 0317 and 0320, are used in woven fabrics and in forming fabrics in paper machines (Fig. 10.1). In processing, monofilament diameter must be controlled carefully because weave consistency depends on having a uniform diameter.

In producing monofilaments, the melt is extruded through a monofilament die and cooled (Table 10.3). The monofilament then passes through draw-roller assemblies to gain high tenacity. As the monofilament exits the first draw assembly, it is heated and passed through a second one running at a different linear speed. It then passes through a third draw assembly where it is spooled.

10.5 Multifilaments

Fortron PPS monofilaments, primarily made from Fortron 0320C0, are used in multifilaments. In processing, multifilament diameter must be controlled carefully because weave consistency depends on having a uniform diameter.

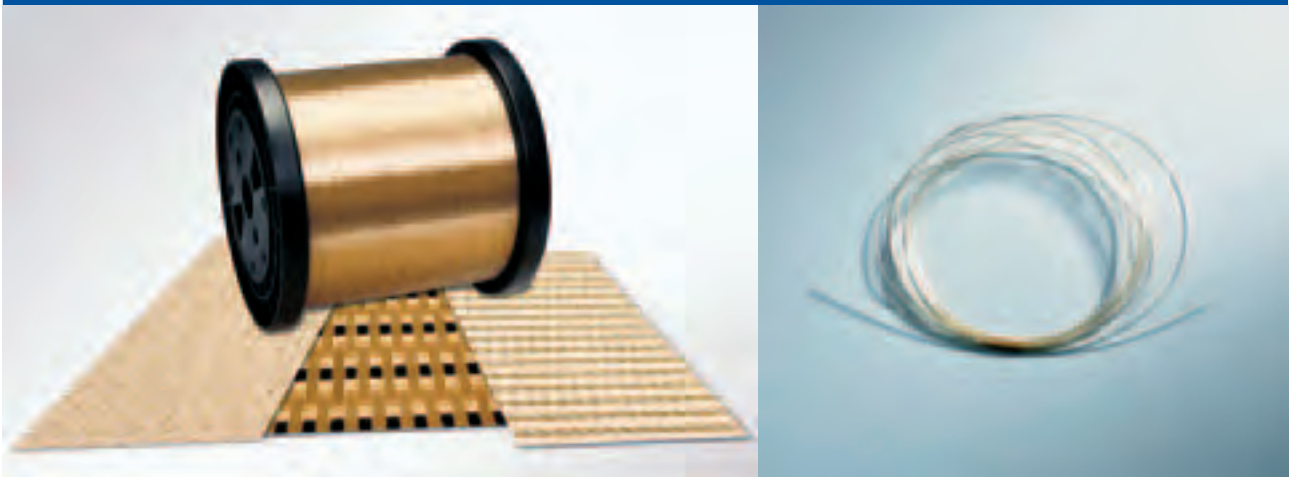
Table 10.2 · Typical spundond process parameters

Parameter	Recommended Values
Extruder	
Zone 1	274 °C
Zone 2	285 °C
Zone 3	296 °C
Zone 4	310 °C
Zone 5	320 °C
Die melt	320 °C
Calendar, engraved/smooth	107/107 °C
Basis weight, g/m²	34.0 – 68.0 g/m²

Table 10.3 · Typical monofilament process parameters

Parameter	Value
Extruder average temperature	300 – 320 °C
Flange temperature	300 – 310 °C
Head temperature	300 – 310 °C
Melt temperature	300 – 310 °C
Oven temperature	140 – 210 °C
Draw ratio	3 – 4
Pack pressure	25 – 100 kg/cm²
Air Quench	Yes

Fig. 10.1 · Drying belts made from monofilaments using Fortron PPS 0320C0



Fortron® PPS 0320C0 enables the production of very tough and high tenacity multifilaments.

Their temperature resistance up to 170 °C and chemical resistance make them suitable for rubber vulcanisation. Several trials have shown the compatibility of Fortron® PPS and conventional elastomers and additives used in the automotive industry.

The combination of Fortron® PPS multifilaments and rubber leads to a very good flexibility of the rubber hoses. Fortron® PPS multifilaments combine high tenacity and required elongation to allow the radial expansion of the hoses according to volume and pressure increases. The dimensional stability of Fortron 0320C0 ensures a very good and uniform shrinkage behaviour of the multifilaments (shrinkage below 1 %).

References

1. 2003, Chemical Economics Handbook, SRI International
2. Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., vol. 17, John Wiley & Sons, 1996, pp. 336-368.

11. Assembly and finishing

Manufacturers have many choices when it comes to the assembly and finishing of Fortron PPS parts. Selecting among them involves an informed decision that balances design, the grade used, end use and other practical considerations to gain the greatest efficiency at the lowest cost.

11.1 Annealing

Fortron PPS parts processed with mold wall temperatures ≥140 °C are well crystallized. They shrink little when exposed to high temperatures afterward, so annealing to counter post-molding shrinkage effects is not needed (Fig. 11.1).

A test of post-shrinkage on Fortron PPS parts with a 3 mm wall thickness made at mold temperatures of 140 °C showed that the 11401L4 and 6165A4 grades had just 0.09% and 0.10% shrinkage when annealed for 2 hours at 230 °C, respectively. Similarly, shrinkage for these grades was 0.10% and 0.12% when annealing occurred at 230 °C for 24 hours.

Strain at break, tensile strength and heat deflection temperature of annealed (3 hours at 200 °C) and non-annealed samples of Fortron 1140L4 as a function of mold wall temperature appear in Figure 11.2, 11.3 and 11.4. These show the critical importance of higher mold wall temperatures in minimizing post-mold shrinkage and optimizing mechanical and thermal properties.

Fig. 11.1 · Shrinkage of Fortron 1140L4 tensile test bars (ISO 3167) as a function of mold wall temperature, annealing conditions: 3 h, 200 °C

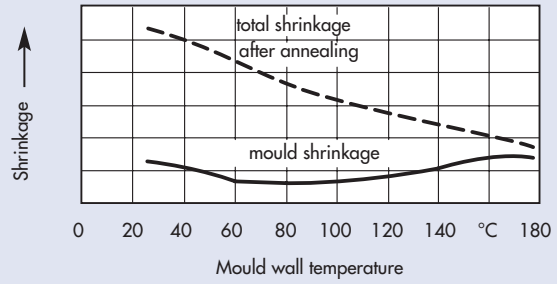


Fig. 11.2 · Relation between tensile strength and mold wall temperature of annealed and non-annealed samples of Fortron 1140L4

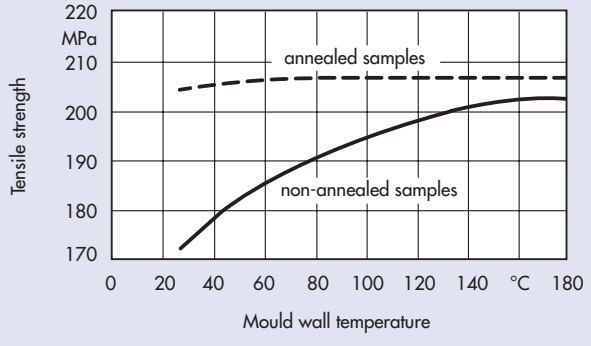


Fig. 11.3 · Relation between strain at break and mold wall temperature of annealed and non-annealed samples of Fortron 1140L4

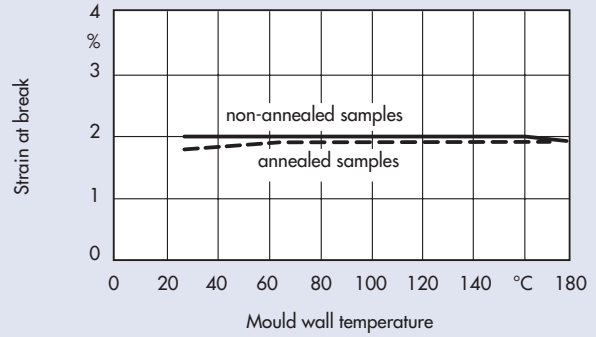
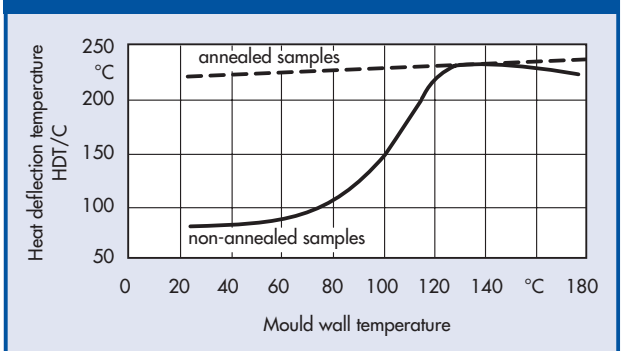


Fig. 11.4 · Relation between heat deflection temperature HDT/C and mold wall temperature of annealed and non annealed samples of Fortron 1140L4



11.2 Machining

Fortron PPS can be machined with the same routers, sanders, saws, lathes and other tools used for metal or wood. Injection molded parts are machined to add features that are uneconomical to mold or that cannot be molded with enough precision, or if there is a need to avoid critical welds. Extruded Fortron PPS shapes are also machined to form components for many applications.

When machining Fortron PPS:

- Keep tools sharp and cool to avoid excessive frictional heat so the plastic does not distort, melt or lose its finish.
- Account for the resin's low thermal conductivity in selecting machining conditions. At high cutting speeds, cool tools with clean, compressed air or conventional cutting fluids, e.g., water, aqueous solutions, ethylene glycol or oil-based fluids. Adjust speed and feed rate according to how the plastic responds, e.g., reduce speed if melting, burning or discoloration occurs.
- Remove chips for optimal cooling. Chips that occur with reinforced or filled Fortron PPS tend to be short and easily removed.
- Recommended cutting speeds vary with the equipment involved, e.g., 50 to 200 m/min for drilling, 250 to 500 m/min for turning and milling, and 500 to 800 m/min for sawing. Recommended feed rates also vary with the process, e.g., 0.1 to 0.5 mm/rev for turning and 0.1 to 0.3 mm/rev for drilling. Tool wear increases at lower feed rates and can impair the quality of the cut surfaces.
- Avoid burr formation in thread cutting by using double-toothed chasers. Also use a diameter-dependent overmeasure with screw taps. Avoid cutting dies because they are likely to continue cutting on the return.
- Machining glass-fiber-reinforced or mineral-filled Fortron PPS grades is best done with carbide- or diamond-tipped tools, especially for high-volume production. Tools made of high-speed steel are likely to have a shorter service life.
- In turning, clearance angles of 6 to 8°, rake angles of 0 to 5°, and cutting edge angles of 45 to 60° are recommended. To gain a smooth cut, increase the cutting profile radiused by at least 0.5 mm.
- In milling, use standard milling cutters having few teeth to gain a larger chip space. This permits a large chip volume so the heat generated is removed with the chips. Clearance angles of 5 to 15° and rake angles of 6 to 10° have proven successful.
- Drilling and reaming are used to enlarge, deepen or remove draft from holes. Bits designed for plastics give the best results. These usually have one or two polished or chrome-plated flutes, narrow lands and large helix angles so they expel chips quickly and minimize friction. Bits should be sharp and may need to be withdrawn often in deep holes to eject chips.
- When using metalworking twist drills, it is best to have twist angles of 12 to 16°, clearance angles of 5 to 10°, rake angles of 10 to 30° and cutting edge angles of 90°. For deep holes, ensure adequate chip removal, e.g., smooth helical grooves. Pilot drilling of large diameters is recommended.
- Avoid unnecessary heat build-up from friction in sawing by using a thin saw blade. Use a tooth geometry with a clearance angle of 15 to 30°, a rake angle of 0 to 5°, and tooth pitch of 3 to 5 mm.

11.3 Assembly of Fortron moldings

Fortron PPS components can be produced separately and then assembled by a variety of thermal, adhesive and mechanical methods.

11.3.1 Thermal welding

In thermal welding, the bond line between two parts is melted to form a weld. This method is a fast, economical and safe way to join Fortron PPS elements. Manufacturers can choose from among ultrasonic welding, spin welding, vibration welding, hot-plate welding, induction welding and laser welding.

The best welding strength occurs with high-quality components that are based on well-designed and well-molded parts having close tolerances and good dimensional stability. The choice of method for an application is governed by joint shape and design, Fortron grade, and part profile.

- **Ultrasonic welding**, which applies high-frequency energy at the interface between parts normally takes less than 2 seconds per weld. It forms continuous, leak-proof joints between Fortron PPS

elements that that can be as strong as the PPS itself (Fig. 11.5). Pinch-off welds formed at 20 to 40 kHz are often optimal, although tapered pinch welds having a welding distance of over 1 mm are also viable.

Fortron PPS is suitable for near- and far-field ultrasonic welding. The alternating strains absorbed by PPS in ultrasonic welding can cause localized damage. Avoid this by designing the weld properly and by optimizing welding, time, pressure and other machine settings. Fortron grades with reinforcement loading to 40% give good welding results. Weldability deteriorates above this level.

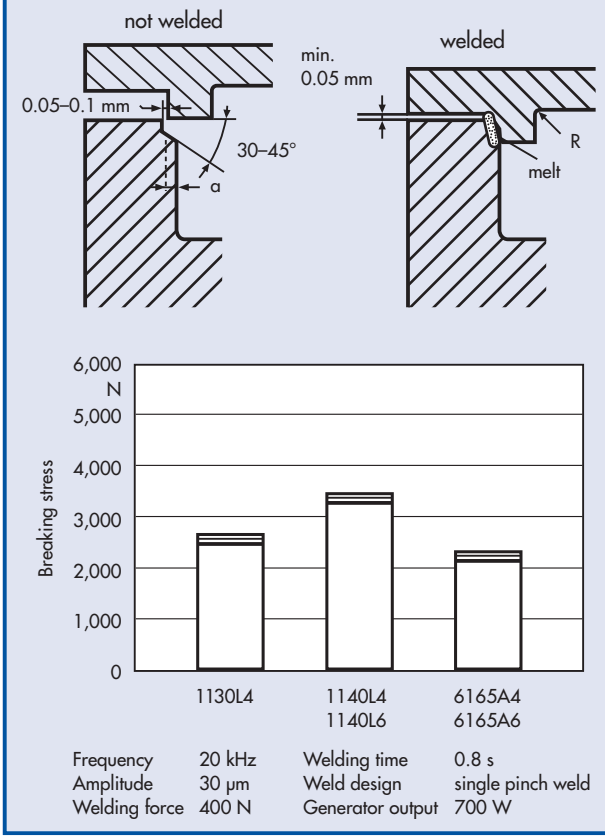
– **Spin welding** joins parts having rotationally symmetrical joint faces. It calls for relatively simple equipment that holds one part steady and while pressing a rotating part against it at a set pressure. With Fortron PPS, gas-tight, high-strength welds usually forms in less than 3 seconds. Welding conditions, such as surface speed, contact pressures and rotational speeds, depend on grade and part geometry, and should be defined in optimizing trials.

– **Vibration welding** rubs parts together to create frictional heat, usually at amplitudes of 2.5 to 5 mm and frequencies of 120 and 240 Hz. This method forms strong joints quickly and works best with large parts that have irregular joint interfaces. It is an excellent alternative if part geometry or size do not allow for ultrasonic or spin welding.

– **Hot-plate welding** works well for joints exposed to mechanical stress in service, large joint surfaces or part geometries that preclude other welding methods. The hot tools used must be designed for the high temperatures needed in working with PPS.

– **Induction or electromagnetic welding** excites fine, magnetically sensitive metallic or ceramic particles in a preform with a radio-frequency magnetic field. Heat induced in the preform placed at the joint fuses Fortron PPS parts as they are pressed together to form gas-tight, high-strength joints. Induction welding allows the insertion of metal parts and can be used for difficult joints where other methods fail.

Fig. 11.5 · Load bearing capacity of ultrasonically welded test specimens produced from various Fortron grades



– **Laser welding** transmits a light beam through one part so it is absorbed and heats the surface of a second part. With Fortron PPS, the laser permeable part should be made of an unfilled grade and less than 2 mm thick. The other element should be made of reinforced Fortron PPS because these grades have good absorption behavior. Consult with the laser welding system manufacturer when carrying out trials for this method.

11.3.2 Snap-fits and other molded-in features

Fortron PPS has limited suatability for snap fits. The design of Fortron PPS snap-fit joints[1] should account for how permissible outer-fiber strain depends on wall thickness, as well as for the orientation of the glass fiber. Guide values for the upper limit of outer-fiber strain are:

Fortron PPS 1131L4 ITT, 1140L4, 1140L6:	1.3%
Fortron PPS 4184L4, 4184L6:	1.1%
Fortron PPS 6165A4, 6165A6:	0.8%

The friction factor needed for the calculation depends on the sliding partners, surface roughness and surface pressure. Typical friction factors with Fortron PPS are 0.3 to 0.4 for Fortron on Fortron and 0.4 for Fortron PPS on steel. Trials are recommended for snap-fits and other molded-in assembly features.

11.3.3 Adhesive bonding

Fortron PPS is bonded through contact adhesion. The process is fast, economical and requires little or no part preparation or special equipment. It also creates excellent liquid and gas seals and causes no assembly stresses.

Depending on the application, two-part adhesives based on epoxy resin, methacrylate or polyurethane and one-part adhesives based on cyanoacrylate or hot melt adhesives can be used. Select the adhesive based on end-use service temperature. Joint surfaces should be free of grease, mold release compound and other contaminants that can spoil a bond and may need to be roughened or etched.

Joints for adhesive bonding can take many forms and should be tested in use. Close contact with the adhesives industry is recommended during adhesive trials.

11.3.4 Screws and other mechanical fasters

Fortron PPS can be used with molded threads, molded-in inserts, and bolting with through bolts and direct bolts (e.g., self-tapping screws). The method chosen depends on end-use requirements and part design. Fortron PPS expands little and is sensitive to notches, so areas of the part likely to be stressed during the attachment of mechanical fasteners should be carefully designed. Stress can also be limited by selecting the appropriate fastener and use of torque-limiting drivers during assembly. Be sure to consult fastener makers during trials.

Threaded metal inserts permanently installed in molded bosses eliminate the need for a nut, so assembly can be done from one side. These can involve female threads, threaded male studs, locating pins and bushings. Ultrasonically installed inserts are strong and relatively free of stress compared to many other type of inserts.

When using self-tapping screws, size the hole properly to avoid excessive hoop stress in the boss. Also, make the hole deep enough so the screw does not bottom out and make the wall of the boss thick enough to resist the stress created by the screw.

Metal rivets create permanent assemblies that install rapidly. The rivets used should have large heads so they spread the load. Form the rivet against the metal part of the assembly or against a metal washer, if the parts being joined are made of plastic.

11.4 Finishing

Manufacturers can turn to many surface finishing methods to improve appearance, add identifying marks and protect against heat, radiation, chemicals, electromagnetic noise and abrasion. These methods include laser marking, painting, printing and metallization.

Such methods often call for pretreatment, because finishing is usually most effective when surfaces are free of oil, mold release agents and other contaminants. Cleaning often involves solvents and detergents, although surface preparation using primers, etching, sanding, flame treatment and other methods may be needed.

11.4.1 Laser marking

Non-contact marking of text, patterns, symbols and codes on Fortron PPS surfaces uses a Nd:YAG laser (at 1064 nm). These lasers produce dark, matt marks on Fortron PPS.

11.4.2 Painting

Articles made from Fortron can be painted using conventional topcoat systems after pretreatment with a suitable primer. The choice of system depends on the properties needed, e.g. weathering resistance, chemical resistance or scratch resistance. It is important to ensure the paint system can cope with the thermal stresses involved in an end use.

11.4.3 Printing

Printing on Fortron PPS can be done via gravure, flexographic, pad, offset, screen, digital and other methods. Before printing, the surface must be pretreated so it is free of grease. Depending on the application, inks based on epoxy resin, acrylic resin, cellulose ester or two-pack inks based on urethane can be used.

11.4.4 Metallization

Fortron PPS parts can be metallized by wet- or electro analysis and vacuum metallizing. Since a flawless part surface is essential for metallization, the mold must be well vented during processing.

In electroplating, Fortron PPS parts are acid etched to create microporous surfaces that improve electroplate adhesion. A thin layer of copper or other metal is deposited by immersing parts into an electrolyte bath. Next, the electroplate is formed as a relatively thick, durable layer of such metals as copper, nickel, chrome, brass, silver or gold. Parts should be smooth and without such flaws as weld lines and sink marks.

11.4.5 Heat-based processes

Hot stamping uses raised-image dies to transfer lettering and designs ranging from solid colors, wood grains, metallic finishes and other effects from foils or tapes. The die is heated to near the melting point of the plastic. Heat transfer uses a heated flat die or roller to bond multicolor designs onto the surface from a composite film.

References

1. Ticona GmbH, Design Calculations for snap fit joints in plastic parts. Issued in August 1996 / 2nd Edition. © 2004 Ticona GmbH, Kelsterbach

12. Subject Index

Conversion

11.1 · Unit conversion factors

	— Multiply by →	
	← Divide by —	
Length		
Inch (in)	0.0254	Meter (m)
Foot (ft)	0.305	Meter (m)
Area		
Square inch (in^2)	6.45×10^{-4}	Square meter (m^2)
Square feet (ft^2)	0.0929	Square meter (m^2)
Volume		
Cubic inch (in^3)	1.64×10^{-5}	Cubic meter (m^3)
Cubic feet (ft^3)	0.0283	Cubic meter (m^3)
Mass		
Pound (lb)	0.454	Kilogram (kg)
Force		
Pound force (lbf)	4.45	Newton (N)
Kilogram force (lbf)	9.81	Newton (N)
Pressure		
Newton/meter^2 (N/m^2)	–	Pascal (Pa)
lbf/in^2 (psi)	6.897×10^3	Pascal (Pa)
lbf/in^2 (psi)	6.897×10^{-3}	Mega Pascal (MPa)
kg/cm^2	9.81×10^4	Pascal (Pa)
bar	10^4	Pascal (Pa)
Viscosity		
Poise	0.1	Pascal · second (Pa · s)
Energy		
Calorie (cal)	4.2	Joule (J)
Calories/gram (cal/g)	4.2	Kilojoule/kilogram (kJ/kg)
Joule/kilogram (J/kg)	2.33×10^3	BTU/lb
Technical fabrics		
Yarn size		
1 tex	9	Denier
1 dtex	0.1	mg/m
Tenacity		
1 cN/tex	0.1132	gf/denier

11.2 · Tensile or flexural property conversion

Strength		Modulus	
MPa	**psi**	**MPa**	**psi x 10^6**
75	10,900	6,000	0.87
100	14,500	8,000	1.16
125	18,000	10,000	1.45
150	21,800	12,000	1.74
175	25,400	14,000	2.03
200	29,000	16,000	2.32
225	32,700	18,000	2.61
250	36,300	20,000	2.90
275	39,900	22,000	3.19
300	43,500	24,000	3.48

11.3 · Length Conversion

inches	inches	mils	cm	mm
1	1	1000	2.54	25.4
1/2	0.5	500	1.27	12.7
1/4	0.25	250	0.635	6.35
1/8	0.125	125	0.32	3.2
1/16	0.0625	62.5	0.16	1.6
1/32	0.0313	31.3	0.08	0.8
1/64	0.0156	15.6	0.04	0.4

11.4 · Temperature Conversion

Degrees Centigrade (°C)	Degrees Fahrenheit (°F)
0	32
10	50
20	68
50	122
75	167
100	212
125	257
150	302
175	347
200	392
225	437
250	482
275	527
300	572
325	617
350	662
375	707
400	752

Conversion factor: °F = 1.8 (°C) + 32

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17 SUCCESSFUL APPLICATION OF BIOLOGICAL ACTIVATED CARBON PROCESS FOR REMOVING SULFOLANE FROM GROUNDWATER

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INTRODUCTION

Since mid-1982, Occidental Chemical Corporation (OxyChem) has operated a groundwater treatment system at a former pesticide manufacturing site in Lathrop, California (Figure 1). About 600 gal/min of groundwater is extracted from a shallow aquifer using seven extraction wells, treated in two parallel 40,000 lbs upflow carbon adsorbers for removing organic contaminants, and finally discharged through two injection wells to a deeper (310 ft below the surface) saline aquifer. The primary target chemicals for carbon treatment are the fumigant pesticides dibromochloropropane (DBCP) and ethylene dibromide (EDB). Sulfolane (tetramethylene sulfone), an important process chemical due to its excellent solvent properties for many organic compounds/polymers and stable nature, is also present in the groundwater. Since sulfolane is soluble in water, it is not effectively removed in the existing carbon adsorption system. Toxicity evaluation conducted during the original design of the remedial program concluded that specific treatment for sulfolane was unnecessary because no toxicity was expected due to its low concentration (3000 ppb) in the groundwater.[1] Concentrations for sulfolane, DBCP, EDB and other groundwater contaminants have since declined significantly as shown in Table 1 which also presents the effluent discharge limits. Sulfolane removal is now required due to considerations for reclassifying the deep saline aquifer in the Lathrop area for productive uses. Many treatment options, including biodegradation, chemical oxidation, and adsorption using a different activated carbon or other adsorbents, were reviewed. The task of removing sulfolane at such a low initial concentration is made even more difficult because of the large volume of water to be treated and its high salt content (total dissolved solids about 8000 mg/L and hardness about 2300 mg/L). In early 1989, a call-for-proposal was sent to several California universities active in environmental research for development of a cost-effective treatment process for sulfolane

Figure 1. Location map of the Lathrop site.

49th Purdue Industrial Waste Conference Proceedings, 1994 Lewis Publishers, Chelsea, Michigan 48118. Printed in U.S.A.

Table I. Composition of Lathrop Groundwater and Discharge Limits

Feed Sample	DBCP (ppb)	EDB (ppb)	Sulfolane (ppb)
treatability study (1981)	1200	15	3000
1 year after remediation began (8/83)	300	15	1000
BAC pilot study (3/1991)	20	6	500
typical recent feed	18	1	400
discharge limits before 1994[a]	1.0	none	none
typical effluent quality[b]	0.6	0.1	400
current discharge limits[c]	0.2	0.02	57
analytical detection limits	0.1	0.02	19

[a]The basis for the design of the existing treatment system.
[b]Before the latest inoculation on 9/30/92.
[c]More frequent carbon replacement implemented to meet the new limits on DBCP and EDB.

removal. Since none of the proposed research projects could result in such a treatment process within a year, OxyChem decided to undertake an inhouse investigation.

A biological activated carbon (BAC) column process was selected for development since sulfolane was know to be removed (to form biomass, carbon dioxide and sulfate) in biological wastewater treatment processes[2,3,4] as well as the availability of the large carbon adsorbers at the Lathrop site. Furthermore, OxyChem already had success with the BAC column process for wastewater treatment.[5,6,7] With the combined treatment mechanism of biodegradation and adsorption, the BAC column can remove most organic pollutants and some heavy metals present in a wastewater stream.[8] Since periodical replacement of activated carbon is unnecessary, due to continuous bacterial utilization of adsorbed organic compounds, the BAC column process is very cost efficient.[9] A five-step laboratory feasibility and treatability study employing three benchscale BAC columns was conducted from May through November 1989. The results showed that virtually all sulfolane was removed in small BAC columns. To verify the bench BAC column performance in actual groundwater treatment, TreaTek-CRA was engaged to perform a two-phase on-site demonstration program. The first phase demonstration, employing four 10-lb pilot-scale BAC columns, was conducted from March through June 1990, further proved the BAC process capability for removing sulfolane. The second phase full-scale demonstration performed in 1992 resulted in total removal of sulfolane in the carbon adsorbers of the existing groundwater treatment system. This paper presents a summary of the laboratory and the on-site pilot study results[10] and some highlights of the full-scale BAC demonstration program. Table II presents the analytical method, methylene chloride extraction of sample followed by GC/FID analysis, developed in this project for measurement of sulfolane in water samples.

LABORATORY FEASIBILITY/TREATABILITY STUDY RESULTS

The bench laboratory feasibility and treatability study consisted of five steps: 1) carbon adsorption isotherm experiments, 2) synthetic sulfolane feed using three bench carbon columns inoculated with bacteria in a sewage treatment plant effluent, 3) BAC columns inoculated with acclimated and non-acclimated bacteria, 4) acclimated BAC columns treating Lathrop groundwater, and 5) newly inoculated, pre-saturated (with sulfolane) carbon columns for treating Lathrop groundwater.

Carbon isotherm experiments were first performed for sulfolane, DBCP, and EDB; capacity for sulfolane was found to be much less than DBCP and EDB (Figure 2). Four series of bench scale BAC column experiments were then performed. A synthetic groundwater feed (sulfolane in tapwater) was used in the first two series of column experiments, and a Lathrop groundwater sample was used in the third and fourth series. Three small (30 g Calgon F-400) carbon columns were initially inoculated with bacteria contained in an effluent sample from the trickling filter located at the OxyChem Technology Center. Breakthrough of sulfolane occurred as predicted by the isotherm capacities indicating absence of biodegradation (Figure 3). Bacteria originated from two activated sludge systems were then utilized to re-inoculate the BAC columns in the second set of bench column runs (from Day 106 through 175) in which a common flowrate of 3.0 mL/min was employed. Column 1 and Column 2 were re-inoculated with a batch reactor content which began with a petrochemical plant activated sludge sample containing sulfolane degrading bacteria; Column 3 was re-inoculated with another reactor content which began with a local POTW activated sludge sample. Sulfolane disappeared from effluent samples from Column 1 and 2 within a few days of inoculation, while its concentration decreased only slightly in Column 3 effluent. On Day 148, Column 3 was fed with the combined effluent from

Table II. Analytical Method for Measurement of Sulfolane

A. Extraction

2.0 mL of aqueous sample was extracted with 2.0 mL of methylene chloride in a small glass vial by hand-shake for 1 minute. The bottom layer which contains sulfolane in methylene chloride was withdrawn and analyzed.

B. Analysis

Instrument:	Hewlett Packard 5840 GC with Auto Sampler Model 7672A	
Detector:	Flame ionization detector	
Column:	DB-624 fused silica megabore colum	
	30 m × 0.53 mm i.d., 0.25 μm film thickness	
Injection mode:	splitless	
Injection volume:	4 μL	
Temperature program:	Initial temperature	100°C
	Initial time	2 minutes
	Program rate	7.5°C per minute
	Final temperature	260°C
	Final time	10 minutes
	Injector temperature	250°C
	Detector temperature	275°C
	Carrier	Helium at 6 cc/min

External standard: Sulfolane in methylene chloride
The retention time for sulfolane is 10.4 minutes

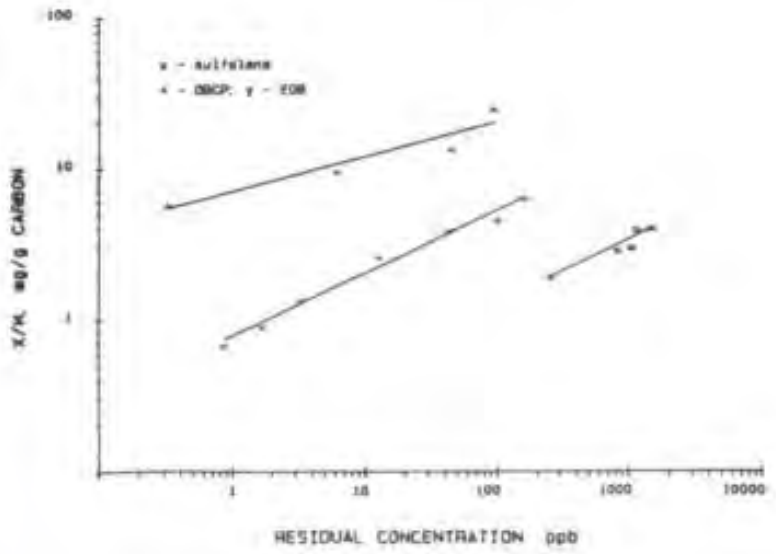

Figure 2. Adsorption isotherms for sulfolane, DBCP, and EDB.

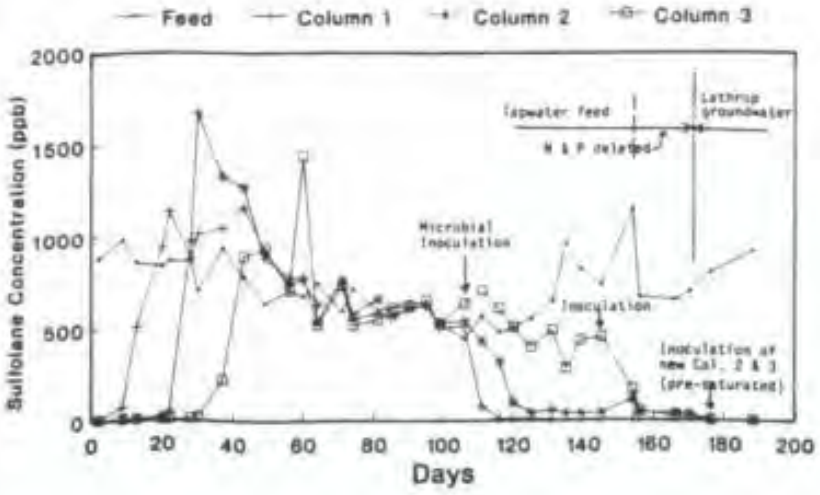

Figure 3. Bench BAC column performance data.

Column 1 and 2 for 20 hours to re-inoculate the column with sulfolane degrading bacteria in the effluent, and, within a few days, sulfolane disappeared from its effluent.

During the third set of column runs which began on Day 175, the three acclimated BAC columns were fed a Lathrop groundwater sample (pH = 6.9, dissolved oxygen = 1.9 ppm, total organic carbon = 4.2 ppm, total inorganic carbon = 84 ppm) received in a 55-gal steel drum. Columns 1, 2 and 3 were fed the as-received groundwater, aerated groundwater, and aerated groundwater spiked with 10 ppm of sugar, respectively. Sulfolane was still at or near detection limits in all effluent samples indicating similar results were achievable in treating actual groundwater even without additions of extra source of organic carbon (sucrose), nutrients (N and P) and dissolved oxygen. During the fourth set of bench BAC runs (Day 180 through Day 190, feed rate = 3.0 mL/min), Column 2 and Column 3 were cleaned and then each was repacked with 30 g of pre-saturated carbon. 0.5 g of sugar was added to about 5 liters of supernatant of the pre-saturation test solution (15 L of 2.6 mg/L which was reduced from 23.8 mg/L after adsorption on 60 g of carbon), and aeration was provided overnight to allow mass culturing of sulfolane-degrading bacteria. The broth was then utilized to inoculate the columns. Sulfolane disappeared from effluent samples within three (Column 3) to five days (Column 2). This finding was significant in that it had predicted removal of sulfolane in the existing fullsize carbon adsorbers after inoculation with sulfolane-degrading bacteria and conversion to the BAC mode of operation. Column 1 continued to remove all sulfolane in the same manner as before.

ON-SITE PILOT-SCALE TREATABILITY STUDY RESULTS

The objectives for the pilot scale on-site demonstration program were to duplicate bench-scale sulfolane removal results using the actual Lathrop groundwater and to observe and define potential full-scale operating issues such as mass-culturing and column inoculation techniques, flow pressure drop due to microbial growth, effect of biocide addition, and effluent quality stability. The pilot demonstration equipment was fabricated in TreaTek-CRA's laboratory in Grand Island, New York and shipped to the Lathrop site for installation. The primary treatment section consisted of four 4 inches diameter × 6 feet long clear PVC columns, each packed with approximately 10 pounds of Calgon F-400 activated carbon. The four columns were piped in parallel and were equipped with individual flow meters and sampling ports. Two 25 gallon tanks were connected to the inlet manifold to these columns. One tank was dedicated for mass culturing and column inoculation, while the other served as a feed or surge tank for the extracted groundwater. The feed to the pilot columns was the feed to the full size carbon adsorbers. Each of the four pilot carbon columns was fed initially at a rate of 30 L/hr (empty bed residence time = 22 min vs. 30-50 min for the existing adsorbers) to quickly saturate these pilot columns with sulfolane in the groundwater. After 35 days, the feed rate was reduced to 15 L/hr to duplicate actual plant operation.

Sulfolane-degrading bacteria were mass-cultured on site using microbial seeds prepared in the laboratory. The culturing step utilized sucrose, sulfolane, and inorganic nutrients as a source of food and vigorous aeration and agitation as means for oxygen transfer. Once the appropriate cell density was reached in the culture tank, the microbial broth was fed or "inoculated" onto the pilot columns. One of the four columns (Column 1) were not inoculated and thus served as the "control" column. The other three "BAC" columns were inoculated up to four times during the first month of operation to provide a high initial bacterial density. The four pilot columns were operated and their treatment performance monitored for a total of 83 days, starting on 3/14/90. After only two weeks of continuous operation, significant microbial growth was observed on all four carbon columns. Biocide (chlorine dioxide) addition to the groundwater feed was performed once on Day 66. Columns 1 and 2 were exposed to the biocide, while Columns 3 and 4 were shutoff from the feed stream until the chlorine concentration in the feed returned to the background level.

The effluent data for the four pilot columns showed a significant reduction in the sulfolane level during the first phase demonstration program. As expected, very low sulfolane concentrations were found in the early stage effluent samples due to physical adsorption by the fresh activated carbon. Beyond this initial carbon adsorption phase (the first two weeks), significant removal of sulfolane had continued because of biodegradation (Figure 4). The treatment performance of the four pilot columns were very similar. In fact, sulfolane removal in the non-inoculated column (Column 1) was about the same as the three inoculated columns. This was a result of inadvertent inoculation of the control column with the acclimated bacteria due to cross-contamination of the sulfolane degrading bacteria present in the effluents from the three inoculated columns which were recycled back to the collection/feed sump of the Lathrop groundwater treatment system (Figure 5). There were no noticeable visual differences in microbial growth between the four columns after biocide addition. Rapid adsorption of the free chlorine on activated carbon[12] eliminated any adverse effects of chlorination on the bacterial culture established in the pilot BAC columns. The pilot BAC columns achieved a sulfolane removal

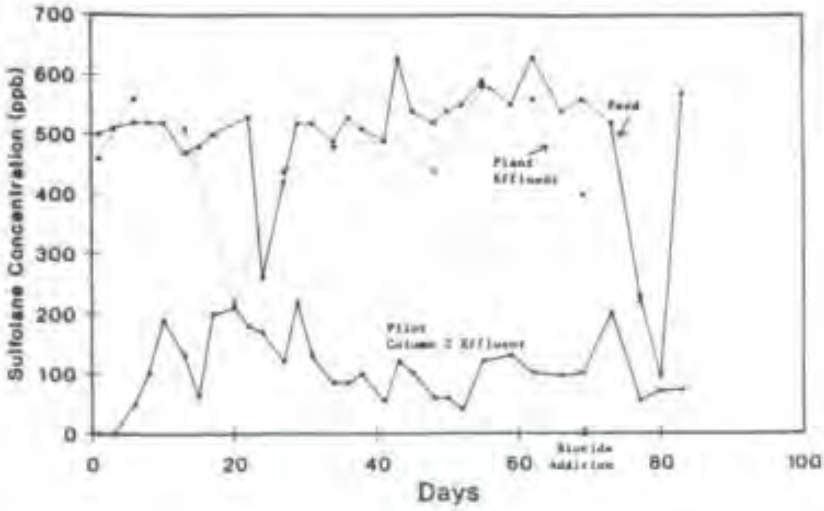

Figure 4. Pilot BAC column performance data.

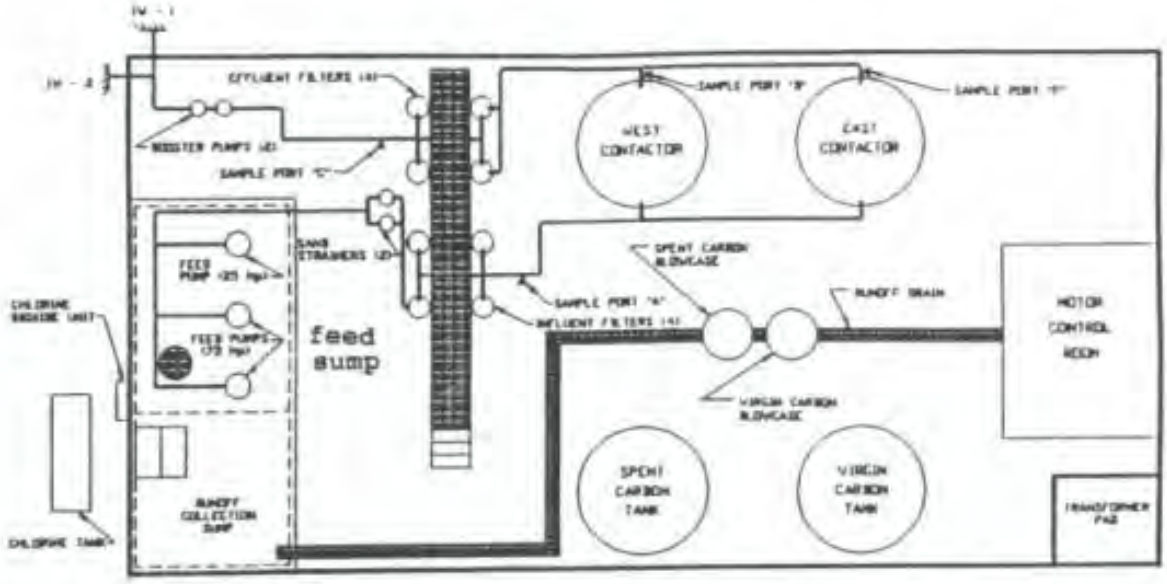

Figure 5. The Lathrop groundwater treatment system.

efficiency of 70–80% relative to the 10% removal in the existing adsorption system. If biodegradation did not take place in these columns, complete breakthrough would have occurred on or before Day 40 (based on the isotherm capacity of 2.4 mg/g for a feed of 500 ppb). The fumigants DBCP and EDB were also monitored during the pilot study; they were removed to below the discharge limits by carbon adsorption. The results thus demonstrated that the treatment capacities for removing EDB and DBCP would be maintained after conversion of the existing carbon adsorbers to the BAC mode of operation.

FULL SCALE DEMONSTRATION OF THE BAC PROCESS FOR SULFOLANE REMOVAL

The full scale demonstration was first conducted in March 1992. The sulfolane concentration in the adsorber effluent was not significantly lowered as a result of bacterial inoculation performed in a manner similar to the pilot demonstration program, except that a larger inoculation system was employed. Less than a sufficient number of sulfolane degrading bacteria were present in the inoculating culture solution (viability of the bacterial culture was not checked) and a very low dissolved oxygen (DO) in the influent were suspected to be the major causes for the failure. The West Adsorber was inoculated again on September 30, 1992. The second inoculation employed a specially prepared culturing solution which was extensively checked to ensure a high density of sulfolane degrading bacteria (see details given in the next two paragraphs), and the influent DO was raised (from about 1 to 4 ppm) by aeration at the sump. Within a few days, sulfolane had disappeared from all effluent samples (Table III). Active sulfolane degrading bacteria had populated not only in the West Adsorber

Table III. Sulfolane Data for Lathrop Groundwater Samples Taken Before and After Bacterial Inoculation[a]

Sample Date (1992)	Influent (Port A)	Effluent West Ads. (Port B)	Effluent East Ads. (Port F)	Effluent Combined (Port C)
9/14	390			340
9/21	350			530
9/23	390			440
9/28	580			450
10/05	140			49
10/07		26		
10/09		ND[b]		
10/12	370	ND	ND	ND
10/19	110	ND	ND	ND
10/21		62		
10/23		ND		
10/26	ND	62	ND	36
10/28		ND		

[a]In ppb (μg/L). Inoculation of the West Adsorber was performed on 9/30.
[b]Less than 19 ppb.

but also in the East Adsorber, as a result of cross contamination which was also observed during the pilot BAC column program. With the exception of increasing the influent DO, no other system modifications or re-inoculation of the BAC adsorbers were required to sustain the complete removal of sulfolane from the Lathrop groundwater.

Isolation and Maintenance of Sulfolane Degrading Bacteria

Mixed culture bacteria capable of degrading sulfolane were isolated from a petrochemical plant activated sludge sample; such previous samples were employed to prepare the inoculation solutions for seeding the bench and pilot BAC columns. An examination of the growth characteristics of these cultures on solid media containing sulfolane as the sole source of carbon showed the presence of at least two different bacterial species. None of these single colonies were capable of utilizing sulfolane, suggesting that the sulfolane degradation was catalyzed by microbial co-metabolic activities. Liquid cultures of sulfolane degrading bacteria were maintained in the TreaTek-CRA laboratory by regular replacement of a portion of the active cultures with fresh mineral salt media (the Stanier's mineral salt media, see Table IV), containing sucrose (100 ppm) and sulfolane (200 ppm). This task was conducted weekly to ensure an adequate supply of nutrients and organic carbon to maintain viability. Sulfolane biodegradation was checked weekly. On average, 200 ppm of sulfolane was consumed within a five day period.

Table IV. Composition of Mineral Salt Media

Stanier's Mineral Salt Media (in g/L):

- 5.9 $Na_2HPO_4 \times 7H_2O$
- 1.5 KH_2PO_4
- 0.3 NH_4Cl
- 2.0 KNO_3
- 0.1 $MgSO_4 \times 7H_2O$
- 5 mL Trace Element Solution (in g/L)
  - 50.0 EDTA
  - 22.0 $ZnSO_4 \times 7H_2O$
  - 5.54 $CaCl_2$
  - 5.06 $MnCl_2 \times 4H_2O$
  - 4.99 $FeSO_4 \times 4H_2O$
  - 1.10 $(NH_4)_6Mo_7O_{24} \times 4\ H_2O$
  - 1.57 $CuSO_4 \times 5H_2O$
  - 1.61 $CoCl_2 \times 6H_2O$

Large-Scale Biomass Production

The microbial biomass required for field inoculation was produced in the TreaTek-CRA laboratory using conventional fermentation techniques. Five gallon fermenters, filled with sterilized mineral salt media were supplemented with sucrose (1000 ppm) and sulfolane (1000 ppm). The fermenters were then inoculated with sulfolane degrading cultures (15% v/v). The fermenters were supplied with air to provide the microorganisms with the necessary DO and maintained at room temperature. Each batch of fermentation required typically a 72 hour incubation period to reach maximum growth and a cell density in the range of 10^9 colony forming units per milliliter culture (CFUs/mL). During this period, both biomass density and sulfolane degradation were monitored as part of the laboratory quality assurance program.

For the inoculation of one of the two 40,000 lb carbon adsorbers (the West Adsorber), a 20 gallon batch of fermentation broth was used to provide a minimum inoculum density of 10^6 cells/gm of activated carbon. The inoculum was shipped from the lab to the site overnight in 5 gallon plastic bottles and the bottles were packed on ice inside coolers.

BAC Treatment Performance Assessment

To optimize the sulfolane degradation process within the activated carbon beds and identify potential rate-limiting factors, DO, total organic carbon (TOC), alkalinity, turbidity, pH, nutrients (ammonia nitrogen and orthophosphate phosphorous), and biomass density were measured for many groundwater, adsorber influent and effluent samples.

Dissolved Oxygen

Biodegradation of sulfolane is an aerobic process depending on the presence of DO. Table V shows that with aeration in the sump, DO in the adsorber influent was sufficient for maintaining an aerobic environment in the adsorber, as evidenced by the more than 1 ppm DO in the effluent. The low DO (0.9 ppm) recorded before implementing the aeration was at least partially responsible for the less effective sulfolane removal observed during the first phase pilot-scale BAC demonstration program.

Nutrient Requirements

Table VI shows that TOC in groundwater decreased from 3.4 ppm in the influent to 2.1 ppm in the combined adsorber effluent, indicating a very small amount of possible increase in biomass (resulting from utilization of sulfolane and other organic contaminants) which, combined with the low turbidity of the influent, would not cause a high pressure drop problem. pH of the groundwater was nearly neutral, ideal for bacterial growth, and it would not change substantially (due to bacterial activities in the adsorbers) since the groundwater had a high alkalinity level. There were more than measurable amounts of ammonia nitrogen and orthophosphate in the groundwater samples before and after carbon treatment (Table VII). Assuming a C:N:P ratio of 100:10:1 for typical biomass, very small amounts of nitrogen and phosphorous (<1 ppm) were consumed during biodegradation of sulfolane

Table V. Dissolved Oxygen Data

Sample Date	Influent (mg/L)	Effluent-Combined (mg/L)
3/ 3/92	0.9	0.9
11/11/92	3-4	NA[a]
11/18/92	2-3	NA
11/25/92	7-8	NA
12/ 2/92	5-6	NA
12/ 9/92	4.0	2.2
12/16/92	4.5	1.7
12/23/92	1.9	3.2
12/30/92	3.5	1.2
1/ 6/93	4.2	1.7
1/13/93	4.2	1.6
2/ 8/93	4.1[b]	

[a]Not analyzed.
[b]Dropped to 2.7 mg/L 45 minutes after aeration was stopped.

Table VI. TOC, Alkalinity and Turbidity Data[a]

Sample	TOC (mg/L)	Total Alkalinity (mg $CaCO_3$/L)	Turbidity
Influent	3.4	313	< 1
Effluent-West	1.3	300	< 1
Effluent-East	2.0	300	< 1
Effluent Combined	2.1	300	< 0.1
EW-1	3.2	225	< 1
EW-2	1.8	225	< 1
EW-3	7.2	525	< 1
EW-4	4.3	400	< 1
EW-5	6.7	275	< 1
EW-6	4.3	350	< 1
EW-7	4.4	275	< 1
PW22-71	7.3	400	12

[a]For samples taken on 12/9/92.

Table VII. pH and Nutrient Data

	pH		Ammonia-N (mg/L)		Orthophosphate-P (mg/L)	
Sample	12/9/92	2/8/93	12/9/92	2/8/93	12/9/92	2/8/93
Influent	6.8	7.0	52	90	1.3	3.0
Effluent-West	6.9	6.9	51	92	1.3	2.9
Effluent-East	6.8	6.9	52	87	1.5	3.3
Effluent-Comb.	6.9	6.9	52	88	1.4	2.9
EW-1	7.2	NA	19	NA	1.1	NA
EW-2	7.2	NA	8	NA	1.3	NA
EW-3	6.7	NA	278	NA	1.3	NA
EW-4	7.0	NA	26	NA	1.4	NA
EW-5	6.7	NA	227	NA	1.6	NA
EW-6	6.8	NA	54	NA	1.3	NA
EW-7	6.9	NA	33	NA	1.4	NA
PW22-71	6.5	NA	202	NA	1.5	NA
Sump	NA	NA	NA	91	NA	4.2

[a]For samples taken on 12/9/92.

in the BAC adsorbers. Therefore no nutrient supplementation is required to sustain the BAC treatment performance.

Biomass Density

The effectiveness of BAC removal of sulfolane was dependent on the number of sulfolane degraders in the carbon adsorbers. Table VIII shows that total microbial counts in the range of 10^5 to 10^6 CFUs/gm carbon, with at least 50% sulfolane specific degrading bacteria, were found in two spent carbons samples taken several months after conversion of the full size adsorbers to the BAC mode of

Table VIII. Microbial Characterization of Lathrop Carbon Samples[a]

Sample Date[b]	Total Microbial Counts (TMC)	Sulfolane Counts (SSMC)	% Ratio (SSMC/TMC)
4/10/92	7.90×10^3	NA	NA
2/ 8/93	1.12×10^6	7.96×10^5	71
3/25/93	8.97×10^6	4.72×10^6	53

[a]Colony forming units (CFU) per g. The results are an average of microbial counts for carbon from East and West Adsorbers.
[b]Biocide was applied for 24 hours each on the following dates: 3/2/93, 3/5/93, 3/12/93, 3/19/93, and 3/26/93.

operation. Table IX shows that large numbers of viable bacteria, mostly sulfolane degraders, were found in the groundwater sump, adsorber influent and effluent samples and, more significantly, that such numbers were not substantially reduced after repetitive additions of biocide.

SUMMARY

Since October 1992, sulfolane has been removed from Lathrop groundwater (Figure 6) in the full scale application of the BAC treatment process which was developed in the OxyChem's Grand Island Technology Center, utilizing an acclimated seed obtained from a Texas activated sludge system employed for treating a sulfolane containing petrochemical plant wastewater. For more than ten years, activated carbon adsorption treatment at the Lathrop groundwater remediation site was not effective in removing sulfolane since the carbon's capacity for sulfolane was much smaller than for the target compounds (DBCP and EDB). Maintaining a large population of viable sulfolane degrading bacteria in the inoculant and optimizing the treatment conditions (e.g., providing > 2 mg/L dissolved oxygen in the feed) were the keys to the successful removal of the poorly adsorbed sulfolane from more than 600 gal/min of groundwater in the two existing 40,000 lb carbon adsorbers. Therefore, a

Table IX. Microbial Characterization of Lathrop Groundwater Samples[a]

Sample Date[b]		Total Microbial Counts (TMC)	Sulfolane Counts (SSMC)	% Ratio (SSMC/TMC)
2/ 8/93	Influent	22.7	10.3	45
	Effluent-West	19.4	7.9	41
	Effluent-East	18.2	7.9	43
	Effluent-Combined	17.5	8.0	46
	Sump	18.4	8.4	46
3/ 1/93	Influent	15.4	8.8	57
	Effluent-West	22.2	15.9	72
	Effluent-East	19.8	15.2	77
	Effluent-Combined	18.6	14.8	80
	Sump	NA	NA	NA
3/ 3/93	Influent	14.0	8.7	62
	Effluent-West	16.2	12.3	76
	Effluent-East	15.3	9.0	59
	Effluent-Combined	17.2	12.9	75
	Sump	7.9	6.0	76
3/ 8/93	Influent	14.4	8.1	56
	Effluent-West	15.3	9.0	59
	Effluent-East	9.0	7.1	79
	Effluent-Combined	14.2	10.6	75
	Sump	6.6	5.4	82
3/15/93	Influent	6.7	2.8	42
	Effluent-West	7.9	1.9	24
	Effluent-East	7.0	2.1	30
	Effluent-Combined	6.3	2.2	35
	Sump	11.2	5.0	45
3/22/93	Influent	18.8	8.0	43
	Effluent-West	13.5	6.3	47
	Effluent-East	9.1	6.6	72
	Effluent-Combined	6.8	4.5	66
	Sump	2.8	1.0	36
3/29/93	Influent	13.8	8.7	63
	Effluent-West	32.4	22.2	69
	Effluent-East	15.9	8.4	53
	Effluent-Combined	24.0	16.2	68
	Sump	1.4	0.8	57

[a]In 1000 CFU/mL.
[b]Biocide was applied for 24 hours each on the following dates: 3/2/93, 3/5/93, 3/12/93, 3/19/93, and 3/26/93.

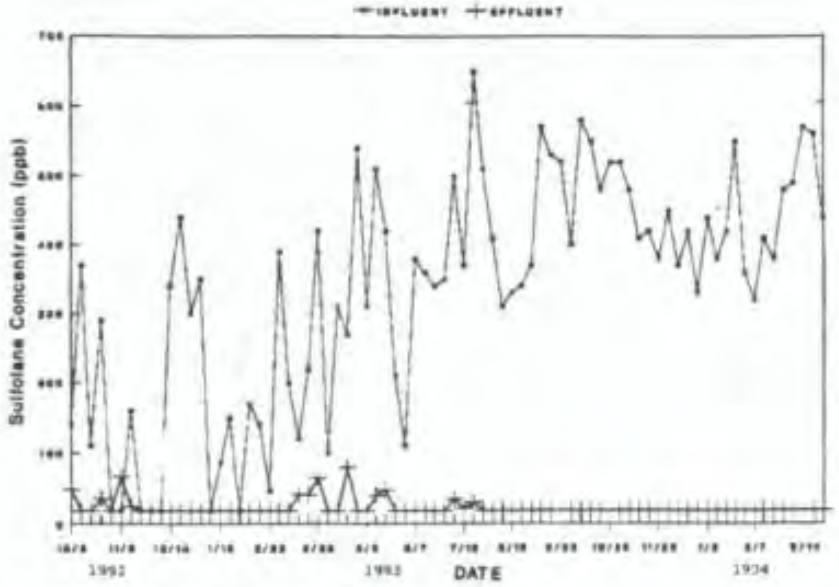

Figure 6. Full scale BAC adsorber performance data.

Table X. Typical Treatment Performance Data[a]

Sample Date (1993)	Influent (Port A)			Effluent West Ads. (Port B)			Effluent Combined (Port C)			Effluent East Ads. (Port F)		
	DBCP	EDB	SULF	DBCP	EDB	SULF	DBCP	EDB	SULF	DBCP	EDB	SULF
7/26	11	1.5	510				ND	ND	ND			
Composite 7/21, 7/23, 7/26				ND	ND	22				ND	ND	20
7/28	11	1.8	380				ND	ND		0.17	ND	
7/30	10	1.4	350				ND	ND				
8/2	10	1.4	410				ND	ND	ND			
Composite 7/28, 7/30, 8/2				0.21	ND	21				ND	ND	ND
8/4	11	1.5	380	ND	ND		ND	ND				
8/6	10	1.4	320				ND	ND				
8/9	9.7	1.3	310				0.13	0.022	ND			
Composite 8/4, 8/6, 8/9				ND	ND	26				ND	ND	ND
8/11	10	1.5	330				ND	ND		0.14	0.03	
8/13	10	1.6	310				ND	ND				
8/16	9.0	1.4	330				0.19	ND	ND			
Composite 8/11, 8/13, 8/16				0.18	ND	ND				0.16	0.024	ND
8/18	9.4	1.3	350	0.24	0.03		0.19	ND				
8/20	13	1.7	350				0.28	0.05				
8/23	13	1.8	340				0.29	0.05	ND			
Composite 8/18, 8/20, 8/23				0.33	0.052	ND				0.23	0.039	ND
8/25	11	1.5	310				0.27	0.05		0.28	0.04	
8/27	11	1.2	400				0.23	0.03				
8/30	11	1.2	370				0.16	0.023	ND			
Composite 8/25, 8/27, 8/30				0.13	ND	ND				0.22	0.059	ND
9/1	9.8	1.3					ND	ND				
9/3	9.9	1.2					ND	ND				
Composite 9/1, 9/3				0.15	ND	ND				ND	ND	ND
9/8	8.3	1.1					ND	ND		ND	ND	
9/10	8.1	1.1					ND	ND				
9/13	9.0	1.6					ND	ND				
Composite 9/8, 9/10, 9/13				ND	ND	ND				ND	ND	ND
9/15	8.3	1.3					0.22	0.062				
9/17	8.3	1.3					0.18	0.057				
9/20	9.1	1.2					0.19	0.037				
Composite 9/15, 9/17, 9/20				ND	ND	ND				0.16	ND	ND
9/22	8.8	1.4					0.25	0.029		0.27	0.023	
9/24	8.5	1.3					0.29	0.049				

[a]In ppb (μg/L). Analytical detection limits for sulfolane, DBCP, and EDB are 19, 0.1, and 0.02 ppb, respectively.

potentially very costly requirement for removing sulfolane from Lathrop groundwater has been met at no incremental cost to the remediation project. Table X presents typical Lathrop groundwater treatment performance data showing excellent adsorption removal of DBCP and EDB as well as complete biodegradation of sulfolane in the BAC adsorbers.

ACKNOWLEDGMENTS

The activated sludge samples, which contained sulfolane degrading bacteria, employed in this project as the seeding culture were provided by Dr. Charles C. Chou of Shell Development Company. Donald McLeod managed the pilot-BAC demonstration program. Karen Jackson and Gregory Bonk assisted in microbial identification, culture maintenance, biomass production and samples analyses.

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11 BIOLOGICAL ACTIVATED CARBON PROCESS FOR REMOVING SULFOLANE FROM GROUNDWATER

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INTRODUCTION

Since mid-1982, Occidental Chemical Corporation (OxyChem) has been operating a groundwater remedial program at a former pesticide manufacturing site in Lathrop, California (Figure 1). The program includes a continuous groundwater extraction system, an activated carbon treatment system (two parallel 40,000 lbs upflow adsorbers) for removing chemicals from the groundwater, and a two-well reinjection system for returning the treated groundwater into a deep (310 ft below the surface) saline aquifer. The target chemicals for this remedial program are the fumigant pesticides dibromochloropropane (DBCP) and ethylene dibromide (EDB). The treatment level of below 1 ppb for each fumigant has been consistently met since the start of the remedial program.

Along with the fumigants, there is also a detectable level of a compound known as sulfolane (tetramethylene sulfone, see Figure 2) in the groundwater. Sulfolane is an important process chemical for the petroleum and chemical industries. It has outstanding solvent properties for most classes of organic compounds and many common polymers and is chemically and thermally stable. Since sulfolane is soluble in water, it is not effectively removed in the existing carbon adsorption system. Toxicity evaluation conducted during the original design of the remedial program concluded that specific treatment for sulfolane was unnecessary because of no toxicity was expected due to its presence at the low concentration (about 2000 ppb) was found in the groundwater.[1] The level of

Figure 1. Location map of the Lathrop site.

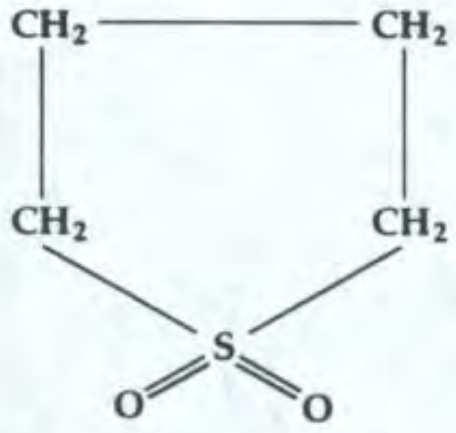

Figure 2. Structure of sulfolane.

46th Purdue Industrial Waste Conference Proceedings, 1992 Lewis Publishers, Inc., Chelsea, Michigan 48118. Printed in U.S.A.

sulfolane in the Lathrop groundwater has since declined to about 500 ppb at the present time; concentrations for DBCP, EDB and other fumigants have also declined during the same period.

Recent considerations for reclassifying the deep saline aquifer in the Lathrop area for productive use have prompted the California Water Quality Control Board to request OxyChem to review potential treatment options for removing sulfolane prior to reinjection. Several treatment alternatives, including biodegradation, chemical oxidation, and adsorption using a different activated carbon or other adsorbents, were reviewed. The task of removing sulfolane at such a low initial concentration is made even more difficult because of the large volume of water (500 gal/min) to be treated and its high salt content (total dissolved solids about 8000 mg/L and hardness about 2300 mg/L). In early 1989, a call-for-proposal was sent to several California universities which were known to be active in environmental research for development of a cost-effective treatment process for sulfolane removal. Since none of the proposed research projects would produce actual treatment results in the first year, OxyChem decided to undertake an in-house investigation.

A biological activated carbon (BAC) column process was selected for development since sulfolane was reported to be removed (to form biomass, carbon dioxide and sulfate) in biological wastewater treatment processes[2,3,4] and the availability of the large carbon adsorbers at the Lathrop site. Furthermore, OxyChem already had success with the BAC column process for wastewater treatment.[5,6,7] With the combined treatment mechanism of biodegradation and adsorption, the BAC column can remove most organic pollutants and some heavy metals present in a wastewater stream.[8] Since periodical replacement of activated carbon is unnecessary, due to continuous bacterial utilization of adsorbed organic compounds, the BAC column process is very cost efficient.[9] A five-step bench scale feasibility and treatability study was conducted from May thru November 1989. The results showed that virtually all sulfolane was removed in small BAC columns. To verify the bench BAC column performance in actual groundwater treatment, TreaTek, Inc., the environmental service subsidiary of OxyChem, was engaged to perform a two-phase on-site demonstration. The first phase demonstration, employing four 10-lb pilot BAC columns, was conducted from March thru June 1990. This pilot study further proved the BAC process capability for removing sulfolane. The second phase full-scale demonstration will soon begin. This paper presents the experimental results from the bench- and pilot-scale BAC column studies.

EXPERIMENTAL SECTION

A. Analytical Methods

Considerable effort was devoted to develop a GC method for measuring sulfolane at the low concentration levels found in the feed and effluent samples. Ten mL of acidified (to pH 2 using 9N H_2SO_4 to prevent or stop biodegradation) water samples was pipetted into a glass tube (16 cm x 150 mm) equipped with a Teflon-lined screw cap. One and one half ml of methylene chloride was added, and the capped mixture was shaken for 10 min on a shaker (Model S-500 by Kraft Apparatus, Inc), followed by 10 minutes of centrifugation. The bottom (methylene chloride) layer was then transferred

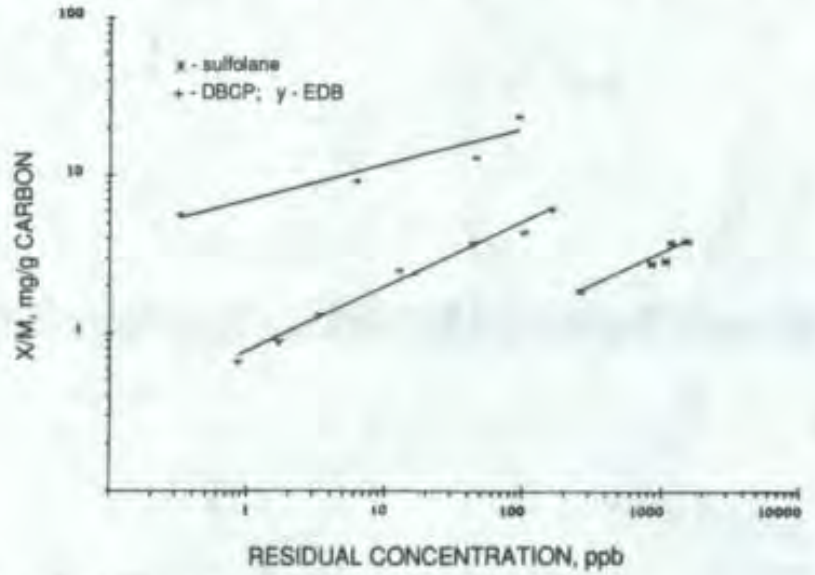

Figure 3. Adsorption isotherms for sulfolane, DBCP, and EDB.

Table I. GC Area Count Data for Sulfolane Standard Solutions

Standard solutions were prepared in methylene chloride.

250 pbb	500 pbb	1 ppm	2 ppm	5 ppm	10 ppm	1 ppm[a] Spike
118	276	542, 671	1432	3437, 3691	7738	2588, 2664 2512
60, 97 72, 107	278,294 303, 314	588, 525	1250, 1270	3362, 3656	7214, 6788 6470, 6375	2327, 2235 2395
	216	526, 569	1319, 1139	3460	7034	2150, 2211

[a] Acidified water solution;

$$\text{Sulfolane (ppb)} = \frac{\text{corrected count}}{2281} \times 1000$$

$$\text{Corrected count} = \text{observed count} \times \frac{\text{2 ppm count}}{1260}$$

to a sample vial for GC/FID analysis. With both methylene chloride and aqueous standard solutions run along with each batch of samples, the method was capable of detecting sulfolane at 10 ppb, even though the GC area counts did vary from time to time. Table I presents three series of the calibration results (performed on different dates during the study) and the procedure for calculation of sulfolane concentration. DBCP and EDB concentration were measured by hexane extraction followed by GC/ECD analysis; a 1 ppb detection limit was established for these two compounds.

B. Feasibility and Treatability Study

The bench laboratory feasibility and treatability study consisted of five steps: (1) carbon adsorption isotherm experiments, (2) synthetic sulfolane feed using three bench carbon columns (30 g) inoculated with bacteria in a sewage treatment plant effluent, (3) BAC columns inoculated with acclimated and non-acclimated bacteria, (4) acclimated BAC columns treating Lathrop groundwater, and (5) newly inoculated, pre-saturated (with sulfolane) carbon columns for treating Lathrop groundwater.

Carbon isotherm experiments were performed for sulfolane, DBCP, and EDB. The experimental procedure and test results are shown in Tables II and III. Two activated carbons—Calgon F-400 (the carbon in the existing adsorbers) and Polifos Actibon (a wood based carbon)—were tested for adsorptive capacity for sulfolane in pure water.

Four sets of bench scale BAC column experiments were performed. Synthetic feed (sulfolane in tapwater) was used in the first two column sets, and a Lathrop groundwater sample was used in the third and fourth sets. Three small (30 g Calgon F-400) carbon columns were first inoculated with bacteria contained in an effluent sample from the trickling filter located at the OxyChem Technology Center. Table IV presents the details for the first set of bench BAC column runs which lasted for 106 days. The objective was to induce biodegradation of sulfolane in bench carbon columns or to produce a large reduction in sulfolane concentration of the effluent after breakthrough. Figure 4 depicts the equipment layout for the bench BAC column runs.

Bacteria originated from two activated sludge samples were utilized to re-inoculate the BAC columns in the second set of bench column runs (from Day 106 thru 175) in which a common flowrate of 3.0 mL/min was employed. An acclimated sludge was obtained from a Gulf coast Shell refinery activated sludge system which was treating a sulfolane-containing wastewater,[2] and a non-acclimated sludge was obtained from the Niagara Wheatfield POTW. Each of the two sludge samples was diluted (to 50%) and placed in a 1-L bottle. A batch air-stripping and biodegradation experiment was performed by aerating a 2 ppm sulfolane solution and the spiked (to 2 ppm sulfolane) diluted sludge solutions. Sulfolane was re-spiked several times to the batch bottle reactor containing the Shell refinery sludge to replenish the amount biodegraded. Table V summarizes the results of the batch aeration study. Column 1 and Column 2 were then re-inoculated with the reactor content started with the Shell sludge; Column 3 was re-inoculated with the reactor content started with the POTW sludge. On Day 148, Column 3 was fed with the combined effluent from Column 1 and 2 for 20 hours to re-inoculate the column with sulfolane degrading bacteria in the effluent.

The third set of column runs began on Day 175. The three acclimated BAC columns were fed at a common flowrate of 3.0 mL/min with a Lathrop groundwater sample (pH = 6.9, dissolved oxygen = 1.9 ppm, total organic carbon = 4.2 ppm, total inorganic carbon = 84 ppm) received in a 55-gal

Table II. Carbon Adsorption Isotherm Data for Sulfolane

Isotherm sample volume: 50 mL sample + 4 mL total of blank water and carbon slurry
(A - 5 mg/mL, B - 20 mg/L)
Carbon type: pulverized activated carbons - Polifos Actibon, Calgon F-400

Experimental Procedure:
Add the specified amount of carbon slurry/blank water to each of the 125-mL Erlenmeyer flask containing 50 mL of the sample. Shake for two hours, and then separate the carbon, by filtration, to produce a clear filtrate. Measure sulfolane concentration using GC. Calculate the carbon capacities (X/M)[a].

No.	Carbon dose/ slurry/blank (mg)/(mL)/(mL)	Calgon F-400 ppb (GC count)	Calgon F-400 X/M (mg/g)	Polifos Actibon ppb (GC count)	Polifos Actibon X/M (mg/g)
Control	0/0.0/4.0	1852 (966,4)[b]		1852	
1	5/A1.0/3.0	1490 (777,5)	3.91	1836 (958,3)	0.17
2	10/A2.0/2.0	1143 (596,5)	3.83	1645 (858,4)	1.17
3	15/A3.0/1.0	1041 (543,6)	2.92	1478 (771,3)	1.35
4	20/B1.0/3.0	822 (429,3)	2.78	1775 (926,2)	0.21
5	30/B1.5/2.5	571 (298,5)	2.79[c]	1428 (745,4)	0.76
6	50/B2.5/1.5	253 (132,2)	1.86	1503 (784,4)	0.38

Freundlich adsorption isotherm parameters $X/M = k \times C_f^{1/n}$

k	0.1805
1/n	0.4168
Correlation coefficient	0.9511

[a] Adsorptive capacities of carbon for sulfolane in the distilled water is calculated for each isotherm sample.

$$X/M\ (mg/g) = (C_0 - C_f,\ ppb) \times V\ (liter) / carbon\ dose\ (mg)$$

[b] Average GC count and number of measurements.
[c] Excluded from the isotherm correlation.

steel drum. Columns 1, 2 and 3 were fed the as-received groundwater, aerated groundwater, and aerated groundwater spiked with 10 ppm of sugar, respectively.

Two newly inoculated pre-saturated carbon columns were employed in the fourth set of bench BAC runs (Day 180 thru Day 190, feed rate = 3.0 mL/min). About 60 g of Calgon F-400 carbon was added to 15 liters of sulfolane solution prepared from the combined BAC effluent of the third set runs. After seven hours of agitation, sulfolane concentration decreased from 23.8 to 2.6 ppm. The carbon was saturated since the sulfolane loading of 5.3 mg/g was above the 4.8 mg/g estimated from Figure 3. Column 2 and Column 3 were cleaned and then each was repacked with 30 g of the pre-saturated carbon. 0.5 g of sugar was added to about 5 liters of supernatant from the pre-saturation test solution, and aeration was provided overnight to allow mass culturing of sulfolane-degrading bacteria. The broth was then utilized to inoculate the columns.

C. Pilot BAC Demonstration

The objectives for the pilot scale on-site demonstration program were to duplicate bench-scale sulfolane removal results using the groundwater feed at the Lathrop site and to observe and define potential full-scale operating issues such as mass-culturing and column inoculation techniques, flow pressure drop due to microbial growth, effect of biocide addition, and effluent quality stability.

The pilot demonstration equipment was fabricated in TreaTek's laboratory in Grand Island, New York and shipped to the Lathrop site for installation. The pilot unit was assembled in a skid-mounted module for ease of shipment and operation. The equipment layout and flow schematic is shown in

Table III. Carbon Adsorption Isotherm Data DBCP and EDB

Water sample: Lathrop groundwater sample spiked with 600 ppb of dibromochloropropane (DBCP) and 300 ppb of ethylene dibromide (EDB) by adding 4 mL of DBCP solution (600 mg/L - 50 μl per 180 mL pure water) and 2 mL of EDB solution (600 mg/L - 50 μl per 190 mL pure water) to 1 gallon of the groundwater sample

Isotherm sample volume: 43 mL (40 mL groundwater sample and 3 mL total of carbon slurry and distilled water

Carbon type: pulverized Calgon F-400; carbon slurry - 1 mg/mL and 10 mg/mL

pH = 7.0 (unadjusted)

Experimental Procedure:

Add a total of 3 mL of carbon slurry and distilled water, in accordance with the following table, and then fill the vial with spiked groundwater sample (about 40 mL). Shake for at least two hours, and then separate the carbon, by settling and then centrifugation, to produce a clear supernatant. Analyze the sample for DBCP and EDB.

		DBCP		EDB	
No.	Carbon Dose[a]	conc. (ppb)	X/M[b] (mg/g)	conc. (ppb)	X/M (mg/g)
Control 1	0/0.0/1	657		300	
1	1/1.0/1	93	24.04	162	6.11
2	2/2.0/1	45	13.05	101	4.36
3	3/3.0/1	6.2	9.26	43	3.74
4	5/0.5/10	0.32	5.60	12.6	2.51
5	10/1.0/10	<0.30		3.3	1.29
6	15/1.5/10	<0.30		1.7	0.87
7	20/2.0/10	<0.30		0.85	0.65
Control 2	0/0.0/1	648		308	

Freundlich adsorption isotherm parameters $X/M = k \times C_f^{1/n}$

k	6.7438	0.7442
1/n	0.2285	0.4143
Correlation coefficient	0.9475	0.9928

[a] Values shown are, respectively, weight of carbon per sample (mg), volume of carbon slurry (mL), and concentration of carbon slurry (mg/mL).

[b] X/M (mg/gm carbon) = (Co - C_f, ppb) × V (liter) / carbon dose (mg)

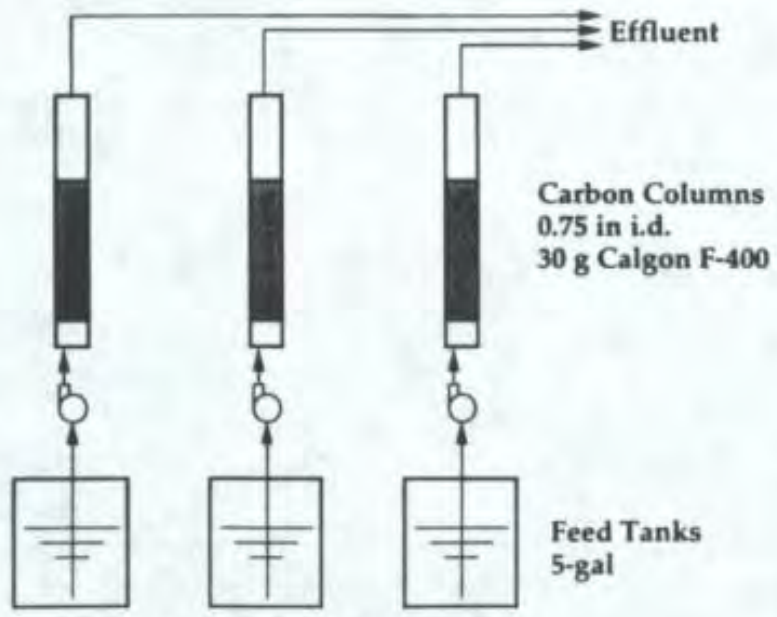

Figure 4. Equipment layout for the bench BAC column study.

Table IV. Bench BAC Column Experiments for Removing Sulfolane

A. BAC Column Start-Up Procedure:

1. Charge each glass column (0.75 inch i.d.) with 30 g of Calgon F-400 carbon.
2. Wet and then drain the carbon column with three 100-mL aliquots of tapwater.
3. Prepare the feed solution - 1 mg sulfolane/L (nominal) by diluting a stock 2000 mg/L. Add 50 mL of the OxyChem Techology Center trickling filter effluent and 1 mL of nutrient solution (1 mg NH_4-N and 0.2 mg PO_4-P per mL) to two liters of the feed solution, and aerate the solution overnight. Seed the column with the inoculated batch of feed by pumping it upflow thru the carbon column at the specified flowrate.
4. Switch to a feed batch containing no TF effluent, and continue pumping thru the column at the specified flowrate.
5. Take daily effluent samples. Analyze the effluent sample, by GC, for sulfolane, and record on the data sheet.
6. Calculate sulfolane concentration by comparing the area counts with that of the 2 ppm standard (prepared in methylene chloride).

B. BAC Column Operating Conditions[a]:

Column Number	Carbon Type	Feed Composition Sucrose (mg/L)	Feed Composition Sulfolane (mg/L)	Flowrate (mL/min)	EBRT - (min)	Note
1	F-400 (fresh)	0	1	3.0	22	b
2	F-400 (fresh)	10	1	3.0	22	c
3	F-400 (fresh)	10	1	1.8	36	d

Notes:

[a] The equipment layout for the BAC column experiment is shown in Figure 4.

[b] Control run, with no readily degradable sucrose serving as food to the seed bacteria. The empty bed residence time (EBRT) is equivalent to a 40,000 lb adsorber treating groundwater at a rate of 500 gal/min.

[c] Same as 1, except for the addition of sucrose in the feed. Bacterial culture will establish in the column as a result of utilization of sucrose.

[d] The EBRT for an adsorber treating groundwater at a flowrate of 300 gpm.

Figure 7. The primary treatment section consisted of four 4" diameter × 6' long clear PVC columns, each packed with approximately 10 pounds of Calgon F-400 activated carbon. The four columns were piped in parallel and were equipped with individual flow meters and sampling ports. Two 25 gallon tanks were connected to the inlet manifold to these columns. One tank was dedicated for mass culturing and column inoculation, while the other served as a feed or surge tank for the extracted groundwater. The feed to the pilot unit was the feed to the full size carbon adsorbers. The effluent from the four pilot columns and any spills or overflows were drained directly back to the water collection sump within the existing Lathrop treatment system complex. This sump served as both a drain collection tank and a feed tank for the carbon treatment adsorbers.

The experimental strategy for this pilot biological treatment program was based on several key operating parameters including hydraulic and sulfolane loadings, microbial inoculation, biocide exposure and analytical monitoring.

Table V. Batch Air Stripping and Biodegradation Data

Days	Non-Seeded Stripping Reactor	POTW Seeded Reactor	Shell Seeded Reactor
0	1400	1400	600
1			25/625[a]
3	1375	1320	
4	1350		190/1180
6			ND_{10}/1500
7			ND_{10}/1500
10	1275		ND_{10}
14		1100	
24		ND_{10}	

[a] Sulfolane concentration before and after spike

1. System Feed Rate. Each of the four pilot carbon columns was fed initially at a rate of 30 L/hr (empty bed residence time = 22 min vs. 30–50 min for the existing adsorbers) to quickly saturate these pilot columns with sulfolane in the groundwater. This would eliminate physical adsorption as a factor for further sulfolane removal and enable the study to focus on biodegradation. With a flow rate of 30 L/hr and a feed sulfolane concentration of 495 ppb, the pilot carbon columns were expected to be fully loaded (i.e., reaching the isotherm capacity of 2.4 mg/g, Figure 3) in about 35 days. Following this period, feed was reduced to 15 L/hr to duplicate actual plant operation.

2. Microbial Inoculation. Sulfolane-degrading bacteria were mass-cultured on site using microbial seeds prepared at TreaTek's laboratory. The culturing step utilized sucrose, sulfolane, and inorganic nutrients as a source of food and vigorous aeration and agitation as means for oxygen transfer. Once the appropriate cell density was reached in the culture tank, the microbial broth was fed or "inoculated" onto the pilot columns. One of the four columns (Column 1) were not inoculated and thus served as the "control" column. The other three "treatment" columns were inoculated up to four times during the first month of operation to provide a high initial bacterial density.

3. Biocide Exposure. One of the more important operating issues not addressable during the bench-scale study was the effect of biocide addition on sulfolane removal in BAC columns. Chlorine dioxide, as a biocide, has periodically been applied to the Lathrop groundwater feed to prevent excessive growth of bacteria in the inlet zone which would produce a high pressure drop across the carbon adsorbers. To observe any adverse effect resulting from biocide addition, one of the three treatment columns and the control column were exposed to the groundwater feed when biocide was added, while the other two treatment columns were shut off until the chlorine level in the feed returned to the background level.

4. Column Performance Monitoring. A sampling protocol was designed for this pilot demonstration to assess both sulfolane biodegradation and its potential adverse effects on treatment efficiency for removing DBCP and EDB. A single feed sample to the pilot columns was taken three times a week for analysis of sulfolane, DBCP and EDB. Individual effluent from the four pilot columns was also analyzed for sulfolane, DBCP and EDB on a similar frequency. These results were compared to the effluent quality from the full-scale treatment plant. Several random feed and effluent samples were also taken and characterized for biodegradation by-products. To ensure the proper QA/QC protocol was used for this pilot study, all feed and effluent samples from the pilot columns were analyzed along with the routine Lathrop plant samples. Weston Analytics, the analytical laboratory responsible for Lathrop plant monitoring for the past eight years, performed the analyses for the study.

RESULTS AND DISCUSSION

A. Feasibility and Treatability Study

1. Carbon Adsorption Isotherm Experiments. Table II shows that the bituminous coal-based Calgon F-400 had a higher adsorptive capacity for sulfolane than the wood-based Actibon, and Table III shows that the Calgon carbon's capacities for DBCP and EDB were much higher than for sulfolane. Figure 3 shows that carbon (Calgon F-400) had a much lower capacity for sulfolane than either DBCP or EDB. Breakthrough of sulfolane is thus expected from an carbon adsorber designed and operated for removing DBCP or EDB.

2. Bench BAC Column Experiments. Figure 5 results show that sulfolane concentrations in the effluent samples started to increase after one week for Column 1 (3.0 mL/min, without sugar), three weeks for Column 2 (3.0 mL/L, with 10 mg/L sugar), and five weeks for Column 3 (1.8 mL/min, with 10 mg/L sugar). The delayed breakthrough of sulfolane in Column 2 (relative to Column 1) might due to adsorption of the compound on the large amount of biomass resulting from bacterial utilization of the sucrose in the feed.[10] Calculated at the times of complete breakthrough, the cumulative removal of sulfolane were 1.56 mg/g, 2.59 mg/g, and 2.95 mg/g in Columns 1, 2 and 3, respectively. Up to the breakthrough times, no significant bacterial utilization of sulfolane had taken place since the removals were all below the isotherm capacity (about 3 mg/g, Figure 3). The sulfolane concentration of effluent samples from all three carbon columns were only slightly lower than the feed from Day 60 thru 105, indicating the adsorptive capacity of these columns for sulfolane was nearly exhausted.

Table V shows that no appreciable loss of sulfolane was observed in a control reactor (without sludge) showing sulfolane was not removed by air stripping. Rapid decline in sulfolane concentration was found in the bottle reactor containing the acclimated refinery sludge but not in the other reactor containing the non-acclimated POTW sludge. Sulfolane concentration in the POTW sludge reactor

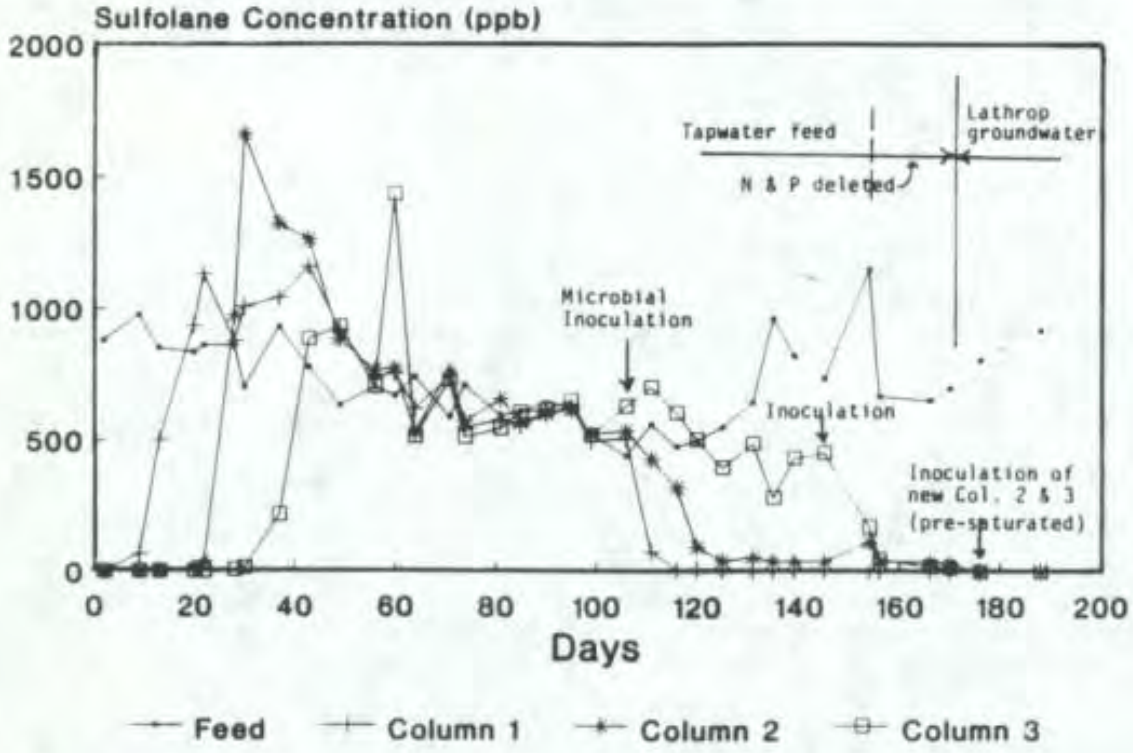

Figure 5. Bench BAC column performance data.

declined after two weeks, indicating gradual acclimation. The Figure 5 results for Day 106 thru 175 show that sulfolane was removed in the two bench BAC columns inoculated with the highly acclimated bacteria originated from the refinery sludge. Column 1 having no sugar in its feed actually performed better; sulfolane was not detected (less than 10 ppb) in the effluent only one week after the inoculation. Figure 6 shows GC spectra for the effluent samples taking on Day 125 – no sulfolane in the Column 1 effluent, trace quantity in the Column 2 effluent, and a high residual sulfolane concentration in the Column 3 effluent. On about Day 150, contamination or inadvertent inoculation of sulfolane-degrading bacteria to the feed solution tanks had resulted in active biodegradation of sulfolane causing its disappearance in the feed solutions within two days after preparation. The feed solution tanks were subsequently washed with soap to prevent bacterial utilization of sulfolane. Column 3 which was inoculated with acclimated bacteria originated from the Wheatfield POTW sludge achieved only partial removal of sulfolane. Sulfolane concentration decreased steadily and finally disappeared in the effluent from Column 3 after feeding on Day 148 for twenty hours at the normal flow rate with the combined effluent from Column 1 and Column 2 containing active bacteria capable of degrading sulfolane. Complete removal of sulfolane continued in the sugar-free column (Column 1) after deleting N-P nutrient from the feed on Day 170.

The Figure 5 results for Day 175 thru 190 show that the three BACs, having established a capability for removing sulfolane from the tapwater solution, were capable of removing sulfolane in the ground-

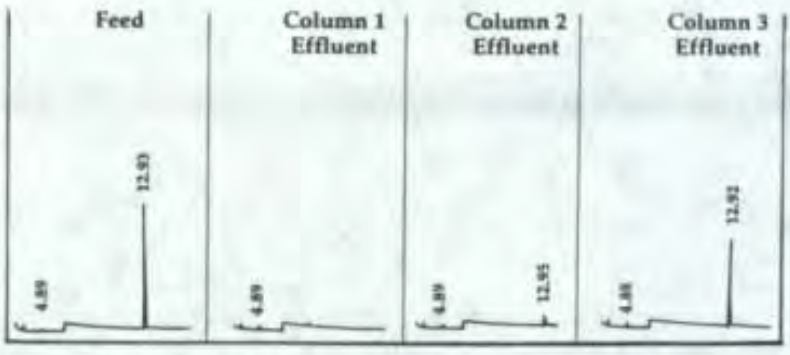

Figure 6. GC spectra for bench BAC column effluent samples.

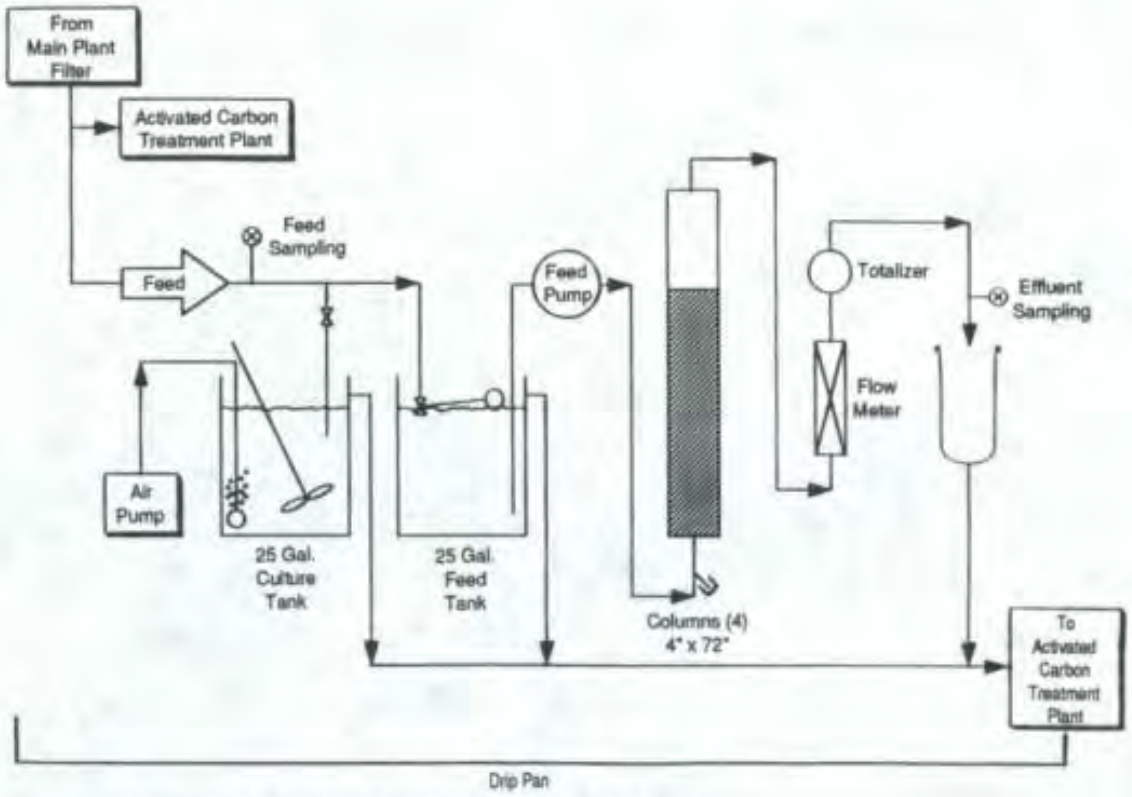

Figure 7. Equipment layout for the pilot BAC column study.

water sample, even without additions of extra organic carbon (sucrose), nutrients (N and P) and dissolved oxygen. The groundwater sample became cloudy upon aeration as a result of precipitation of iron hydroxide and/or calcium carbonate. The Figure 5 results for Day 180 thru 190 show that sulfolane disappeared from effluent samples within three (Column 3) to five days (Column 2) after starting up the two newly inoculated columns filled with sulfolane-saturated carbon. This finding is significant in that it predicts removal of sulfolane in the existing full-size carbon adsorbers once they are properly inoculated with sulfolane-degrading bacteria and converted to the BAC mode of operation. Column 1 continued to remove all sulfolane in the same manner as before.

B. Pilot BAC Demonstration

The four pilot columns were operated and their treatment performance monitored for a total of 83 days, starting on 3/14/90. Columns 2, 3, and 4 were inoculated with organisms on Days 1, 17, and 24. Column 1 was not inoculated and designated as the control column. After only two weeks of continuous operation, significant microbial growth was observed on all four carbon columns. Biocide (chlorine dioxide) addition to the groundwater feed was performed once on Day 66. Columns 1 and 2 were exposed to the biocide, while Columns 3 and 4 were shutoff from the feed stream until the chlorine concentration in the feed returned to the background level. To better compare the performance of each individual pilot column and assess treatment trends as impacted by inoculation and biocide exposure, the pilot results are presented in Figures 8, 9, and 10.

Figure 8 shows that the treatment performance of the four pilot columns were very similar; sulfolane removal in the non-inoculated column (Column 1) was about the same as the three inoculated columns. Presumably this was the result of inadvertent inoculation of the control column with the acclimated bacteria due to cross-contamination and/or natural growth of the sulfolane degrading bacteria present in the effluent (from the other three columns) which was recycled back to the collection sump of the on-site treatment system. There were no noticeable visual differences in microbial growth between the four columns after biocide addition. Rapid adsorption of the free chlorine on carbon[11] would reduce or eliminated any adverse effects of chlorination on the bacterial culture established in the pilot BAC columns. The sulfolane concentration data obtained during the pilot demonstration program are summarized in Table VI. The pilot BAC columns achieved a sulfolane removal efficiency of 70 to 80% relative to the 10% removal in the existing adsorption system. It is important to note that there were no definitive increases in sulfolane concentration in effluent

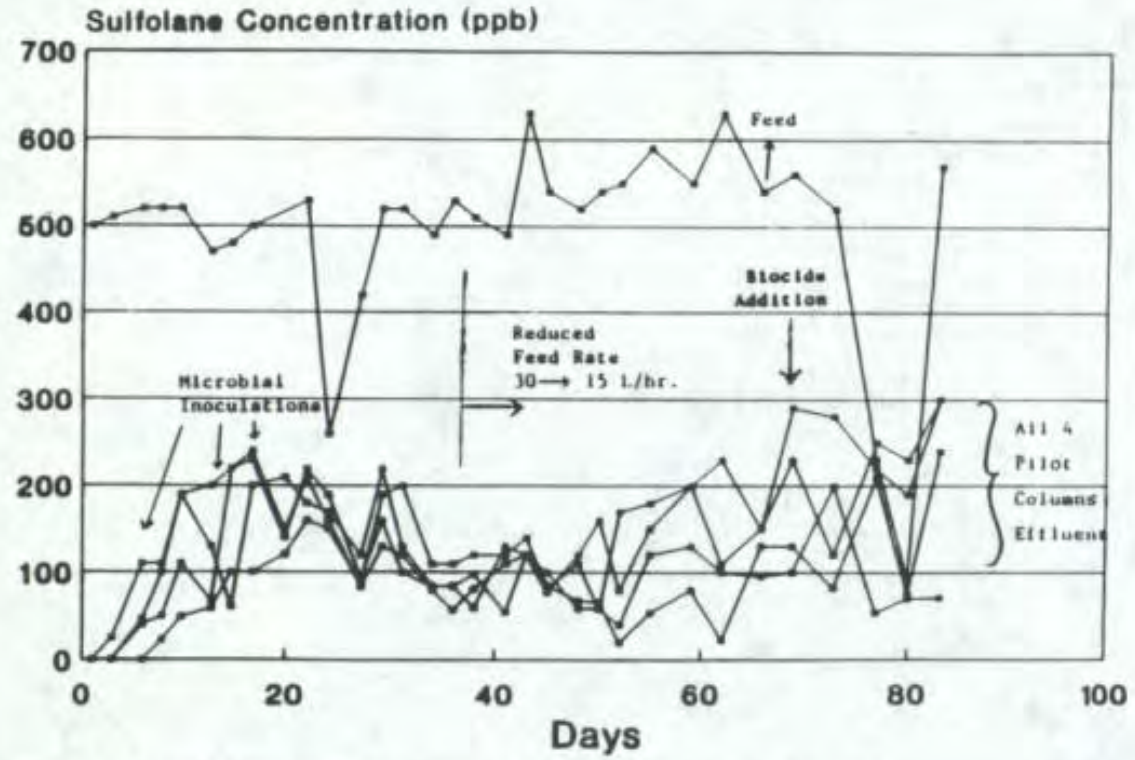

Figure 8. Pilot BAC column performance data – sulfolane (four columns).

samples after the first two weeks of the BAC operation. Without biodegradation taking place in these columns, complete breakthrough would have occurred on or before Day 40.

The effluent results from the four pilot columns showed a significant reduction in the sulfolane level during the demonstration period. As expected, extremely low sulfolane concentrations were

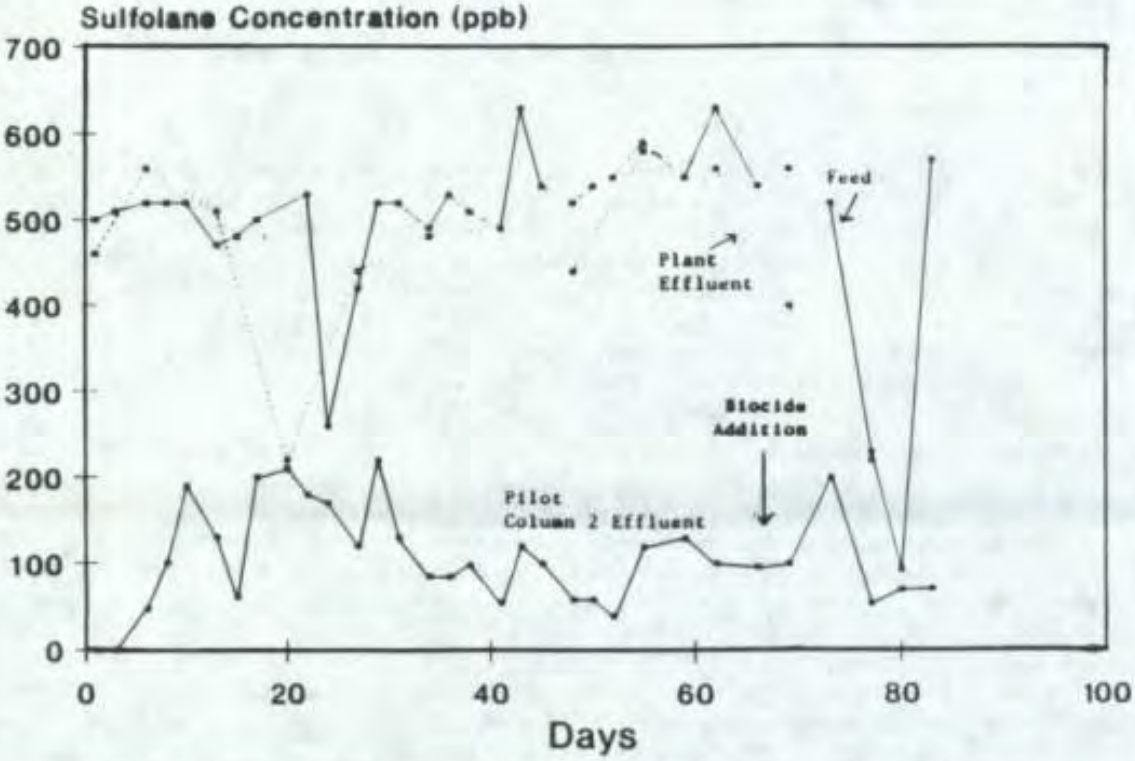

Figure 9. Pilot BAC column performance data – sulfolane (Col. 2 vs full size adsorber).

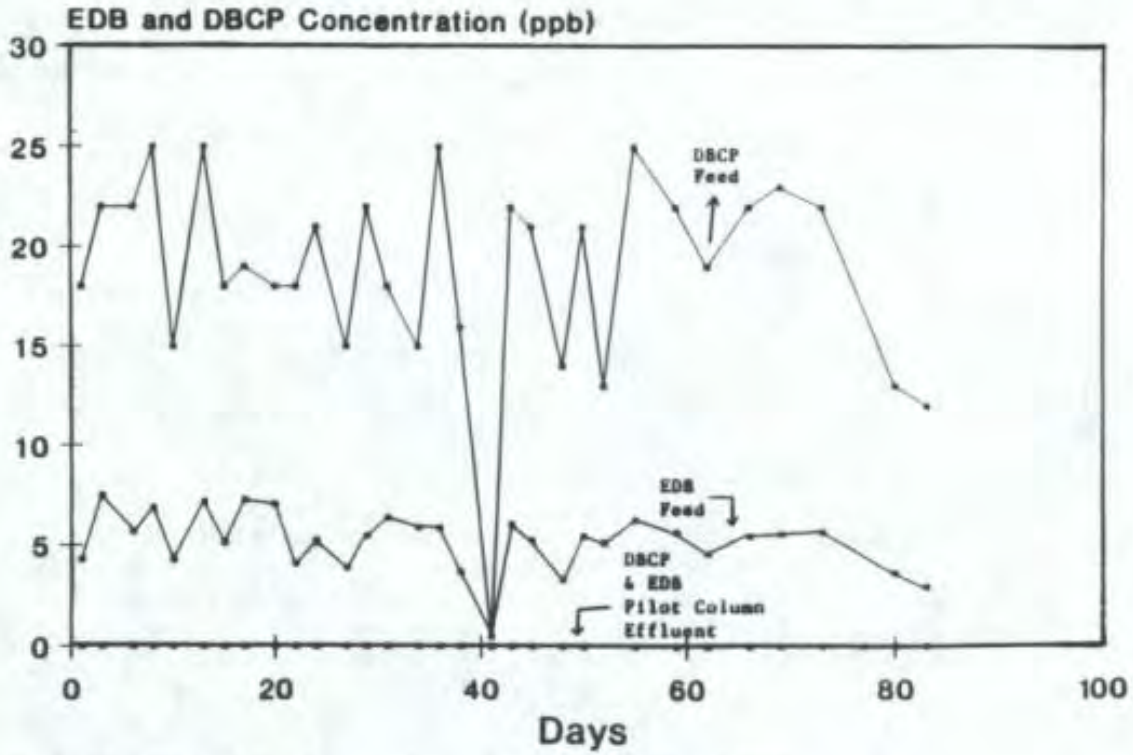

Figure 10. Pilot BAC column performance data - DBCP and EDB.

found in the early stage effluent samples due to physical adsorption by the fresh activated carbon. Beyond this initial carbon adsorption phase (the first two weeks), significant removal of sulfolane had continued because of biodegradation. Contribution by biodegradation to the overall removal of sulfolane observed in each BAC column is calculated and presented in Table VII. At the end of the pilot study the BAC columns continued to remove up to 88% (feed – 570 ppb, Column 2 effluent – 71 ppb) of sulfolane, the fraction (31 to 39%) of removal due to biodegradation would have been larger if the pilot demonstration program had lasted longer.

Table VI. Sulfolane Concentrations Found During the Pilot Study

	High	Low	Average
Feed	630	93	495
Lathrop Plant Effluent	580	220	447
Pilot Effluent 1	240	ND_{10}	97
Pilot Effluent 2	220	ND_{10}	106
Pilot Effluent 3	300	ND_{10}	142
Pilot Effluent 4	300	ND_{10}	143

Unit in ppb.

Table VII. BAC Pilot Study Results

	Column 1	Column 2	Column 3	Column 4
Total Sulfolane Removed	17,800	17,400	15,800	15,800
Max. Carbon Adsorption Loading for Sulfolane	10,900	10,900	10,900	10,900
Sulfolane Removed via Biodegradation or Enhanced Bioadsorption	6,900	6,500	4,900	4,900

Unit in mg.

The fumigants were also monitored during this pilot study. Figure 10 shows both DBCP and EDB were removed to non-detect level by carbon adsorption. The present treatment capacities for removing EDB and DBCP will be maintained when the existing carbon adsorption system is converted to the BAC column process, since biomass density in the carbon bed will remain the same as addition of extra organic carbon is not required for the BAC treatment for removing sulfolane.

CONCLUSIONS

A. Bench Feasibility and Treatability Study

1. Activated carbon, such as Calgon F-400 used in the Lathrop adsorbers for treating groundwater, had a much lower capacity for sulfolane than for either DBCP or EDB, hence sulfolane was found in the effluent before DBCP or EDB.
2. Sulfolane broke through bench carbon columns even they were inoculated with bacteria in sewage treatment plant effluent, and the breakthrough time was predicted by the isotherm capacity.
3. Inoculation of carbon columns with acclimated bacteria originated from a sludge sample taken from a refinery activated sludge plant employed for treating sulfolane-containing wastewater resulted in quick and complete removal of sulfolane.
4. Complete removal of sulfolane from the Lathrop groundwater was achieved without pre-aeration nor addition of organic substrate (sucrose) and inorganic nutrients (ammonia and phosphate).
5. Mass culturing, using sugar and N/P nutrients, of acclimated bacteria in aerated groundwater produced effective seed solution for inoculation of pre-saturated carbon columns, and the resulting BAC quickly removed sulfolane from the feed.

B. Pilot BAC Demonstration

1. The addition of microorganisms to activated carbon enhanced the removal of sulfolane from groundwater. Significant portion of the total sulfolane removal was due to biodegradation during the three months pilot study.
2. After receiving a loading equivalent to the isotherm capacity (Day 30–40), the four pilot columns continued to achieve an average sulfolane removal of 73% vs. 10% removal for the existing full-scale adsorbers.
3. Addition of biocide did not adversely affect the BAC column performance in removing sulfolane.
4. As expected, fumigants DBCP and EDB were both consistently removed to non- detectable levels during the pilot demonstration. The BAC process did not adversely impact carbon adsorption treatment capacity for the fumigants. As a result of the successful on-site pilot-scale demonstration of the BAC column treatment efficiency for removing sulfolane, the second phase full- scale demonstration program, converting one of the existing carbon adsorbers for the BAC mode of operation for at least six months, will soon begin to evaluate the long-term removal of sulfolane, DBCP and EDB as well as to assess effects of periodic biocide addition and carbon change on the treatment performance.

ACKNOWLEDGMENTS

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