SULFOLANE TECHNICAL ASSISTANCE AND EVALUATION REPORT

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ACRONYMS AND ABBREVIATIONS

ADEC	Alaska Department of Environmental Conservation
BAC	Biologically activated carbon
BC	British Columbia
bgs	Below ground surface
BTX	Benzene, toluene, and xylenes
CCR	CCR Technologies Ltd.
CO_2	Carbon dioxide
°C	Degrees Celsius
°F	Degrees Fahrenheit
DBCP	Dibromochloropropane
DIPA	Diisopropanolamine
DMSO	Dimethylsulfoxide
DOC	Dissolved organic carbon
EDB	Ethylene dibromide
EPA	U.S. Environmental Protection Agency
g/L	Grams per liter
H_2S	Hydrogen sulfide
HCl	Hydrochloric acid
K_{oc}	Organic carbon partition coefficient
LDEQ	Louisiana Department of Environmental Quality
$\log K_{ow}$	Log octanol/water partition coefficient
m^3	Cubic meters
MCL	Maximum contaminant level
mg/kg	Milligrams per kilogram
mg/L	Milligrams per liter
mmHg	Millimeters of mercury
MO-2	Management Option 2
MPR	MPR Services, Inc.
MSDS	Material Safety Data Sheet
NMP	N-methyl pyrolidone
OASIS	OASIS Environmental, Inc.
PCL	Protective Concentration Levels
POPCO	Pacific Offshore Pipeline Company
ppb	Parts per billion
ppm	Parts per million
PPS	Polyphenylene sulphide
RCRA	Resource Conservation and Recovery Act
TCEQ	Texas Commission on Environmental Quality
TSCF	Transpiration stream concentration factor
VSS	Volatile suspended solids

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EXECUTIVE SUMMARY

Research was conducted by OASIS Environmental, Inc. on behalf of the Alaska Department of Environmental Conservation (ADEC) to investigate sulfolane and report on its physical properties, chemical properties, uses of, breakdown processes, attenuation information, substitutes, and case histories. The information collected and presented in this report provides background information on sulfolane and will aid in better understanding how sulfolane is used in the oil and gas industry, its potential to cause corrosion in process equipment and piping, case histories of reported sulfolane spills and remediation, and regulation of sulfolane.

Sulfolane is a readily available commodity chemical. The most common uses of sulfolane are in aromatics extraction in the oil refining process and CO_2 extraction in the natural gas sweetening process. Sulfolane is an organosulfur compound that is readily soluble in water. In pure form, sulfolane is a clear, colorless liquid that is heavier than water. Sulfolane does not volatilize from water or soil, nor does it readily adsorb to organic matter. The primary attenuation mechanism appears to be biodegradation in an aerobic environment. Research suggested that sulfolane is present in industrial wastewater from refineries and gas processing facilities at approximately 10 ppm or less (Chou 1983). Sulfolane concentrations in the wastewater are generally able to be treated by the activated sludge in biotreaters in the on-site industrial wastewater treatment system.

Sulfolane is not considered corrosive to steel; corrosion of steel from using sulfolane generally occurs from by-products of sulfolane decomposition. The root cause of corrosion related to sulfolane use is the presence of impurities in sulfolane extraction units that degrade sulfolane. Specifically, oxygen or chlorides in contact with sulfolane cause degradation. Sulfolane is thermally stable until approximately 220°C, when it starts to break down into sulfur dioxide and a polymeric material. Although corrosion is a problem in sulfolane processes due to degradation, research did not indicate that corrosion ever became severe enough to cause leakage or spills of sulfolane outside of plants. Generally, the degradation of the sulfolane would cause process problems prior to causing severe corrosion resulting in leaks or spills.

Internationally, Environment Canada is the most progressive regulatory authority in establishing environmental quality guidelines for sulfolane contaminated soil and groundwater. The U.S Environmental Protection Agency does not regulate sulfolane, nor is the transportation of sulfolane regulated in the United States as a hazardous material or dangerous good. Texas is the only state that has established maximum contaminant levels (MCLs) for sulfolane.

Because sulfolane is used in proprietary processes which are considered confidential, it has not been thought to be highly toxic, and it is not generally regulated as a water or soil contaminant, limited information is readily available. This report summarizes OASIS' sulfolane research findings.

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1. INTRODUCTION

OASIS Environmental, Inc. (OASIS) was contracted by the ADEC to research background information on the chemical sulfolane. Sulfolane is used in the refining process to extract aromatics and is present in certain refined products in limited quantities. Sulfolane has been identified as a contaminant in groundwater in the vicinity of the Flint Hills refinery in North Pole, Alaska.

The objective of this work was to investigate the use of sulfolane in industry, including transportation, use, and disposal practices, as well as determine the potential of sulfolane to cause equipment corrosion and subsequent spills. In addition, OASIS conducted global research to identify case histories of sulfolane spills and remediation strategies implemented at sulfolane contaminated sites through contacting regulatory agencies, manufacturers, and consultants worldwide.

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2. SULFOLANE PROPERTIES

Sulfolane was developed by Shell Oil Company in the late 1950s for use in purifying butadiene. It is known by various synonymous names that are provided in Appendix A. The International Union of Pure and Applied Chemical (IUPAC) name is thiolane 1,1-dioxane. The Chemical Abstract Service (CAS) number is 126-33-0; the European Commission (EC) or European Inventory of Existing Chemical Substances (EINECS) number is 204-783-1; and the Beilstein Registry number is 107765.

2.1. Physical Properties

The chemical sulfolane in pure form is a clear, colorless liquid, but in industry it often takes on a light yellow color due to interaction with air. Its chemical formula is $C_4H_8O_2S$ with a molecular weight of 120.17 grams per mole (g/mol). The melting point is 27.5 degrees Celsius (°C; 81.5 degrees Fahrenheit [°F]), and the boiling point is 285°C (545°F) with a specific gravity of 1.261 grams per milliliter (g/mL). The autoignition temperature of sulfolane is 528°C (982°F), and its flash point is 165°C (329°F). The hazard symbol is XN (harmful).

The National Fire Protection Agency rates sulfolane with the following hazards:

• Health Hazard	2	Intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury.
• Flammability Hazard	1	Must be heated before ignition can occur.
• Reactivity Hazard	0	Normally stable even under fire exposure conditions.

Additional hazard ratings include the following:

• R22	harmful if swallowed
• S23	do not breathe vapor or fumes
• S24	avoid contact with skin
• S25	avoid contact with eyes

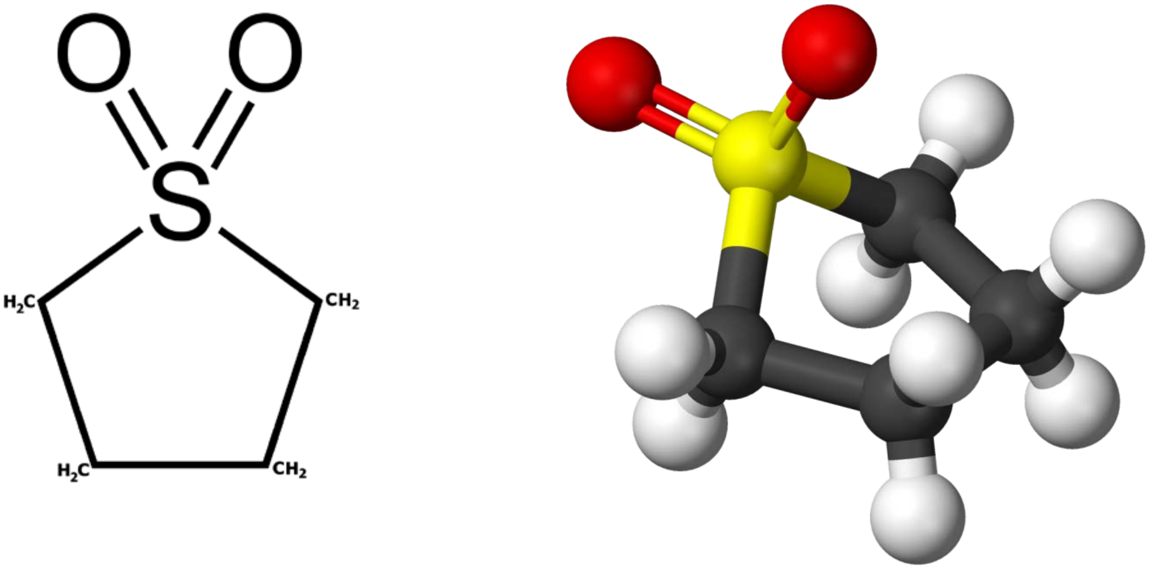
Two manufacturers' Material Safety Data Sheets (MSDSs) are included in Appendix B.

2.2. Chemical Properties

Sulfolane is an organosulfur compound, containing a sulfonyl group with a sulfur atom double-bonded to two oxygen atoms. The structure is shown in Figure 1. It is synthesized by hydrogenating sulfolene, the product of a reaction between butadiene and sulfur dioxide. The double bond is highly polar, but the carbon ring has high non-polar stability. The vapor pressure increases from 0.01 millimeters of mercury (mmHg) to 421.4 mmHg between the temperatures of 20°C and 260°C (68°F to 500°F) (CCME

2006). The vapor density is 4.2 g/L relative to air, where air is 1 g/L (CCME 2006). Sulfolane is thermally stable until approximately 220°C, when it starts to break down into sulfur dioxide and a polymeric material. It is chemically stable in the presence of many chemical substances except sulfur and aluminum chloride (Kirk-Othmer 1999).

FIGURE 1: CHEMICAL STRUCTURE OF SULFOLANE



A complete list of chemical properties with referencing is shown in Table 1 as found for the Canadian Environmental Quality Guidelines for Sulfolane Scientific Supporting Document. For comparison purposes physical and chemical properties for benzene are included in Table 2.

2.3. Water Interaction

Sulfolane is readily soluble in water due to the highly polar sulfur–oxygen double bonds. Shell Chemical found the solubility to be 1,266 g/L at 20°C (68°F). The Canadian Environmental Quality Guidelines reports solubility at 1,000 g/L. Sulfolane is miscible at 25°C (77°F) (CCME 2006).

2.4. Breakdown Processes

Sulfolane breaks down into acidic byproducts as described further in Section 4. Most typically in the refining process, the breakdown occurs in the presence of oxygen or chlorides. Additionally, sulfolane breaks down at high temperatures into butadiene and sulfur dioxide. Various processes are used to remove the reaction byproducts and “clean” the sulfolane, as discussed further in Section 4.

The oxidation of sulfolane under ideal conditions is as follows.

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

TABLE 1: PHYSICAL AND CHEMICAL PROPERTIES OF SULFOLANE

Property	Units	Value	Reference
CAS registry number		126-33-0	
Molecular formula		$C_4H_8SO_2$	Kirk-Othmer (1999)
Molecular weight	$g \cdot mol^{-1}$	120.17	Lide (1996)
Melting point	°C	28.5	Kirk-Othmer (1999)
Boiling point	°C	287.3	Kirk-Othmer (1999)
Specific gravity			
30° C (sulfolane) /30° C (water)	-	1.266	Kirk-Othmer (1999)
100° C (sulfolane) /4° C (water)	-	1.201	Kirk-Othmer (1999)
Flashpoint	°C	165-178	Kirk-Othmer (1999)
Density at 15° C	$g \cdot cm^{-3}$	1.276	Kirk-Othmer (1999)
Vapour density (air=1)	$g \cdot L^{-1}$	4.2	Shell Chemical Company (1976)
Vapour pressure			
20° C	mm Hg	0.01	Shell Chemicals Europe Limited (1994)
118° C	mm Hg	5	Verschueren (1996)
150° C	mm Hg	14.53	Mellan (1977)
160° C	mm Hg	21.55	Mellan (1977)
200° C	mm Hg	85.23	Mellan (1977)
210° C	mm Hg	115.1	Mellan (1977)
260° C	mm Hg	421.4	Mellan (1977)
n-Octanol-water partition coefficient (K_{ow})	log	-0.4	Travis and Arms (1988)
	log	-0.77	Shell Chemicals Europe Limited (1994)
Organic carbon partition coefficient (K_{oc})	log	0.07	Shell Chemicals Europe Limited (1994)
Henry's law constant	$atm \cdot m^{-3} \cdot mol^{-1}$	8.9×10^{-10}	Shell Chemicals Europe Limited (1994)
Solubility in water			
20° C	$g \cdot L^{-1}$	1,266	Shell Chemicals Europe Limited (1994)
25° C	$g \cdot L^{-1}$	379, miscible	Witzaney and Fedorak (1996)
30° C	$g \cdot L^{-1}$	miscible	Windholz (1983)
PKa	-log K	12.9	Coetzee (1977)
Soil water partition coefficient (Kd)			
montmorillonite	$L \cdot kg^{-1}$	0.94	Luther *et al.* (1998)
kaolinite	$L \cdot kg^{-1}$	0.18	Luther *et al.* (1998)
humus-rich soil	$L \cdot kg^{-1}$	0.099	Luther *et al.* (1998)
soils/aquifer materials (average of 4)	$L \cdot kg^{-1}$	0.08	Luther *et al.* (1998)
Dielectric constant	-	43.3	Kirk-Othmer (1999)
Dermal permeability coefficient (K_p)	$cm \cdot hour^{-1}$	0.0002	US EPA (1992)

(CCME 2006)

TABLE 2: PHYSICAL AND CHEMICAL PROPERTIES OF BENZENE

Property	Units	Value	Reference
CAS registry number		71-43-2	
Molecular formula		C_6H_6	
Molecular weight	$g*mol^{-1}$	78.11	Budavari et al. 2001
Melting point	°C	5.5	Budavari et al. 2001
Boiling point	°C	80.1	Budavari et al. 2001
Specific gravity		0.877	Watts (1998)
Flash point	°C	-11	Budavari et al. 2001
Density at 20°C	$g*cm^3$	0.8765	Watts (1998)
Vapour density	$g*L^{-1}$	2.8	Watts (1998)
Vapour pressure at 20°C	mm Hg	75	Budavari et al. 2001
n-Octanol-water partition coefficient	Log Kow	2.05	HSDB 2007; Karickhoff 1981; Kenaga 1980
Soil adsorption coefficient	Log Koc	1.8-1.9	HSDB 2007; Karickhoff 1981; Kenaga 1980
Henry's Law Constant	$atm*m^{-3}*mol^{-1}$	.00548	Mackay and Leinonen 1975
Solubility in water at 25°C	mg/L	1770	Watts (1998)

2.5. Attenuation Information

Attenuation of a compound generally occurs though volatilization, degradation, or adsorption. Sulfolane does not adsorb, as shown by the log octanol/water partition coefficient (log K_{ow}) of -0.77. The organic carbon partition coefficient (K_{oc}), estimated at 0.07, shows that the compound is highly mobile in soil. Studies performed by the University of Queensland in 2000 concluded that hydrogeologic properties of the aquifer have little influence on sulfolane adsorption (Kim et al. 2000) whereas studies conducted by the University of Alberta indicated that sulfolane had higher adsorption to clay (Luther et al. 1998). An investigation in sulfolane attenuation completed at Mount Royal College in Calgary found that sorption capacity was not affected by temperature (St. Fort 2006)

Sulfolane does not volatilize from water or soil, evidenced by its low vapor pressure and Henry's Law Constant of 8.95×10^{-10} atmosphere-cubic meters per mole (atm-m^3/mol) at 25°C. The primary attenuation mechanism appears to be biodegradation in an aerobic environment. However, some evidence of biodegradation under specific anoxic conditions has been documented. Further data regarding biodegradation are included in Section 5.

3. INDUSTRY USES AND STANDARDS

Information was gathered about chemical uses, transportation, storage, manufacturing, and disposal of sulfolane in general practice in industry.

3.1. Uses

The most common uses of sulfolane are in aromatics extraction in the oil refining process and CO_2 extraction in the natural gas sweetening process. However, other industries use the chemical in smaller quantities. Details are described in the following sections.

3.1.1. Oil Refining–Sulfolane Extraction Process

Sulfolane is a solvent used in liquid–liquid aromatic extraction units to dissolve the aromatics benzene, toluene, and xylenes from a hydrocarbon stream. Since aromatic extraction units can use solvents other than sulfolane for extraction, sulfolane extraction unit is the more common name for those specifically using sulfolane as the extractive solvent.

Three licensers of the sulfolane extraction process technology were identified, UOP Honeywell, LyondellBasell, and Sinopec Tech. UOP is the predominant licenser; other licensers may exist, but were not encountered through this research. Overall, there are more than 150 sulfolane extraction units licensed throughout the world (TTC 2010). Sulfolane extraction units are generally custom designed and implemented for a refining operation by large petroleum companies in coordination with engineering firms who gain the appropriate licensure.

In aromatics extraction using sulfolane, the hydrocarbon feed liquid (most often naphthas, distillates, and kerosene in the C6–C8 range) mixes with the sulfolane liquid to selectively dissolve aromatics into the sulfolane. Sulfolane is the preferred solvent for this process due to its high selectivity for the aromatics of interest and its capacity for dissolving large quantities of aromatics in relatively low quantities of solvent. For its selectivity, capacity, and low boiling temperature, the sulfolane extraction process is less expensive to operate than similar processes using other solvents.

Following extraction, more non-aromatics are removed from the sulfolane and aromatic stream using extractive distillation. After extractive distillation, the aromatics must be separated from the sulfolane using an aromatics recovery column. This column separates the components by employing the large difference in boiling temperature. Sulfolane has a very low boiling temperature (545°F) relative to other solvents, which makes it especially valuable in the recovery process. In a well-maintained system, the separated aromatics are of high purity (> 99% by weight) and most of the aromatics are recovered (> 99%). At a sulfolane loss of approximately 5-10 ppm of feed for a 10,000 BPD feed plant, about 10,500 pounds of solvent is lost per year, resulting in a sulfolane recovery rate greater than 99% (TTC).

Once the aromatics and non-aromatics are removed from the solvent, most of the solvent is recovered, regenerated, and recycled. A whitepaper on the sulfolane process published by UOP is included in Appendix C.

3.1.2. Liquid Natural Gas Treating–Sulfinol® Process

Sulfolane is a component of a solvent solution used to remove carbon dioxide (CO_2), hydrogen sulfide (H_2S), carbonyl sulfide (COS), mercaptans, and organic sulphides from natural gasses. These compounds are poisonous and corrosive and when contained in natural gases, the gases are often called “acid gases” or “sour gases.” The process, called the Sulfinol® process, was developed by Shell Oil Company and is now licensed by Jacobs Nederland, Chiyoda Corporation, and JGC Corporation. Sulfinol® is a registered trademark of Shell International.

The solvent used in the Sulfinol process is composed of diisopropanolamine (DIPA) or methyldiethanolamine (MDEA), sulfolane, and water. Sulfolane usually comprises between 15% and 35% of the solvent, depending on the solvent manufacturer and the composition of the liquid natural gas feed stream. This composition allows the solvent to have both physical and chemical absorption of the compounds depending on which is more cost effective. The Shell proprietary names of the solvent used in the Sulfinol process are Sulfinol-D™ and Sulfinol-M™.

Like the sulfolane extraction process, the Sulfinol process is a liquid–liquid extraction, blending liquid gas feed into liquid solvent feed to dissolve the sulfur compounds of interest. Sulfur compounds are separated from the solvent by heating, and then the compounds are condensed and recovered as sulfur. The solvent is regenerated and reused.

The Sulfinol process is used in a variety of industries for removal of unwanted CO_2 and H_2S including production of ammonia or hydrogen, petroleum refining without a cracking unit, enhanced oil recovery, ethylene plants, and landfill gas facilities (WorleyParsons Whitepaper).

3.1.3. Other

Sulfolane is used as a solvent in a wide variety of smaller applications including the following, which will not be discussed further in this document:

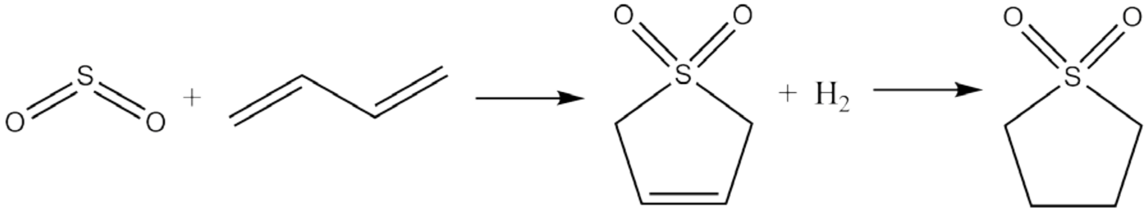
- Separation of compounds with similar boiling points in extractive distillation
- Fractionation of saturated and unsaturated compounds in fatty acids, i.e., soap
- Production of insecticides, herbicides, and fungicides such as captan
- Enhancement of the color fastness of dispersed dyes in hydrophobic synthetic fibers
- Component of electrolyte solvents in lithium or light-metal anode batteries
- Process solvent in pharmaceutical manufacturing

- Synthesis of Cephalosporins
- Polymerization solvent in polymer production
- Component of ink for jet printing to increase storage ability, reduce clogging of printer nozzles, improve fixation on substrates, and water resistance
- Solvent in spinning and casting of synthetic fibers and fabrics
- Circuit board cleaning
- Photoresist stripper for processing liquid crystal and semiconductors
- Plasticizer and curing agent

3.2. Manufacturing

Sulfolane is a readily available commodity chemical. The synthesis process involves reacting sulfur dioxide and butadiene to create 3-sulfolene and then hydrogenating 3-sulfolene to form sulfolane. The chemical process is shown in Figure 2.

FIGURE 2: CHEMICAL SYNTHESIS OF SULFOLANE



The chemical is commercially available to purchase as anhydrous sulfolane or aqueous sulfolane. Aqueous sulfolane is provided at approximately 3%–5% water content to ensure that the chemical remains liquid during transport and storage. Sulfolane becomes solid at 27°C (80°F). Sulfinol-D™ and Sulfinol-M™ are the common solutions of sulfolane used in the Sulfinol process for gas treatment.

ChevronPhillips Chemicals is the primary manufacturer of sulfolane in the United States and also has manufacturing centers in Belgium and Singapore. In Europe, Novasol is the primary manufacturer of sulfolane and is located in Belgium. A few manufacturers in China produce sulfolane, including Liaoyang Guanghua Chemical Company, Ltd. In terms of industrial process chemicals, sulfolane is considered expensive at $20–$40 per gallon to replenish if losses occur (CCR 2010).

Research indicated that Oklahoma State University is working with ChevronPhillips to improve process efficiency in sulfolane production. The report indicated that there is much waste reduction potential in this process.

3.3. Transportation and Handling

Transportation of sulfolane occurs in bulk in liquid form, typically accomplished using a trucking company familiar with transporting bulk hazardous liquid chemicals. At the chemical manufacturer or distributer warehouse, the truck is filled with nitrogen gas that is displaced when the truck is loaded with sulfolane. A similar process occurs when off-loading the chemical into a tank on site of use. The nitrogen blanket helps to ensure limited chemical degradation due to oxygen exposure.

The Department of Transportation, Air Transport Association, International Maritime Association, and International Carriage of Goods by Road do not regulate the transportation of sulfolane as a hazardous material or dangerous good. However, in the United States, Massachusetts lists sulfolane on its Hazardous Material List making it subject to the hazardous chemical Right to Know Law.

3.4. Storage

Sulfolane is stored with a nitrogen blanket similar to the process for transportation. The chemical should be stored between 30°C (86°F) and 40°C (104°F). Below 30°C the sulfolane becomes solid, and above 40°C degradation can begin to occur as evidenced by color change.

3.5. Disposal

During regular use of sulfolane as a solvent by industrial users, disposal is not encountered because the solvent is used in a closed loop, recovered from the process, and regenerated on-site for continued use. However, sulfolane is lost over time in small quantities to the process through incomplete recovery and needs to be replenished from a fresh tank. UOP estimates that in the sulfolane extraction process, a typical loss rate would be about 5 parts per million (ppm) of the feed rate (UOP 2006). Other evidence suggests that the loss rate can be much higher depending on the feed type, solvent quality, and other factors. The lost solvent is found in the end products of the refining process and in the industrial wastewater. Research by Shell in 1982 suggested that sulfolane is present in industrial wastewater from refineries and gas processing at approximately 10 ppm or less (Chou 1983). Sulfolane concentrations in the wastewater are generally able to be treated by the activated sludge in biotreaters in the on-site industrial wastewater treatment system.

The Site Characterization Work Plan from Flint Hills Refinery suggests that the concentration of sulfolane in its gasoline end product ranged from 24 ppm to 868 ppm between 1992 and 2004. In 2005, the gasoline specification for sulfolane was set at 56 ppm. Between 2005 and 2009, sulfolane concentrations ranged between 2 ppm and 55.5 ppm (Barr 2010).

On infrequent occasions, sulfolane concentrations are found in places other than the wastewater or end refining products. During sulfolane extraction unit turnarounds for cleaning and repair, the remnant solvent that was unable to be drained from the system prior to cleaning is dissolved in the turnaround wash water. Depending on the concentration of the solvent, the wash water is either treated on-site in the wastewater treatment system biotreaters or is sent to a Class I deep well injection facility that is certified for No Migration by the U.S. Environmental Protection Agency (EPA). The concentration of sulfolane that is able to be treated by the biotreaters is facility dependant, but it is generally less than 3,000 ppm (Chou 1983). In rare instances, an entire batch of sulfolane becomes contaminated or degraded to a level that is unacceptable for use in the extraction unit. When a large volume of sulfolane needs disposal, it is returned to the manufacturer for chemical processing into disposable or useful components (TTC 2010).

Sulfolane has also been found in landfill leachate or groundwater aquifers under a landfill. In those cases, it is assumed that spent filters from the Sulfinol process have been improperly disposed in landfills (Greene et al. 1998).

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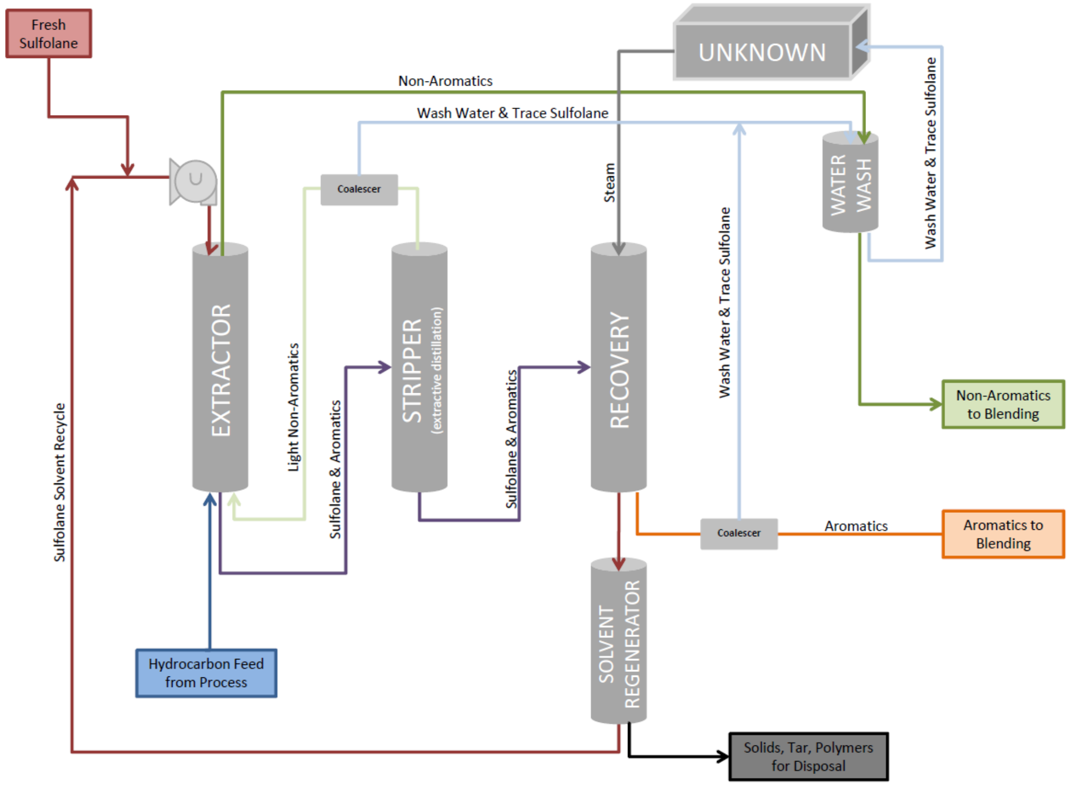
4. SULFOLANE AND CORROSION

The ability of sulfolane to cause corrosion in pipelines or processing facilities was investigated for OASIS by TTC Labs, an engineering consulting firm in the petrochemicals and refining industries. TTC Labs is known for troubleshooting and perfecting refining processes including aromatic extraction, one of the two primary processes that use sulfolane as a solvent. This section summarizes the findings of TTC Labs regarding sulfolane as a corrosive chemical, with additional information included as found by OASIS' research. TTC Labs' full report is included in Appendix D.

4.1. Sulfolane in the Refining Process

Sulfolane extraction units (defined in Section 2.1) employ a liquid–liquid extractor column where sulfolane flows counter-current to the flow of the hydrocarbon feed stream. The sulfolane dissolves aromatics in the extractor column. A subsequent stripper column removes any remaining non-aromatics from the mixture by extractive distillation. The sulfolane/aromatics mixture is fed through a recovery column where aromatics are vaporized and captured. The remaining sulfolane is regenerated to remove impurities and recycled for repeated use. The non-aromatic stream is washed with water to remove sulfolane and is then stored for further use. The wash water with trace sulfolane is captured with an unknown process and used for steam in the recovery column. A simplified flow diagram of this process is shown in Figure 3.

FIGURE 3: SULFOLANE EXTRACTION PROCESS IN REFINING



4.2. Corrosion Mechanisms

Sulfolane is not considered corrosive to steel; corrosion of steel from using sulfolane generally occurs from by-products of sulfolane decomposition. Reactions with impurities in the solvent from upstream processes, reactions with oxygen in air, and high temperatures can cause sulfolane decomposition. Details are included in the following sections.

4.2.1. Oxygen

Oxygen is permitted into the extraction process via air leaking into vacuum processes or via air that is dissolved in the hydrocarbon feed. The reaction of sulfolane with oxygen creates sulfuric and organic acids as well as aldehydes and ketones. Oxygen-degraded sulfolane has a lower pH, a higher acid number, and a darker color than pure sulfolane. Additionally, oxygen-degraded sulfolane tends to become less extractive of aromatics in the aromatic extraction process. Figure 4 shows solvent from one refinery during an oxygen leak detection project performed by TTC Labs. The sample on the right shows sulfolane in the presence of the oxygen leak and the sample on the left shows sulfolane after the oxygen leak was repaired.

FIGURE 4: OXYGEN-DEGRADED SULFOLANE

(TTC 2010)

4.2.2. Chlorides

During the refining process, a process known as catalytic reforming is used to convert hydrocarbon molecules from low octane ratings to high octane ratings. Catalysts used in catalytic reforming usually contain chlorides that are then passed downstream to the extraction units. Chlorides react with organic acid molecules and possibly sulfolane itself to create precipitates. The reaction appears to be aggravated with temperature and time, a problem particularly with sulfolane extraction, as the unit operates at a high temperature. Similar to degradation from oxygen, degradation from chlorides causes an increase in the acid number and a darkening of the sulfolane, but does not change the pH. Given settling time, the precipitates will drop out and the sulfolane will become much clearer.

4.2.3. Temperature

Thermal decomposition occurs in sulfolane at temperatures above 392°F (Kirk-Othmer 1999). Temperature also aggravates the reactions of sulfolane with oxygen and chlorides. Industry research of corrosion problems in sulfolane extraction units reveals that reboiler regenerators and their associated equipment are common focal points for corrosion. Unacceptably high corrosion rates may occur at aromatic stripper reboiler temperatures of 350-380 F in units with oxygen intrusion (Schneider 2004).

4.3. Corrosion Detection Methods

Detecting corrosion that is due to sulfolane use can focus either on the cause or the result. The mechanism for detecting the cause is to monitor the solvent condition. The mechanism for detecting the result of corrosion is to monitor the equipment in contact with the solvent. Each mechanism is described in the following sections.

4.3.1. Solvent Condition

Since sulfolane becomes corrosive as it degrades, one method of corrosion detection is to monitor the condition of the solvent. Solvent condition is monitored in several ways.

As shown in Figure 4, an easy method to detect degradation of sulfolane, and therefore its elevated corrosion potential, is a visual inspection of the color. Pure sulfolane is often referred to as “water white,” while degrading sulfolane becomes yellow to brown to black with increasing opaqueness.

A sample of the sulfolane can be collected from the process analyzed for both qualitative and quantitative parameters. Qualitatively, a precipitate isolation test can be performed with equal parts of sulfolane, water, and non-aromatic stream. Given time to settle, the precipitates formed during degradation will concentrate at the interface between the solvent and the non-aromatics. The thicker the layer of precipitate, the more degraded the sulfolane.

TTC Labs has developed a settling test that measures the separation rate of solvent from the non-aromatic stream. In this procedure, equal parts sulfolane and non-aromatics are mixed and the interface separation timed. Degraded sulfolane will take longer to separate from the hydrocarbons than pure sulfolane, which takes a minimum of 1 inch per second.

As mentioned in Sections 4.2.1 and 4.2.2, degraded sulfolane has an elevated acid number compared to pure sulfolane. ASTM Test Method D974 can be used to test for the acid number of the solvent, with pure sulfolane having an acid number of 0.01. Also, laboratory analyses can be performed to test for the concentration of organic and sulfuric acids, which are the by-products from degradation, or for chlorides, which are a cause of degradation.

4.3.2. Removing the Source of Corrosive Impurities

The root cause of corrosion related to sulfolane use is the presence of impurities in the extraction unit that degrade sulfolane. Specifically, oxygen or chlorides in contact with sulfolane cause degradation.

Oxygen presence can usually be isolated to either the hydrocarbon feed or an atmospheric leak in the process. The most common way for oxygen to enter the hydrocarbon feed is through leaks in the feed tank seals (if present at the refinery) or insufficient nitrogen gas blanketing during storage. If feed tanks are used at a refinery, the feed does not run directly from upstream into the extractor, and the additional storage allows more potential for oxygen intrusion. In refineries that utilize feed tanks, the vapor in the feed tanks can be analyzed to determine the oxygen content. If high oxygen content is detected, a more thorough nitrogen blanket must be used in the feed tanks.

The most common way for oxygen to enter the process is through vacuum leaks in vacuum processing sections of the plant. In this case, each portion of the vacuum process must be tested to determine whether a leak is present. When leaks are identified, they must be repaired to prevent oxygen from entering the process.

Chloride presence must be monitored chemically as a component in the feed stream. The concentration of chloride tends to vary over time. Concentrations between 50 and 100 ppm have been shown to be extremely corrosive in sulfolane extraction units (TTC 2010). Chloride concentrations are related to the catalyst used in the catalytic reforming process, and the relationship must be determined and adjusted.

4.3.3. Removing Degradation By-Products

In order to prevent sulfolane from becoming corrosive and from having limited extraction potential, most sulfolane extraction units incorporate a regeneration component for the solvent. The regeneration unit works to remove the degradation by-products from the sulfolane as it is recycled during use. The solvent regenerator is shown in the extraction process in Figure 3.

Degradation of sulfolane is common in the industry, and support companies specialize in regeneration technologies specifically for extraction processes in oil refining and gas processing. CCR Technologies Ltd. (CCR) and MPR Services, Inc. (MPR) are two companies that work to remove the acids and other byproducts from sulfolane to preserve its integrity as a solvent. CCR uses vacuum distillation, and MPR uses ion exchange. Typical treatments used in other processes in the industry are not useful for sulfolane, such as the use of corrosion inhibitors or alkanolamines (CCR 2001).

General industry opinion is that some refineries, in an attempt for simplicity and money savings, reduce the level of degraded sulfolane by diluting it with fresh sulfolane, known as a “bleed and feed.” In these instances, corrosion rates of the metal in the extraction unit are higher than in sulfolane extraction units that employ solvent regeneration units. The Flint Hills North Pole refinery currently utilizes a solvent regenerator in its sulfolane extraction unit. The regeneration process can be complex to design and maintain in an extraction system. The degradation by-products are not fully known, but are generally categorized as either acids or polymers. In addition, resulting corrosion by-products can be in the solvent stream, including iron solids, acid salts, and polymer solids (Schneider 2004). All impurities in the solvent stream are known as “heavies” in the regeneration process. In order to remove sulfolane from the heavies, vaporization is used. However, with the very low vapor pressure of sulfolane, vaporization can be difficult, as can the condensing for reuse due to the high freezing temperature (Schneider 2004). In addition, the heavies can cause fouling in the system and whether fouling or not, the heavies need to be removed and disposed as waste.

A study of disturbances in biological treatment of wastewater from a refinery indicated that every few months a concentrated phenolic waste (15,000 mg/L) was discharged into the refinery’s wastewater system. The waste originated from a regeneration operation of the “gasoline washery.” During normal operations, the phenols present in the wastewater stream are 10—20 mg/L (Galil 1988). After the phenolic discharge, turbidity would increase, discoloration of the biomass would occur, and strong odor was present. Within a few days, the bioactivity was inhibited and the system was poisoned. Further research showed that up to 100 mg/L concentrations could be treated effectively as long as the feed was steady and continuous (Galil 1988). For this reason, concentrated wastes are stored and gradually fed into the wastewater treatment system.

4.3.4. Tank, Pipeline, and Vessel Condition

Corrosion of tanks, pipelines, or vessels is usually found during routine turnarounds, which happen approximately every four years. During a turnaround inspection, particular components of the extraction process are visually inspected for visible signs of corrosion. Impellers of sulfolane pumps are particularly sensitive components to corrosion due to the velocity of sulfolane against the metal.

Also during a turnaround, the metal in the columns can be tested for metal thickness, evidence of pitting, and other signs of corrosion. If corrosion is present at a level that warrants action, the specific corroded metal will be replaced. This can be as small as one tray in the column, or in extreme cases, it may be the entire column. Support companies are utilized to replace and rework columns during a turnaround such as Tiger Tower Services.

In addition to inspections and possible replacements during turnarounds, corrosion probes or corrosion coupons may be used for continuous monitoring. Corrosion probes may be electrical or electrochemical devices that help determine the composition of the stream based on changed in resistance. Corrosion coupons are small pieces of the same metals used in the system that are placed in the process for a period of time. To gather meaningful results the same metals processed in the same fashion must be used.

The coupon thickness is measured prior to placement and then again after the coupon is removed from the system. The resulting data is a measurement of the loss in thickness of the metal over a period of time, usually represented by millimeters per year.

Support companies are utilized to design and place a corrosion monitoring system for an industrial process. The location of each monitoring device is important as well as the type of device. A vast network of probes and coupons helps to diminish uncertainty in data that stems from variation in the various locations and exposures throughout a system.

4.4. Sulfolane Substitutes in the Refining Process

The extraction process used in oil refining can use various solvents. Sulfolane is popular due to its high solvent to feed ratio, however, other solvents can be used with success. Extractive solvent substitutes include tetraethylene glycol (TTEG), ethylene glycol, diethylene glycol, triethylene glycol (TEG), diglycol amine (DGA), n-methyl pyrolidone (NMP), dimethylsulfoxide (DMSO), dimethylformamide, morpholine, and carbonate derivatives. Other solvents have also been used or researched. Recently, ionic liquids have been getting attention. Details of historical solvents used in various extraction processes are shown in Table 3.

The characteristics that are most important in an extractive solvent are the solvency and the selectivity for compounds of interest. In the case of oil refining, the compounds of interest are benzene, toluene, and xylenes (BTX). However, other characteristics must be taken into account such as the chemical stability, compatibility, availability, price, and environmental hazards.

The efficiency of sulfolane is difficult to exceed with a solvent-to-feed ratio of 3:1 and a BTX recovery of 99% for naptha and kerosene feeds. Additionally, its boiling point allows fairly easy separation of the sulfolane from the extract.

Glycols have historically been used as an extractive solvent in refining prior to the invention of sulfolane by Shell and continue to be used in many units. Sulfolane has a higher polarity than glycols and is therefore a better solvent; however, glycols tend to be easier to separate from extract because of the lesser polarity.

Glycols degrade with oxygen, creating aldehydes, ketones, and organic acids that are generally weaker and less corrosive than the acids created during oxygen degradation of sulfolane. These weaker acids can be neutralized with the ethanolamines diethanolamine (DEA) and monoethanoamine (MEA). Glycol degradation is tested in the same manners as sulfolane degradation: color, acid number, precipitates, separation, etc. Glycols are used during extraction at lower temperatures than sulfolane, making corrosion less extreme and also limiting the effect of chloride concentration on corrosion potential. It is relatively common to switch from sulfolane to glycol in an extraction unit that is burdened with corrosion problems (TTC 2010).

TABLE 3: EXTRACTIVE PROCESSES FOR BTX RECOVERY

Company Process	**Solvent**	**Operating Temperature**	**Contacting Equipment**	**Comments**
Shell Process, UOP	Sulfolane	120°C	Rotating disk contactor, up to 4 m in diameter	The high selectivity and capacity of sulfolane leads to low solvent-feed rations, and thus smaller equipment.
UOP Udex Process	Diethylene glycol Triethylene glycol Tetraethylene glycol	150°C for diethylene glycol and water	Sieve-tray extractor	Tetraethylene glycol and water mixtures are claimed to increase capacity by a factor of four and also require no antifoaming agent; the extract requires a two-step distillation to recover BTX.
Union Carbide Tetra Process	Tetraethylene glycol	100°C	Reciprocating-plate extractor	The extract leaving the primary extractor is essentially free of feed aliphatics, and no further purification is necessary; two-stage extraction uses dodecane as a displacement solvent in the second stage.
Institut Français de Petróle	Dimethyl sulfoxide (DMSO)	Ambient	Rotating-blade extractor, typically 10–12 stages	Low corrosion allows use of carbon steel equipment; solvent has a low freezing point and is nontoxic; two-stage extraction has displacement solvent in the second stage.
Lurgi Arosolvan	N-methyl-2-pyrrolidionone monoethylene glycol	60°C for NMP-glycol, 35°C for NMP-water	Vertical multistage mixter-settler, 24–30 stages up to 8 m in diameter	The quantity of mixing component required depends on the aromatics content of the feed.
SNAM Progetti Formex	N-formylomorpholine	40°C	Perforated tray extractor, FM density at 1.15 aids phase separation	Low corrosion allows use of carbon steel equipment.

(Kirk-Othmer 1999, p. 164)

4.5. Solvent Extraction Substitutes in the Refining Process

Depending on the end product goals of a particular refinery, removal of aromatics may be accomplished without using a solvent extraction unit. Hydrocracking is an alternative most popular when producing lubricant-base oils. In this process, hydrogen is used as a reactant to the feed stock. At high temperatures and pressures and in the presence of a catalyst, polar compounds (sulfur, nitrogen, oxygen) are removed; aromatic hydrocarbons become saturated cyclic hydrocarbons; and heavy polycyclo-paraffins are broken up into lighter saturated hydrocarbons (Boucher and Jones 2010).

The hydrocracking process for removing aromatics is chemical, and therefore can result in greater elimination of aromatics than the solvent extraction physical process of removal. The purity of the end product creates a different end product with different physical and chemical characteristics. Solvent extraction end products are often chemical grade, while the hydrocracking end products are often other grades.

Table 4 shows the carbon atom numbers and boiling range of typical crude oil refining products. Flint Hills' North Pole refinery produces only gasoline, jet fuel, heating oil, diesel, gas oil, and asphalt. They gather crude oil for refining from the Alyeska pipeline on its way from Prudhoe Bay to Valdez. The products that North Pole refines are determined by their ability to be sold into Alaska markets. Other refineries, including Flint Hills' refineries in Minnesota and Texas, refine a broader spectrum of end products than the North Pole refinery, including lubricating oils and waxes.

TABLE 4: REFINED PRODUCT CHARACTERISTICS

Product	Carbon Atoms (Approx. No.)	Boiling Range (°F)
Naphtha (Intermediate)/Gasoline	8	110–212
Kerosene (intermediate)/Jet Fuel	12	350–617
Gas oil/Diesel/Heating oil	16	482–662
Lubricating oil	36	572–700
Residuals (coke, asphalt, tar, wax)	80, multi-ringed	> 1,112

5. SULFOLANE CASE HISTORIES

OASIS conducted global research to identify case histories of sulfolane spills and sites contaminated with sulfolane. This section describes the process and the results of the research. It is important to note that despite the significant effort of making contacts, little information was gathered in the search for information on groundwater spills and cleanup. There are a few reasons for this reality.

Both the sulfolane extraction process and the Sulfinol process are proprietary processes, and associated information is often proprietary. Questions about the process or the chemical are not looked upon favorably. In most situations, although sulfolane is classified as a hazardous chemical, it has not been thought to be highly toxic, and it is not generally regulated as a water or soil contaminant. Therefore, the solvent has not been tested for or deemed as a contaminant of concern by regulatory bodies, so very little information exists. In a few certain locations, sulfolane is regulated, and industrial facility personnel are not willing to provide anecdotal information on environmental problems with the solvent.

5.1. Approach and Methods

Upon commencement of this project, OASIS and ADEC circulated a questionnaire among members of the Association of State and Territorial Solid Waste Management Officials (ASTSWMO) asking about their familiarity with sulfolane. ADEC received assistance from regulators in California and the Agency for Toxic Substances and Disease Registry (ATSDR) in gathering information that led to the derivation of drinking water standards for the State of Alaska.

5.1.1. State Regulatory Contacts

The environmental regulatory agency in each of the 50 states in the U.S. was contacted by phone. Regulators in hazardous waste, remediation, or groundwater were asked if they had experience with the chemical sulfolane or if that state has established maximum contaminant levels (MCLs) for sulfolane. If the regulator expressed interest in the issue, he was sent a questionnaire with a link to the ADEC website about the sulfolane issue at Flint Hill's North Pole refinery and was asked to distribute it to departments and personnel who may be able to provide assistance. The questionnaire is included in Appendix E. Approximately 60% of the states' regulators were sent questionnaires.

Based on responses from the phone survey, Texas is the only state that has established MCLs for sulfolane. The Tier 1 Groundwater Protective Concentration Levels (PCLs) for sulfolane, regulated by the Texas Commission on Environmental Quality (TCEQ), are tabulated in Table 5.

TABLE 5: TEXAS COMMISSION ON ENVIRONMENTAL QUALITY SULFOLANE PCL

Medium	Protective Concentration Level (PCL)
Residential Groundwater for Ingestion	0.49 ppb
Residential Class 3 Groundwater (not suitable for drinking)	49 ppb
Commercial/Industrial Groundwater for Ingestion	1.5 ppb
Commercial/Industrial Class 3 Groundwater (not suitable for drinking)	150 ppb

Key:
ppb: Parts per billion

Appendix E contains Tables 1 through 5 for TCEQ's Tier 1 PCLs for various soils and groundwater media.

5.1.2. Environmental Protection Agency

The EPA does not regulate sulfolane. In Volume 59, Number 249 of the Federal Register in 1994, sulfolane was removed from the priority testing list of the Toxic Substance Control Act's Interagency Testing Committee. However, it is currently included on the High Production Volume (HPV) sponsored chemicals list. HPV chemicals are classified as those chemicals produced or imported in the United States in quantities of 1 million pounds or more per year (http://www.epa.gov/HPV/pubs/update/hpvchmlt.htm). The website for the EPA was searched for sulfolane references as were each EPA region's website in the U.S (http://www.epa.gov/regional).

5.1.3. International Contacts

Various countries were contacted based on prior knowledge of sulfolane issues or the prevalence of the oil refining industry, the stringency of environmental regulations, and the ease of communication. The prevalence of the oil refining industry was determined based on a list from the U.S. Department of Energy, Energy Information Administration showing the oil refining ability by country. The stringency of environmental regulations was determined from The Global Competitiveness Report of the World Economic Forum from 2007. Ease of communication was based on time zone difference from Alaska and speaking the English language.

A combination of regulatory body, industry, laboratory, and manufacturer contacts were phoned, emailed, or contacted by internet form. Approximately 25% responded. In addition, various agencies and companies were researched via the Internet. Information that was attempted to be gathered included cleanup levels for soil or water and case studies on use or misuse of the chemical. A complete list of international contacts is included in Appendix E. Only information on positive responses is included in the following sections.

5.1.3.1. European Union

The regulatory framework for high production volume chemicals applies to sulfolane in Europe through the REACH program (Registration, Evaluation, Authorization, and restriction of Chemicals); however, no information was found to imply that any other standards or cleanup levels apply to the European Union as a whole. A manufacturer and distributor of sulfolane in Belgium, Novasol, was contacted regarding any knowledge of spills or pollution relating to the chemical. They were not aware of any environmental hazards.

5.1.3.2. New Zealand

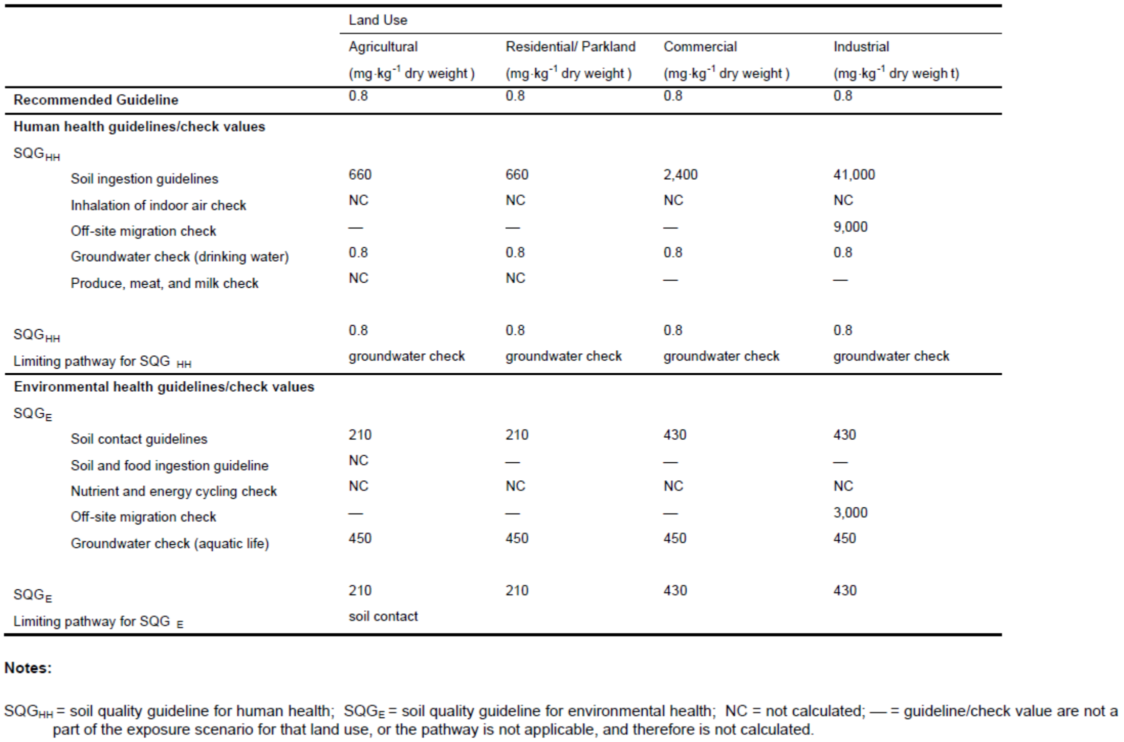
Sulfolane, spelled sulpholane in New Zealand, is managed under several pieces of legislation. A contact with the Northland Regional Council suggested that the Department of Labour covers sulfolane under workplace exposure standards; however, this was unable to be confirmed. Additionally, the chemical is managed under the New Zealand Hazardous Substances and New Organisms Act. In the Marine Pollution regulations under the Resource Management Act, sulfolane is listed as a noxious liquid and cannot be discharged into marine waters. No other indication of the chemical being regulated in New Zealand was found. However, the laboratory contracted by the Northland government has tested for sulfolane in the past relating to refinery products, but at a detection limit of 500 ppb.

5.1.3.3. Canada

The federal environmental regulatory body for Canada, Environment Canada, regulates sulfolane in water and soil through environmental quality guidelines. A document titled *Canadian Environmental Quality Guidelines for Sulfolane: Water and Soil* is a discussion of the chemical with supporting information on the regulation. It is thorough in discussing background information on persistence, effects, toxicity, and remediation of sulfolane. The drinking water guidance for human ingestion is 0.09 milligrams per liter (mg/L). Dermal contact is calculated to be 0.1% of the oral dose and can be disregarded. The soil quality guidelines are shown in Table 6, and the water quality guidelines are shown in Table 7.

The provinces of British Columbia (BC) and Alberta both have guidelines at the province level government. BC has the same water quality guidelines from 2003 as Environment Canada. Alberta includes sulfolane as a Tier 1 contaminant for soil and groundwater remediation through the framework for the management of contaminated sites. For fine soils and also agricultural use, the cleanup level is 0.18 milligrams per kilogram (mg/kg), and for coarse soil the cleanup level is 0.21 mg/kg. The cleanup level for groundwater is 0.09 mg/L for all soils and uses (Alberta Environment 2009). To determine Tier 2 guidelines, guidance levels for various exposure pathways are given for each type of land use. The entire document with the Tier 2 guidelines is included in Appendix E.

TABLE 6: CANADIAN SOIL QUALITY GUIDELINES ON SULFOLANE

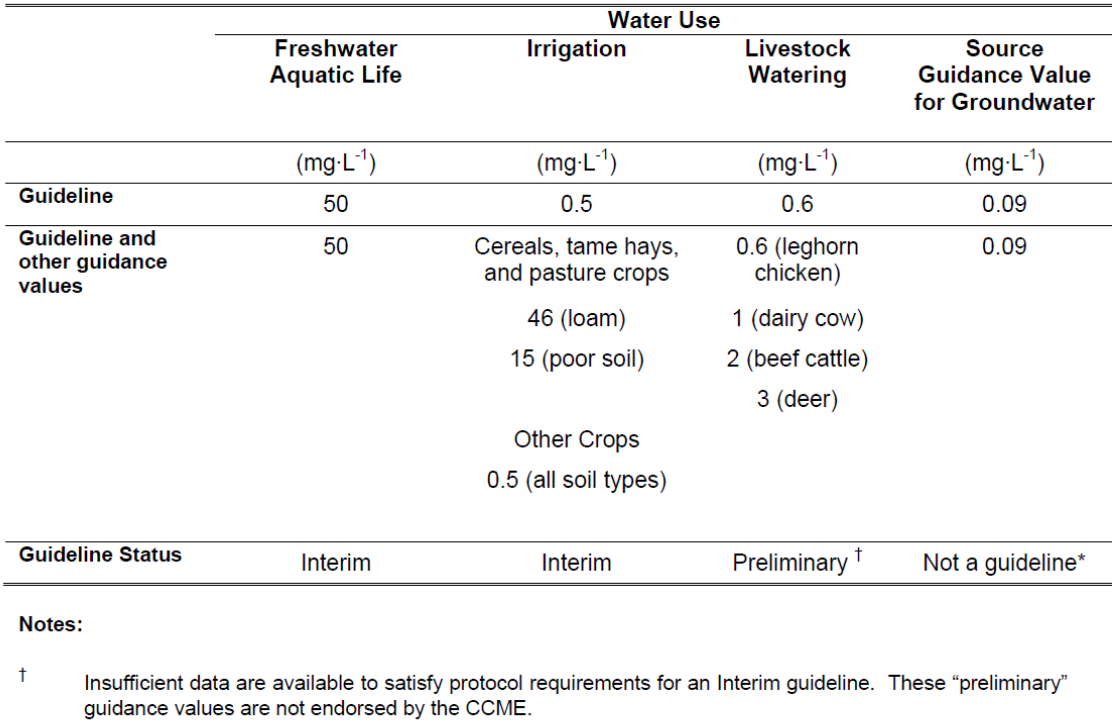


	Land Use			
	Agricultural (mg·kg^{-1} dry weight)	Residential/ Parkland (mg·kg^{-1} dry weight)	Commercial (mg·kg^{-1} dry weight)	Industrial (mg·kg^{-1} dry weigh t)
Recommended Guideline	0.8	0.8	0.8	0.8
Human health guidelines/check values				
SQG$_{HH}$				
Soil ingestion guidelines	660	660	2,400	41,000
Inhalation of indoor air check	NC	NC	NC	NC
Off-site migration check	—	—	—	9,000
Groundwater check (drinking water)	0.8	0.8	0.8	0.8
Produce, meat, and milk check	NC	NC	—	—
SQG$_{HH}$	0.8	0.8	0.8	0.8
Limiting pathway for SQG $_{HH}$	groundwater check	groundwater check	groundwater check	groundwater check
Environmental health guidelines/check values				
SQG$_{E}$				
Soil contact guidelines	210	210	430	430
Soil and food ingestion guideline	NC	—	—	—
Nutrient and energy cycling check	NC	NC	NC	NC
Off-site migration check	—	—	—	3,000
Groundwater check (aquatic life)	450	450	450	450
SQG$_{E}$	210	210	430	430
Limiting pathway for SQG $_{E}$	soil contact			

Notes:

SQG$_{HH}$ = soil quality guideline for human health; SQG$_{E}$ = soil quality guideline for environmental health; NC = not calculated; — = guideline/check value are not a part of the exposure scenario for that land use, or the pathway is not applicable, and therefore is not calculated.

TABLE 7: CANADIAN WATER QUALITY GUIDELINES ON SULFOLANE



	Water Use			
	Freshwater Aquatic Life	**Irrigation**	**Livestock Watering**	**Source Guidance Value for Groundwater**
	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})	(mg·L^{-1})
Guideline	50	0.5	0.6	0.09
Guideline and other guidance values	50	Cereals, tame hays, and pasture crops 46 (loam) 15 (poor soil) Other Crops 0.5 (all soil types)	0.6 (leghorn chicken) 1 (dairy cow) 2 (beef cattle) 3 (deer)	0.09
Guideline Status	Interim	Interim	Preliminary †	Not a guideline*

Notes:

† Insufficient data are available to satisfy protocol requirements for an Interim guideline. These "preliminary" guidance values are not endorsed by the CCME.

5.1.4. Other Contacts

In addition to the regulatory bodies in the U.S. that were contacted, various manufacturers, distributors, transporters, refineries, and other interested parties were phoned or emailed for information. Limited success was found when attempting to gather information from these contacts. Appendix E contains records of correspondence.

5.2. Spill and Contaminated Sites Case Histories

Based on Internet research, literature research, and information gathered from various contacts as described in Section 5.1, eight case histories were discovered. The case studies have different causes of sulfolane contamination, but the most prevalent cause appears to be management of waste and wastewater. Although corrosion is a problem in sulfolane processes due to degradation, research did not indicate that corrosion ever became severe enough to cause leakage or spills of sulfolane outside of the plant. Generally, the degradation of the sulfolane would cause process problems prior to causing severe corrosion resulting in leaks or spills.

In the following case studies, many of the sulfolane concentrations were found in wastewater or groundwater after testing, often for other contaminants.

5.2.1. POPCO Gas Processing Plant, Capitan, California

In January 2008, 100 gallons of sulfolane spilled from the Pacific Offshore Pipeline Company (POPCO) gas processing plant in El Capitan Canyon near Santa Barbara, California. The plant is owned and operated by ExxonMobil. A worker noticed a leak from a flange on a gas processing exchanger unit and suspected a failure in the gasket. The spilled sulfolane ran into the nearby Las Flores Creek, which merges with Corral Creek and drains into the Pacific Ocean only 1.5 miles away (SBCFD 2008).

The POPCO plant operator directed questions to Exxon headquarters. A call to Exxon yielded no response. The California Department of Fish and Game reported that the spill occurred during a heavy rain storm, and the sulfolane was flushed quickly along the creeks. Samples were collected by a contractor, Padre Associates, Inc., from along the creek path and submitted to Associated Laboratory in Orange, CA. Follow-up with Padre Associates, Inc., yielded no response. A contact at the County of Santa Barbara was able to find out the sample results, which were reported at 570 ppb. The county also reported details of the event: the final cause of the leak was determined to be a defective flange on a gas exchanger vessel, the Sulfinol system was immediately shut down, a spill gate in the creek was closed, and a vacuum truck reduced water behind the spill gate. Further investigation was not conducted at the site.

A report of the POPCO spill is included in Appendix F.

5.2.2. Hess Corporation and Hovensa, St. Croix, Virgin Islands

Information was gathered through industry contacts about a possible sulfolane spill in the early 1980s at the Hess Oil Refinery, now Hovensa, located in St. Croix in the Virgin Islands. It was suggested that the sewer line dedicated to aromatics and solvent was assembled using an adhesive that dissolved in the presence of sulfolane. A contact at Hovensa who is currently the most senior employee at the facility believed that this information was hearsay. A contact at UOP, the licenser of the sulfolane extraction unit at the Hovensa plant, had never heard of the issue (TTC 2010). The EPA Region 2 contact at the Virgin Islands office was not aware of the chemical sulfolane.

The Hovensa facility is a Resource Conservation and Recovery Act (RCRA) site related to oil spills and has undertaken remediation efforts to recover hydrocarbons since the early 1990s. In an attempt to discover whether sulfolane was a contaminant of concern for the Hovensa RCRA site, the EPA Region 2 Project Coordinator for the site was contacted. He was unfamiliar with the chemical and did not believe that it had ever been mentioned in relation to the site. He subsequently requested information from Hovensa regarding whether sulfolane had ever been tested for at the site. A Hovensa contact replied that the chemical had not been tested for in either soil or groundwater, but fingerprinting of hydrocarbon samples from 1997 and 1998 showed sulfolane peaks that matched a sulfolane sample extracted from Hovensa's No. 2 sulfolane extraction unit.

The EPA Region 2 Project Coordinator for the RCRA site requested on April 30, 2010, that Hovensa add sulfolane as an analytical constituent for semiannual groundwater monitoring at the six wells that showed sulfolane in the fingerprinting from the 1990s. Information will be available on the concentration of sulfolane following that analysis and sampling event and may eventually become a case of interest.

5.2.3. Shell Gas Processing Plant, Waterton, Canada

A report written by WorleyParsons Komex in 2008 refers to a Shell Energy Canada facility with sulfolane contamination first discovered in the 1980s. Upon contacting the Government of Alberta Environment, it was determined that the site was the Waterton sour gas processing complex in southern Alberta. Shell Waterton is located approximately 90 miles north of Flathead Lake in Montana. The Sulfinol process has been used at this plant since the 1960s, and both sulfolane and DIPA were found in groundwater in the 1980s. The cause of contamination is suspected to be spills, unlined process water storage ponds, and landfills where spent Sulfinol filters and spent catalyst were disposed of (Greene et al. 1998). Similar practices relating to sulfolane use have been identified at many gas processing plants in western Canada, where the natural gas has high sulfur content.

Research on the natural biodegradation of sulfolane in soil and water were conducted by the University of Alberta in Canada at a total of three known contaminated gas processing plants in western Canada. Characterization and remediation have been conducted at the Shell Waterton site from the 1990s to the present. The widespread and historical use of sulfolane in western Canada prompted the Alberta and BC governments to establish limits on sulfolane in soil and water as well as overall Canadian Environmental Quality Guidelines for sulfolane.

A contact at the local Lethbridge, Alberta, office of Alberta Environment did not have information on the Shell Waterton contaminated site and directed questions to a contact at WorleyParsons. The contact at WorleyParsons was unable to give any further background information on the case without receiving approval from appropriate parties.

According to the Shell Canada *Progress Toward Sustainable Development Report* in 1999, sulfolane was found in groundwater around the Waterton plant. Water was provided by Shell to three affected residents nearby until the extent of sulfolane could be delineated and sources could be eliminated. Based on information in the University of Alberta research papers, it can be deduced that the starting concentration of sulfolane in the groundwater at the Shell Waterton plant was between 300 and 700 ppm. The area of impact can be estimated at approximately 1 square mile by plume figures in the WorleyParsons remediation plan.

Eight recovery wells were installed in 2001 to capture sulfolane-contaminated groundwater at the site for onsite remediation and biodegradation. The pilot system was an aerobic biological system with activated sludge from the process wastewater treatment plant and a clarifier. Further remediation information on this site is included in Section 5.4.1.1.

5.2.4. Norco Chemical Plant, Shell Oil Company, Louisiana

The Norco Manufacturing Complex in Norco, Louisiana, was constructed in 1954 to manufacture chemicals. The complex covered 103 acres on the east bank of the Mississippi River and produced sulfolane from 1967 to 1988. Other chemicals manufactured at the site included epichlorohydrin, allyl chloride, hydrochloric acid (HCl), methyl ethyl ketone (MEK), secondary butyl alcohol, calcium chloride, epoxy resins, SHAC® Catalyst, and chlorinated solvents. A review was performed on reports generated from 1995 to 2004 for the EPA and the Louisiana Department of Environmental Quality (LDEQ). These reports are located in Appendix F.

In the 1990s, concentrations of sulfolane were found in the soil and groundwater at four of the 97 solid waste management units (SWMUs) located on the property and in several other locations at the complex. Concentrations of sulfolane were also found in surface water and sediment in storm water ditches on and directly adjacent to the property. Most of the contaminated areas were less than ½ acre in area. The largest of the sulfolane-impacted sites was less than 1.65 acres.

The source of sulfolane contamination appeared to be waste disposal practices such as storage of process water and spent catalysts that were awaiting treatment. No indication of pure sulfolane releases was encountered.

Maximum concentrations of sulfolane were 2,900 ppm in groundwater, 369 mg/kg in soil, 126 ppm in ditch surface water, and 36.1 mg/kg in ditch sediment. Average concentrations were generally in the 10 to 100 ppm range for groundwater. Sulfolane did not appear to be encountered at depths greater than 25 feet below ground surface (bgs) due to confining layers in the soil stratigraphy. Crawfish tissue samples were obtained from affected ditches, but they did not contain levels of sulfolane (LDEQ 2002). Groundwater flows away from the Mississippi River, and contaminants from this site have not been shown to be leaching into the waterway.

Risk Evaluation/Corrective Action Program (RECAP) standards were derived for the site based on a target hazard quotient of 0.1. Groundwater was defined as Classification 1, a source of drinking water. The standards were as follows:

- 69.4 ppb in Class 1 groundwater (Equilon 1998)
- 0.173 mg/kg in soil based on the soil leaching to Class 1 groundwater
- 5.22 mg/kg in soil for industrial/commercial land use considering exposure due to ingestion, inhalation of volatiles, and dermal contact

The receptor population was determined to be limited to on-site workers involved in construction or soil excavation. It was further determined that no affected groundwater would be used for residential or industrial purposes as industrial water wells draw from aquifers several hundred feet bgs and drinking water is taken from the Mississippi River. Therefore, revised screening levels were generated under a Management Option 2 (MO-2). MO-2 screening levels were as follows:

- 14.4 ppm in groundwater with no dilution factor
- 21.6 ppm in groundwater with dilution factor (MO-3)
- 36.0 mg/kg in soil
- 14.4 mg/kg in surface water
- 3.60 mg/kg in sediment (LDEQ 2002)

Three recovery wells operated at one of the sulfolane-affected areas at 19 feet bgs. No data were found supporting their effectiveness. Remedial alternatives for the site included natural attenuation, phytoremediation, and installation of interceptor trenches. Discussions or these remedial strategies can be found in sections 5.4.1.2, 5.4.1.3, and 5.4.3.1, respectively.

5.2.5. Occidental Chemical, Lathrop, California

Occidental Chemical Corporation formerly operated a pesticide manufacturing plant in Lathrop, California, approximately 60 miles east of San Francisco. Sulfolane was used as a process solvent in manufacturing and was found in groundwater near the plant at a concentration of approximately 3 ppm in the late 1970s. The method by which the sulfolane reached the groundwater is not described in available literature.

After initially determining in the 1970s that sulfolane was not a contaminant of concern for the site due to its low concentration and limited toxicity, a groundwater extraction and carbon treatment remediation system was operated from 1982 through the 1990s to treat the other contaminants. However, in the late 1980s sulfolane became a contaminant requiring cleanup because of a change in the classification of the deep saline aquifer in the Lathrop area for productive uses (McLeod 1994).

Treatment options for sulfolane were reviewed, but a successful candidate was not found in part due to the already low concentrations of sulfolane in the groundwater. OxyChem began a research investigation to find a treatment. Three articles found during a literature review revealed that sulfolane was removed using biological wastewater treatment processes. Bench scale testing of biologically activated carbon (BAC) columns was completed in 1989. Pilot testing was completed in 1991.

A sample of groundwater contained 3,000 ppb of sulfolane in 1981 prior to any remediation. After two years of pumping and treating with carbon, the sulfolane concentration was found to be 1,000 ppb. During the time of BAC pilot testing, the sulfolane concentration was 500 ppb. In 1994, the discharge limit was set at 57 ppb. With full-scale implementation of the BAC treatment system, sulfolane was not detected in the effluent. The analytical testing detection limit for sulfolane was 19 ppb.

Further details of the remediation process are included in section 5.4.1.1.

5.2.6. McGregor Lake, Alberta, Canada

The McGregor Lake gas processing plant was owned in 1991 by Coho Resources Limited. Current information on this plant was unable to be found. This gas processing plant used the Sulfinol process for gas treatment prior to 1992, and during routine groundwater monitoring in the late 1990s, it found elevated dissolved organic carbon (DOC) with no known origin. After testing soil and water for sulfolane as a potential cause of elevated DOC, sulfolane was found to be present in half of the monitoring wells on-site (Agatonovic 2005).

In 2003, 11 additional groundwater monitoring wells were placed at a maximum depth of 36 feet bgs, with a total of 54 soil samples collected during placement. Based on an assessment of the data, it was estimated that approximately 12,500 cubic yards of soil had sulfolane concentrations greater than 500 mg/kg. Delineation continued into 2004. The highest concentration of sulfolane found in soil was 3,400 mg/kg (Agatonovic 2005).

In order to meet the 2005 guidelines by the Canadian Council of Ministers of the Environment for the maximum allowable concentration of sulfolane in soil of 2.3 mg/kg and groundwater of 0.26 mg/L, remediation pilot tests were commenced. For soil, bioreactors were used with seven fertilizer treatments. For water, UV irradiation and mineralization were tested for chemical oxidation. Further discussion of remediation at the McGregor site is included in Sections 5.4.1.1 and 5.4.2.1.

5.2.7. Liquid Waste Disposal Facility, Brisbane, Australia

Sulfolane was detected in an aquifer beneath a waste disposal site near Brisbane, Australia. The source of sulfolane is thought to be careless disposal of Sulfinol process waste, such as sludge from an ammonia plant. Further information on the extent or concentration of contamination was not available. An e-mail to the researcher in Australia was not returned.

The ammonia plant responsible for the waste is likely Incitec Pivot, a manufacturer of fertilizer. When contacted, an engineering plant manager for Incitec Pivot stated that the plant no longer uses Sulfinol as the amine blend for CO_2 removal. A few years ago the plant switched to using activated methyldiethanolamine (aMDEA), which has less degradation and uses lower heat. The main reason for changing to a new amine blend was to recover costs from continual solvent loss and need for filters, as sludge caked in the recovery tower (Incitec Pivot 2010).

5.2.8. CAM Environmental, North Pole, Alaska

CAM Environmental, an environmental services company that offers industrial and turnaround support, aided in waste management during a turnaround at the Williams Refinery in North Pole, Alaska, in 2003. During this turnaround, high-pressure water washing was employed as a technique for cleaning residual products from the main crude unit surfaces. This is known as hydroblasting and can occur at a pressure of 10,000 pounds per square inch (PSI), using approximately 30 to 60 gallons of water per minute (Perez 2003). The wash water, now contaminated with the residual products, needed to be handled as wastewater for proper treatment or disposal.

CAM Environmental was hired for the May 2003 turnaround because of waste handling issues encountered during a similar turnaround in 2002. In that instance, high sulfolane concentrations were found in wash water and were unable to be treated by the facility's bioponds without harming the bacteria. Unfortunately, the sulfolane wash water was mixed with other wash water that was able to be treated by the facility's bioponds, but after mixing, all wash water had to be stored and disposed of off-site at an expense.

Based on anecdotal information from industry sources, the management of wash water during hydroblasting in turnarounds is a fairly recent practice. Now, the wash water is gathered in bermed basins surrounding the equipment being cleaned. That water is collected by a vacuum truck and transported to the appropriate area for disposal or treatment. In the past, wash water was not collected after hydroblasting, but was left to evaporate.

5.3. Sulfolane Corrosion Case Histories

Due to sulfolane corrosion being a strictly industrial problem with no apparent crossover into the public realm, it was only possible to find one specific case history on corrosion in the extraction process. However, research did indicate that corrosion in extraction units is a prevalent issue that is dealt with by a large number of refineries and gas plants.

The one specific case of corrosion in a sulfolane extraction unit was reported at the Saudi Aramco Shell Refinery in 1994. In this case, the extraction unit has a history of corrosion problems, specifically in the "fat solvent line to the stripper," the reboiler tubing, and the solvent recovery column. The stripper column was lined with carbon steel, re-lined with 410 stainless steel seven years later, and then re-lined with duplex stainless steel three years later. The reboilers were retubed six times in nine years (Harbi 2004).

The root cause was suspected to be acidic degradation products due to oxygen ingress, lack of filtering, poor performance of the solvent regenerator, and decreased water bleed. Chlorine was found to create HCl in other plant processes that operated at high temperatures. Recommendations for fixing the solvent degradation problem was to check tightness in the vacuum system and do pressure tests at start-up, monitor chlorine content and sea water, drain the regenerator regularly, clean the equipment and lines during turnarounds, limit reboiler temperatures to 175°C, and limit steam condensation temperatures in the reboiler to 250°C (Harbi 2004).

TTC Labs reported that in certain cases the quality of the solvent remains degraded without regeneration for so long that the extraction unit columns require replacement. Of the more than 150 sulfolane extraction units in the world, one or two major columns are condemned and replaced due to corrosion every year (TTC Labs 2010). However, specific case histories were unable to be found to report on the extent and frequency of column replacement due to corrosion.

5.4. Remediation Case Histories

The foundational work on remediating sulfolane from spills at refineries was completed by researchers at Shell in the early 1980s when they were responding to the increased use of sulfolane in industry. The occurrence of spills was assumed to increase with the increased usage of the chemical. Shell responded with an analysis of whether sulfolane could be biodegraded with a typical industrial facility biotreater.

Since the work of Shell, the highest-profile remediation study is related to various gas processing plants in Alberta and BC, Canada, which found sulfolane in groundwater in the 1990s. Independent contractors, university researchers, and the government were highly involved in the case to develop cleanup levels, design remediation systems, research sulfolane responses in the environment, and create regulation of the chemical for Canada.

Case histories relating to remediating sulfolane in water generally originate with companies dealing with industrial wastewater treatment. It appears to be common for industrial processes that use sulfolane as a solvent to have concentrations in their wastewater streams. Shell reported that “sulfolane is usually present in wastewaters from petroleum refining and gas treating plants at levels of about 10 mg/l or less” (Chou 1983). More current information on the concentration of sulfolane in industrial wastewater was not found.

Remediation case histories are summarized in the following sections, with supporting documents included in Appendix F.

5.4.1. Biological

5.4.1.1. Aerobic

Shell Development Company tested a bench scale completely mixed activated sludge system (CMAS) and a bench scale continuously stirred tank reactor (CSTR). The CMAS was used to simulate industrial wastewater treatment with an aerator, clarifier, and sludge recycle pump. Dissolved oxygen, pH, and temperature were controlled. Supplemental alkalinity was always required to maintain pH, likely due to sulfolane conversion to inorganic sulfate. The reactor was seeded with activated sludge from a refinery biotreater. In one week, the system was able to remove more than 80% of sulfolane with a starting concentration of 20 ppm (Chou 1983).

The CSTR system consisted solely of an aerated lagoon that was operated for 4 months. In 24 hours, sulfolane concentration was reduced from 100 ppm to less than 1 ppm. Sulphur was recovered as SO_4^{2-} (Chou 1983).

Occidental Chemical Corporation successfully used biologically activated carbon (BAC) columns in the early 1990s at the Lathrop manufacturing plant for remediation of sulfolane in groundwater. Starting concentrations of 3,000 ppb were reduced to less than 19 ppb at a feed rate of 15 L/hr (McLeod 1994). BAC was chosen for its prior use at the site, its ability to treat additional organic pollutants and heavy metals, and because the activated carbon does not need to be periodically replaced due to bacteria continuously utilizing adsorbed organic compounds. Feasibility and treatability studies were conducted using bench scale and pilot scale systems.

In the bench scale BAC system, columns inoculated with activated sludge from a petrochemical plant treated a Lathrop groundwater sample to the detection limit of 19 ppb in three to five days. The groundwater sample had the parameters of pH = 6.9, dissolved oxygen = 1.9 ppm, total organic carbon = 4.2 ppm, total insoluble organic carbon = 84 ppm (McLeod 1992,1994). The activated sludge was known to contain sulfolane-degrading bacteria, because it had been in use to degrade sulfolane in wastewater at a Texas petrochemical treatment plant.

After a successful pilot scale study, a full treatment system was implemented by adding sulfolane-degrading bacteria to the current remediation system carbon columns. Treatment in 2003 showed influent sulfolane concentrations at 300–500 ppb and effluent concentrations at <19–26 ppb (McLeod 1994). The full report is included in Appendix F.

WorleyParsons Komex designed and operated a pilot treatment system with activated sludge and a clarifier at an Alberta sour gas treatment plant. The pilot system was operated seasonally during 2003 and 2004. Activated sludge from the plant's own process wastewater treatment system was used for the pilot system. The treatment was found to be effective to 0.001 mg/L at a treatment capacity of 150 m^3/day (WPX 2008). Effluent from the pilot system was sent to the plant process wastewater treatment system. At the eastern location, the volume of water treated in 2003 was 3,700 m^3, and the mass of sulfolane removed was 112 kilograms (kg). In 2004, the volume of water treated was 2,400 m^3, and the mass of sulfolane removed was 45 kg. At the southern location, over 12,000 m^3 of water was treated each year, and approximately 25 kg of sulfolane was removed each year (WPX 2008).

Based on pilot system results, a full-scale system was built to the parameters shown in Table 8.

TABLE 8: DESIGN PARAMETERS FOR FULL-SCALE REMEDIATION SYSTEM

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

(WPX 2008)

Five groundwater wells are tied to the fully automated system. Maintenance is performed by the plant personnel as part of the regular plant maintenance. The system was installed during regular plant operation. Acid must be added to the system to prevent scaling in water. The volatile suspended solids (VSS) concentration is indirectly correlated to the sulfolane: low VSS results in high sulfolane. The presentation detailing this process is included in Appendix F.

A treatability study was conducted for the McGregor Lake plant contamination in Alberta. Hydroqual Labs conducted a treatability study of sulfolane-contaminated soil at an average concentration of 1,400 mg/kg. The soil was treated using ammonia nitrogen fertilizer at 83 and 232 mg/kg concentrations and ammonia phosphate fertilizer at 83 and 232 mg/kg concentrations. For all studies, oxygen concentration was maintained at > 10%. After 78 days of incubation, the soil was non-toxic to Microtox® and considered remediated successfully (Agatonovic 2005) Microtox® is an acute toxicity test that uses the bacteria *Vibrio fischeri* to produce light when its metabolism is affected.

Treatability for groundwater was also conducted for the McGregor Lake plant, but by aeration and nutrient amendment in a biotreater. The study was conducted by the University of Calgary Tomographic Imaging and Porous Media Laboratory (TIPML). A 24 hour trial was conducted using groundwater with 1800 mg/L of sulfolane. Ammonia phosphate nutrient was added and continuous aeration was conducted with micro bubble technology to maintain oxygen greater than 7.7 mg/L. After 24 hours, sulfolane was 73% removed to a concentration of 490 mg/L (Agatonovic 2005). The presentation and paper detailing the McGregor Lake treatability studies are included in Appendix F.

In addition to these four bench scale, pilot scale, and full scale systems, numerous laboratory studies have been conducted on various aspects of aerobic degradation. A series of studies completed by the University of Alberta confirmed that aerobic degradation does occur. Degradation rates were dependant on temperature but degradation does occur at temperatures consistent with northern latitude soils (8°C) (Fedorak et al. 1996). Biodegradation rates can be stimulated through nutrient addition, specifically nitrogen and phosphorus (Greene et al. 2001). The bacterial isolates that accomplish sulfolane degradation have been identified and appear to be present in native soils in western Canada (Greene et al. 2000). Bacteria appear to need inoculation with sulfolane prior to achieving substantial degradation, which may not be a concern at a site with historic levels of sulfolane.

5.4.1.2. Anaerobic

Research was conducted by the University of Alberta on anaerobic degradation of sulfolane. A thermodynamic evaluation showed that terminal electron acceptors would be oxygen, nitrate, Mn(IV), Fe(III), sulfate, and CO_2. However, results from the anaerobic microcosms supplemented with sulfolane showed only minimal biodegradation under nitrate and Mn(IV) reducing conditions and no biodegradation under Fe(III), sulfate, or methanogenic reducing conditions. The authors of the literature concluded that although anaerobic degradation may be possible, it probably would not have a noticeable effect on the attenuation of sulfolane (Greene et al. 1998). The complete report is included in Appendix F.

Research on anaerobic degradation was conducted on soil and sludge at the University of Queensland in Brisbane, Australia. The study documented the anaerobic degradation of sulfolane and identified that the presence of thiolane inhibited degradation rates (Kim, 1999). Thiolane is an intermediate breakdown product of sulfolane.

At the Norco Chemical Plant site, natural attenuation was proposed as a remedial alternative. It was known that in the absence of oxygen, sulfolane can undergo oxidative transformations using alternate electron acceptors such as nitrate, ferric iron, sulfate, and CO_2. Spatial patterns of nitrate, sulfate, and carbon dioxide depletion can indicate the occurrence of oxidation. Increases in ferrous iron as ferric iron is reduced are also an oxidation indicator. Sulfolane could also serve as an electron donor for the reductive dechlorination of chlorinated ethenes and ethanes in areas where the constituents occur together (URS Greiner Woodward Clyde 1999b). Natural attenuation monitoring was implemented at the site following its proposal. Subsequent reports were not located to examine for trends.

5.4.1.3. Phytoremediation

Utah State University, in coordination with three Canadian groups, conducted research on the uptake of sulfolane in cattails in 2005. After an exposure to 20 mg/L of sulfolane for 50 days, up to 33,000 mg/kg dry weight was found in cattail leaf tips (Doucette et al. 2005). The transpiration stream concentration factor (TSCF) was calculated at 0.9 for sulfolane in the leaf tip. The results were not expected given that the octanol/water coefficients (log K_{ow}) suggest limited uptake, so a conclusion was made that the relationship between TSCF and log K_{ow} is not well known. The full report is included in Appendix F.

Phytoremediation was proposed as a remedial alternative at the Norco Chemical Plant site. No mention was made of phytoremediating sulfolane specifically, just phytoremediating the group of contaminants as a whole. Surface water and shallow soils were the most promising benefactors. It was suggested that phytoremediation had been occurring due to a drop in contaminant concentrations in surface water across a heavy foliage area on-site. Analytical data for one growing season showed that surface water contaminant concentrations decreased as the growing season progressed. Vegetative surveys and planting of vegetative caps were offered as corrective measures (URS Greiner Woodward Clyde 1999b). No outcomes of the proposed phytoremediation study proposals were found.

5.4.2. Chemical

5.4.2.1. Oxidation

A chemical oxidation trial to determine sulfolane mineralization was completed by the University of Calgary Tomographic Imaging and Porous Media laboratory (TIPML). Hydrogen peroxide was used and expected to be able to mineralize sulfolane in groundwater based on the following equation:

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

To increase the number and stability of hydroxyl radicals, hydrogen peroxide was used in conjunction with UV irradiation. Sulfolane concentration ranged was 63 ppm. Hydrogen peroxide at a concentration of 30% was added to the water at 50 mL/L over 7 days under the influence of a 40 watt fluorescent UV bulb with 350 nanometer emission. The removal ratio was 95% (Agatonovic 2005). The complete report is included in Appendix F.

5.4.2.2. Precipitation

No information was gathered on precipitation as a remediation method for sulfolane. Based on the information gathered from researching corrosion methods, it appears that reacting chlorides with the acids that are by-products of sulfolane oxidation create precipitates.

5.4.3. Physical

5.4.3.1. Filtration

Interceptor trenches were installed at the Norco Chemical Plant site to control groundwater flow and intercept discharge of groundwater to the shallow surface ditches. Two trenches approximately 140 feet long each were dug to a depth of 16 feet bgs where there is a confining soil layer in that area of the site. Four-inch-diameter perforated pipe was placed horizontally in the trenches and connected to vertical 24-inch-diameter sumps. Submersible pumps were placed in the sumps to achieve hydraulic control of groundwater. The trenches were backfilled with filter sand up to 5 feet bgs and covered with a geotextile fabric. Native fill completed the backfill to surface. Two similarly constructed trenches were already in place on the property. Extracted groundwater was sent to an on-site stripper for treatment. It was stated that the trenches were successful in diverting the hydraulic flow away from surface ditches (URS Greiner Woodward Clyde 2002).

Conversations with CCR, a company specializing in the recovery and regeneration of sulfolane from processing, suggested that at concentrations of 500 ppm and below, physical separation via an ultrafiltration membrane may be possible to remove water from sulfolane to concentrate the sulfolane. At 5%–10% sulfolane concentration in water, the sulfolane can be recovered by vacuum distillation and reused in the extraction process. A material known as polyphenylene sulphide (PPS) in the Fortron® line developed by Ticona can be blow-molded or extruded into films and fibers for specialty filtration, including aggressive fluids such as sulfolane. A whitepaper on PPS is included in Appendix F.

5.4.3.2. Adsorption

At the Oxychem plant in Lathrop, California, two parallel 40,000-pound upflow carbon adsorbers were in use to remediate the chemical contaminants DBCP and EDB. This remediation system was in use beginning in 1983 and was successful in remediating DBCP and EDB. However, in more than 10 years of use, it was not successful in remediating sulfolane at an influent concentration of 3,000 ppb. It is likely that this was partly due to the carbon's capacity for DBCP and EBD being much higher than for the sulfolane and is consistent with adsorption potential based on the K_{oc} value (McLeod 1994).

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APPENDIX A

Sulfolane Synonyms List

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APPENDIX B

MSDS

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APPENDIX C

UOP Sulfolane Process Whitepaper

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APPENDIX D

TTC Labs Corrosion Report

APPENDIX E

National and International Research Documents

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APPENDIX F

Supporting Documentation for Case Studies and Remediation

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