Feasibility Study

Reducing Concentrations of Dissolved Metals and Ammonia in Large Passenger Vessel Wastewater Discharges

Prepared for

Alaska DEC

Prepared by

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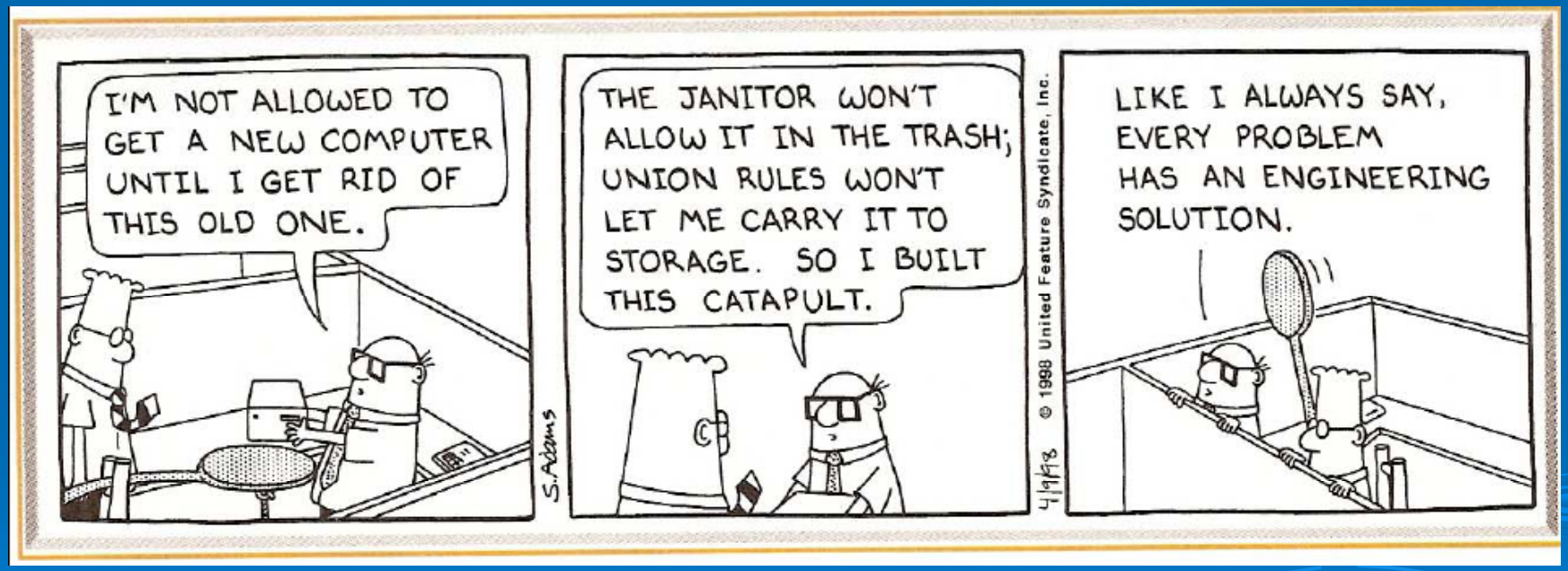
Burns & McDonnell
SINCE 1898

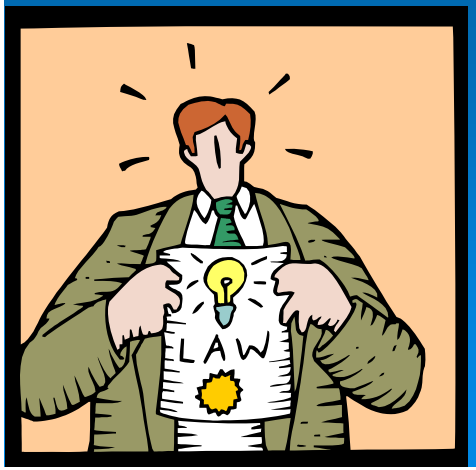
The World According to Engineers



Milestones

- Initiative Passed 2006
- Permits Issued March 2008 w/ interim limits for Cu, Zn, Ni and ammonia
- Data Collection 2008
- Feasibility Assessment (2009 minor edits 6/2010)
- Deadline for Compliance Extended
- Science Advisory Panel Formed 2/2010

The 2010 criteria



[1]

TABLE 2.1: DESIGN CRITERIA FOR END-OF-PIPE POLLUTANT REDUCTION

Parameter	Typical Influent Range (Output from AWTS)	Target Effluent[1] (Removal rate)
Flow	Max 60 m^3/hour and 1440 m^3/day Highly variable[2]	Not to exceed design capacity
Total Suspended Solids (TSS)	1 – 11 mg/l	150 mg/l max
Biochemical Oxygen Demand (BOD) 5-day	3.1 – 126 mg/l	60 mg/l max (50%)
pH	6.2 – 9.5	6.5 min / 8.5 max
Total Residual Chlorine	ND – 0.20 mg/l	0.0075 mg/l max (96%)
Ammonia (NH^3)	4.6 – 150.0 mg/l	2.9 mg/l max (98%)
Nickel (Ni)	7.0 – 44.0 µg/l*	8.2 µg/l max (82%)
Zinc (Zn)	7.0 – 501.0 µg/l*	81.0 µg/l max (84%)
Copper (Cu)	1.0 – 140.0 µg/l*	3.1 µg/l max (98%)

* From 2008 cruise ship testing data. Results were highly variable and at times the target limits were met.

- What Treatment Systems are Currently Used?

TABLE 2.2: AWTS TECHNOLOGIES CURRENTLY USED ON VESSELS DISCHARGING IN ALASKA FOR SHIPBOARD WASTEWATER TREATMENT PHASES

AWTS	Treatment Phase Methods				Vessels with AWTS
	Primary Solids Separation	Secondary Organic Digestion	Tertiary Clarification	Disinfection	
Biopure Marisan	Coarse Screen	Aerobic Biological Oxidation (MBR)	Flotation (DAF) / Microfiltration	UV	1
Hamworthy Bioreactor	Screen Press	Aerobic Biological Oxidation (MBR)	Ultrafiltration Membranes	UV	9
Hydroxyl Cleansea	Coarse Drum Filter	Aerobic Biological Oxidation (MBR)	Flotation (DAF) / Polishing Filter	UV	2
Rochem Bio-filtration	Vibratory Screens	Aerobic Biological Oxidation (MBR)	Ultrafiltration Membranes	UV	2
Scanship	Wedgewire Screen	Aerobic Biological Oxidation (MBR)	Flotation (DAF) / Polishing Filter	UV	4
Triton / Rochem	Vibratory Screens	Aerobic Biological Oxidation (MBR)	Ultrafiltration Membranes	UV	1
Zenon	Coarse Screen	Aerobic Biological Oxidation (MBR)	Ultrafiltration Membranes	UV	6

Do Vessels Currently Meet Standards?

- Vessels are unable to consistently meet 2010 standards for Cu, Ni, Zn and ammonia
- Cruise lines are having the most difficulty meeting the 2010 copper and ammonia standards

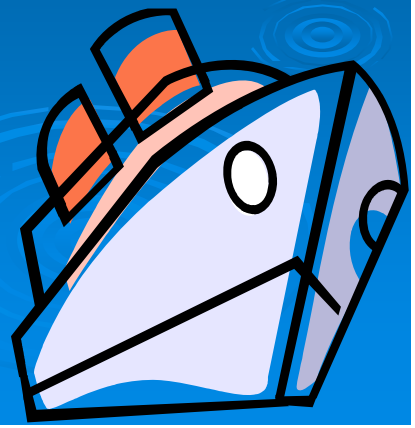
2008 Sampling Results

	Ammonia	Copper	Nickel	Zinc
	mg/L	ug/L	ug/L	ug/L
Interim	80.4	66	180	230
2010 Limits	2.9	3.1	8.2	81
Min	ND	ND	ND	ND
Max	150	140	43.2	501
Avg	35.47	15.67	9.98	89.27

- 3 vessels met zinc standard
- 3 vessels met nickel standard
- 1 vessel within margin of error for copper
- 1 vessel met ammonia standard

Do Any Vessels in the World Meet the Standards?

- Data for vessels not operating in Alaska were not available for review
- In general, Alaska standards are the most stringent in the world
- Unlikely many other vessels meet standards, but data to assess is not available for review



Feasibility Criteria

- Compliance with permit stipulations
- Technology Capability and Availability
- Marine Certification of New Systems
- Cost
- Available Space on Vessels
- Waste Management

Why a Workshop?

- Provide a forum to discuss wastewater treatment technologies and findings from in the draft feasibility study

Feasibility Study Research

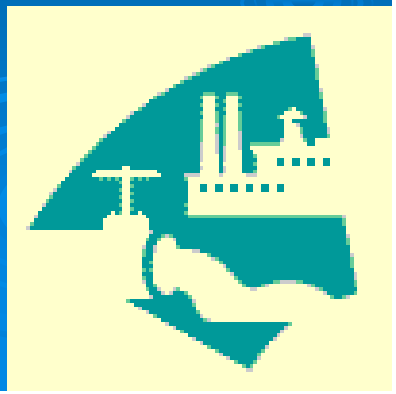
- Contacted more than 45 vendors, academics, or consultants
- Internet Search
- E-mail Solicitations, thousands of contacts
- Web-site

Feasibility Study Research (Cont)

- Involvement of wastewater treatment and marine experts
- Selected technical experts to provide input from a list of 20 national and internationally recognized firms
- Evaluation of existing land based technologies

Results for Existing Land Based Technologies

- Effluent standards can be met based on vendor, academic data, and system performance
  - RO, IX, EDR for metals and ammonia
  - Bio and air stripping for ammonia
  - Chemical precipitation followed by RO or IX for metals only



Land Based Results (Cont)

- Installed land based systems are capable of achieving non-detect limits for all metals
- Applying a land based technology to a vessel can be challenging

Systemic Approach

- Metals and ammonia removal part of overall system
- Multi-stage evaluation and implementation recommended
- Source reduction & substitution
- Recycle & reuse considerations
- Waste characterization & treatability

Properties of Contaminants

- Copper, Nickel, and Zinc
  - Bioaccumulating to marine life
  - All form divalent cations in water
  - Are present primarily in dissolved phase
  - Stable in solution in typical water
  - Sources are vessel source water, evaporators, leaching or impingement from pipes and fixtures, chemical use

Properties of Contaminants (Cont)

- Ammonia
  - Both a nutrient and toxin
  - Exists as a gas at STP
  - Forms ammonium monovalent ion in water
  - Ammonia/ammonium ratio is pH dependent
  - Main source is hydrolysis of human urea in black water

Treatment Alternatives

- Ammonia Only
  - Air/Steam Stripping
  - Aerobic Biological Oxidation / Nitrification
  - Breakpoint Chlorination

Treatment Alternatives (Cont)

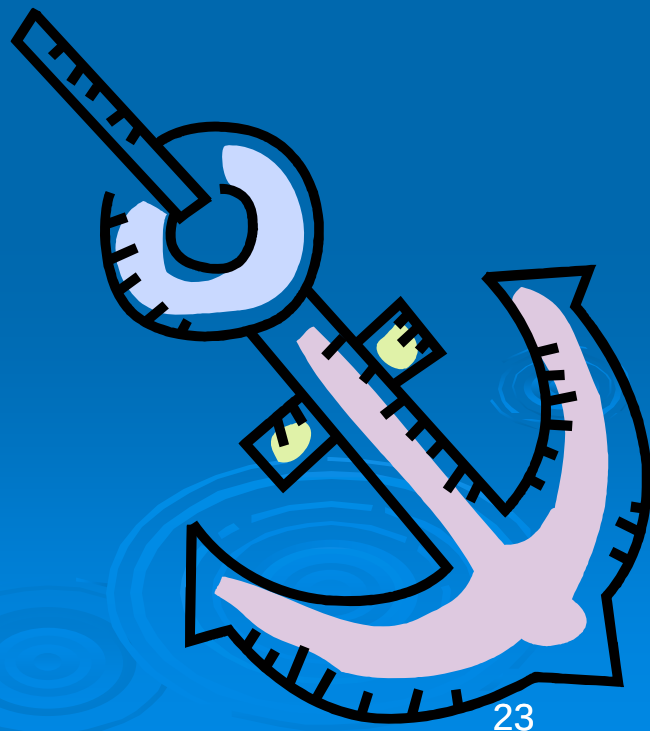
- Metals Only
  - Surface Clay Filtration
  - Electrowinning
  - Chemical Precipitation

Treatment Alternatives (Cont)

- Metals and Ammonia
  - Reverse Osmosis
  - Ion Exchange
  - Electrodialysis

Feasibility Criteria

- Description
- Where Used
- Capabilities/size
- Waste Streams
- Effluent Quality
- Vessel Application



Air/Steam Stripping

- Description
  - Steam or air bubbled through water to volatilize ammonia
- Where Used
  - Industrial applications and some municipal wastewater plants

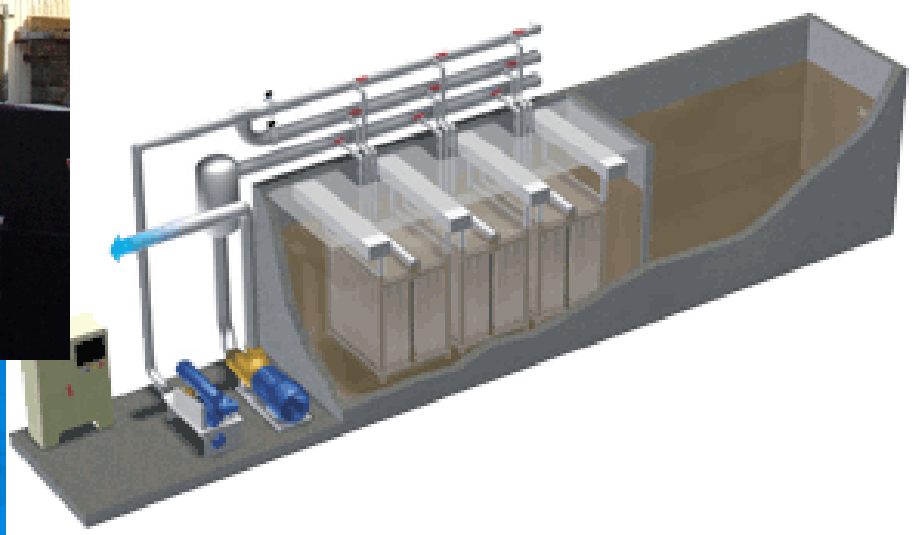
Air/Steam Stripping (Cont)

- Capabilities
  - Removes ammonia only
  - Requires pH adjustment and would be capable of treating wastewater
  - Tanks to store chemicals needed
- Waste Streams
  - Ammonia in air discharge

Air/Steam Stripping (Cont)

- Effluent Quality
  - Capable of meeting permit limits for ammonia
- Vessel Application
  - Not considered suitable for a vessel because of the need for alkaline and acid treatment chemicals, and ammonia air emission

Aerobic Biological Oxidation/Nitrification



Nitrification

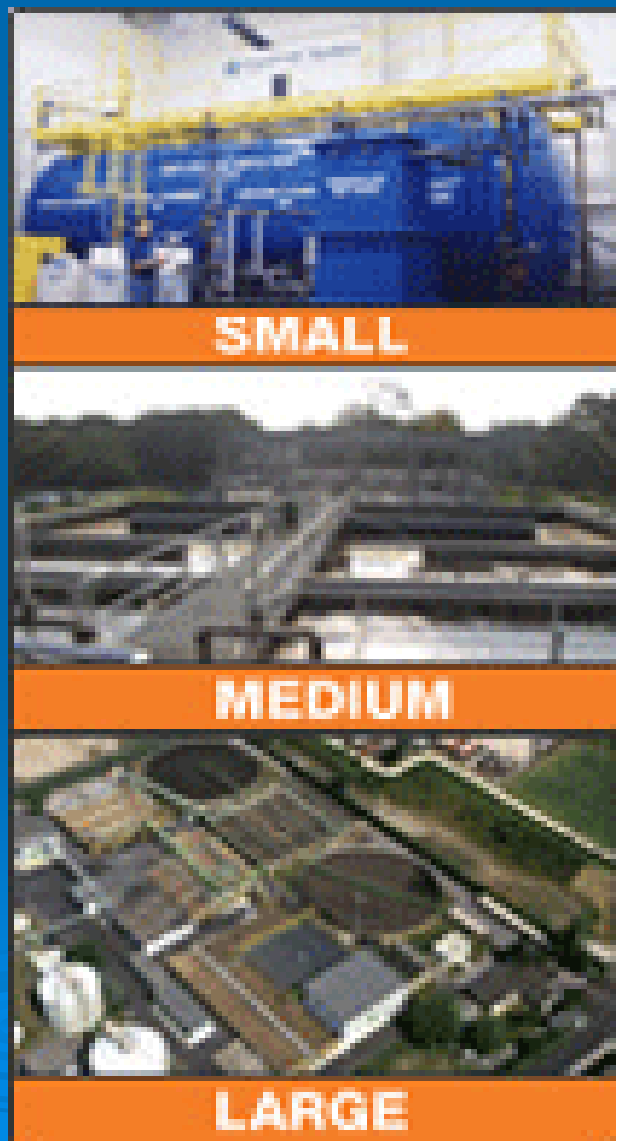
- Description
  - Removal of ammonia by microorganisms
  - Conversion to nitrate
- Where Used
  - This technology is widely used for ammonia removal in municipal and industrial wastewater applications

Nitrification (Cont)

- Waste Streams
  - Generates biological sludge disposed by
    - Land application
    - Composting
    - Dewatering followed by landfilling/incineration
    - Anaerobic digestion followed by energy recovery
- Effluent Quality
  - Removal of ammonia to values less than 1.0 mg/L possible

Nitrification (Cont)

- Capabilities/Size
  - Space requirements depend on flow rates and ammonia concentrations.



Nitrification (Cont)

- Vessel Application
  - Could be compact if membrane technology is used for solids separation (MBR)
  - Most cruise ships already have installed MBR. Modify as needed to meet new limits

Breakpoint Chlorination

- Description
  - Oxidation of ammonia using high concentrations of active chlorine
- Where Used
  - Treatment of drinking water and swimming pools and in pulp and paper industry for bleaching

Breakpoint Chlorination (Cont)

- Capabilities
  - Treatment of ammonia only
  - Requires storage of chlorine or chlorine compounds
- Waste Streams
  - Free chlorine remains in water, potentially exceeding permit limits
  - Dechlorination may be required

Breakpoint Chlorination (Cont)

- Effluent Quality
  - Complete oxidation of ammonia
  - Effluent will contain residual chlorine
- Vessel Application
  - Limited application because of the need for chlorine and additional treatment to remove chlorine from treated water

Surface Clay Filtration

- Description
  - Adsorption of metal ions onto clay filter media surface via ion exchange
  - Older technology
- Where Used
  - Mining and chemical industries
  - Drinking water treatment in developing countries

Surface Clay Filtration (Cont)

- Capabilities
  - Metal removal rates of 95% possible, but difficult to achieve because of low effluent limits
  - Media is inexpensive
- Waste Streams
  - Depleted clay filter media with metal ions
  - Media is not regenerated

Surface Clay Filtration (Cont)

- Effluent Quality
  - Unlikely to meet permit standards consistently
- Vessel Application
  - Pre-treatment of source water on-shore considered for application
  - May require additional treatment for drinking water.

Electrowinning

Electrowinning

- Description
  - Electrodepositing metals from solution onto a cathode using DC current
- Where Used
  - Mining applications, electroplating shops, circuit board mfg. with high dissolved metals concentrations in water

Electrowinning (Cont)

- Capabilities
  - Works best with high concentrations. Surface area would need to be higher for low concentration systems
  - Requires large storage tanks and heaters, may have application to waters concentrated by other processes

Electrowinning (Cont)

- Waste Streams
  - Cathode can be removed and recycled\disposed as a solid
- Effluent Quality
  - Suitable only for metals, effluent concentration generally much higher than permit limits

Electrowinning (Cont)

- Vessel Application
  - Limited to pre-treatment or treatment of concentrated metals waste streams

Chemical Precipitation

- Description
  - pH, precipitate metal hydroxide, clarify, filter out metal waste
- Where Used
  - 90% of Metal Finishing processes use this for heavy metal removal including Cu, Ni, and Zn.
- Capabilities
  - Handle mixed chemistries of metals with high concentrations.

Chemical Precipitation (Cont)

- Waste Streams
  - Generates a heavy metal sludge which on land can be disposed as hazardous waste or recycled. Can dry further to reduce qty
- Effluent Quality
  - On land based systems can consistently get Cu & Ni to below levels of 1 ppm. Zn can be removed to levels around 0.1 ppm. May not meet permit levels.

Chemical Precipitation (Cont)

- Vessel Application
  - More difficult to adapt than RO or IX because of inclination.
  - May still need to be combined with other technology to meet specific effluent requirement

Reverse Osmosis

Reverse Osmosis (RO)

- Description
  - Use of Membranes under pressure to physically separate compounds and ions.
  - Osmosis - Water will move across membrane into wastewater until the contaminant concentrations of both liquids are equal.
  - Reverse Osmosis – Apply pressure to contaminant side of membrane to allow water to flow in reverse.
  - Contaminants will be blocked by pore size of the membrane filter and/or the electrostatic charge on the membrane

Reverse Osmosis (Cont)

- Where Used
  - Refineries
  - Metal Finishing including recycling of water to process
  - Groundwater Remediation
  - Cruise ships

Reverse Osmosis (Cont)

- <u>Effluent Quality</u>
  - Depending on influent qualities, ppm or ppb levels can be achieved.
  - Capable of using to recycle treated graywater and blackwater for other uses

Reverse Osmosis (Cont)

- Capabilities
  - Technology can be used on source or wastewater.
  - Application can require a single or multiple pass setup of equipment.
  - May have to be used in conjunction with other technologies like Ion Exchange

Ion-Exchange (IX)

Ion Exchange

- Description
  - Adsorb contaminant - release exchange element.
  - Well established technology, uses an engineered resin as exchange medium in a reactor vessel
- Where Used
  - Currently used in water and wastewater treatment and as a polishing process in industry

Ion Exchange (Cont)

- Capabilities
  - Competing ions affect treatment achieved and unit sizing
  - Treat both metals and ammonia.
  - May have to be used in conjunction with other technologies like Reverse Osmosis

Ion Exchange (Cont)

- <u>Waste Streams</u>
  - Resin is regenerated as needed, concentrated waste must be disposed
  - Resin can be contracted for regeneration.

Ion Exchange (Cont)

- Effluent Quality
  - In land based systems nearly complete metals removal possible
  - Ammonia removal to meet limits.
- Vessel Application
  - Relatively few vessel related issues identified, dependent upon amount of media required

Electrodialysis

Electrodialysis

- Description
  - Membrane filtration with addition of current to enhance treatment
- Where Used
  - Metal finishing for recovery of nickel and copper and purification of drinking water

Electrodialysis (Cont)

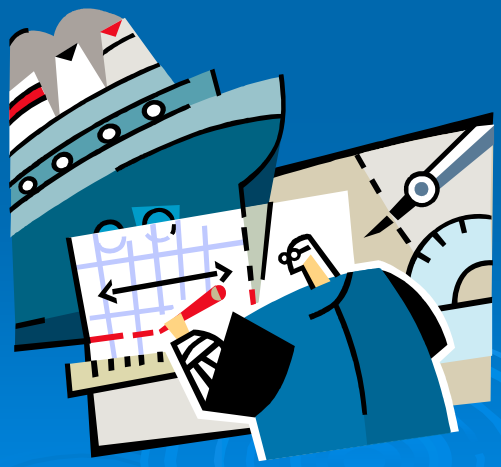
- Capabilities/size
  - Treats both metals and ammonia
  - Chlorine tolerant
- Waste Streams
  - Metals concentrated solution

Electrodialysis (Cont)

- Effluent Quality
  - Technology is capable meeting permit limits
- Vessel Application
  - Treatment would be post tertiary

Vendor Proposals

Several vendors provided proposals or information regarding conceptual systems.



CASTion

- Combination Treatment
  - Ammonia recovery process followed by Ion exchange
    - Multimedia Filters
    - Cartridge Filters
    - Softener Unit
    - Ammonia Recovery Unit
    - Cation Exchanger
    - Metal Ion Exchanger
    - Sulfate Concentration Unit

Det Norske Veritas AS with Norwegian University of Science and Technology

- Combination moving bed biofilm bioreactor with membrane filtration unit
- Applicable to ammonia removal only.

Evac Oy

- MBR System with integrated metals precipitation
- Inconclusive chemical addition agents other than hydrogen sulfide

Ferrate Treatment Technologies

- Oxidation of Ammonia and Zinc with Ferrate

Filter Flow Technology

- Electrochemical technology to remove trace metals and the ammonium ion
- Electro-oxidation
- Zeolite Pre-filter
- Aeration
- Sorbent Dosing
- Precipitation

GE Water and Process Technologies (Zenon)

- Reverse Osmosis
- Electro Dialysis
- MBR Upgrade Systems

NORAM Engineering (Presenter)

- Stage 1 Ammonia Oxidation by ozone or hypochlorite or breakpoint chlorination
- Stage 2 Metal oxidation via iron particles.

Ohio University (Presenter)

- Electrolysis to oxidize ammonia.
- Potential for electrolysis for metals treatment.

ROCHEM (Presenter)

- Multi-membrane (MF, UF, NF and RO) stack for independent and MBR units to remove ammonia and metals

Emerging Technologies

- Removal of Ammonia as Magnesium Ammonium Phosphate
- Ammonia Removal by Thermally Activated Charcoal
- Anaerobic Ammonium Oxidation
- Electrolytic Treatment of Aqueous Media
- Biosorption by Immobilized Microorganism

Implementation Stages

- System balance and source evaluation
- Source substitution
- Optimize water sources
- Evaluate wastewater collection and use
- Ship constraints
- Pre and post treatment options
- Source reduction, substitution, optimization

Summary of Technology Status

- Emerging technologies
  - Likely not solutions for 2010 because of short timeframe available to field systems
  - May offer effective solutions based on further evaluation to demonstrate effectiveness
- Land based technologies
  - Are able to meet standards
  - Require marine regulatory approval
  - Need to be modified for marine environment and waste streams

Summary of Technology Status (Cont)

- Ship safety and space limitations must be accommodated
- Unintended effects, e.g. new waste streams

Implementation

Implementation Considerations

- General
  - Implementation is cruise line responsibility
  - Implementation will be very specific to each vessel and each technology
  - Implementation discussed here to give non-maritime readers and idea of the process

Implementation Considerations (Cont)

- General (Cont)
  - More data to follow once technology is narrowed down and classification agencies weigh in
  - Once identified, needed technologies usually adapt for marine use over time.

Implementation Considerations (Cont)

- Selection of Treatment Systems
  - Systematic Vessel Wastewater Evaluation
    - System Balance and Source Evaluation
    - Source Substitution/optimization
    - Pre and post treatment options

Implementation Considerations (Cont)

- Selection of Treatment Systems (Cont)
  - Selection of Preferred Treatment Alternative
    - Analyze multiple treatment alternatives
      - Each alt. contains source, influent, effluent treatment +
      - Various treatment devices
    - Select Optimum Alternative

Implementation Considerations (Cont)

- Regulatory Approval of Device
  - Device “approved” prior to being installed
  - If device is defined as sewage treatment
    - International agreement IMO Annex 26 MEPC.159(55) states discharge standards

Implementation Considerations (Cont)

- Regulatory Approval of Device (Cont)
  - If device not sewage treatment
    - Classification agency is likely approval authority for foreign flagged vessel
    - General marine machinery approval rules apply
      - Temperature, humidity, inclinations, construction and standards

Implementation Considerations (Cont)

- Installation of Device
  - Concept Design
    - Laboratory based treatability study
    - Comprehensive review of all design parameters and costs
  - Performance Conformation
    - If concept design cannot adequately quantify risks, use onboard testing

Implementation Considerations (Cont)

- Final Selection
- Installation
  - Installation Design
  - Plan Submittal to Classification Agency
  - Construction and Testing.

Summary of Findings

TABLE 8.1: SUMMARY OF FINDINGS FOR TREATMENT METHODS

Treatment Method	Effective for		Technical Feasibility	Implementation Feasibility	Vendor Interest	Other Considerations
	Ammonia	Dissolved Metals				
Chemical Precipitation		✓	Moderate	Moderate	Evac Oy, Filter Flow	Retention time
Ion Exchange	✓	✓	High	Moderate	DOW, CASTIon	Resin recharge
Reverse Osmosis	✓	✓	High	High	GE, ROCHEM	Low chlorine tolerance
Surface Clay Filtration		✓	Low	Moderate	-	
Electrowinning		✓	Low	Moderate	-	
Electrodialysis	✓	✓	High	Moderate	GE	
Air / Steam Stripping	✓		Moderate	Low	-	Air emission limit on ammonia
Aerobic Biological Oxidation / Nitrification	✓		Moderate	High	-	Retention time
Breakpoint Chlorination	✓		Moderate	Low	NORAM	Discharge limit on chlorine
Oxidation using Hydrous Ferric Oxide/Iron		✓	-	-	NORAM	
Magnesium Ammonium Phosphate	✓		-	-	-	Research Only
Thermally Activated Charcoal	✓		-	-	-	Research Only
Anaerobic Ammonium Oxidation	✓		-	-	-	Research Only
Electrolytic Treatment	✓		-	-	Ohio University	Research Only
Biosorption by Immobilized Microorganisms		✓	-	-	-	Research Only