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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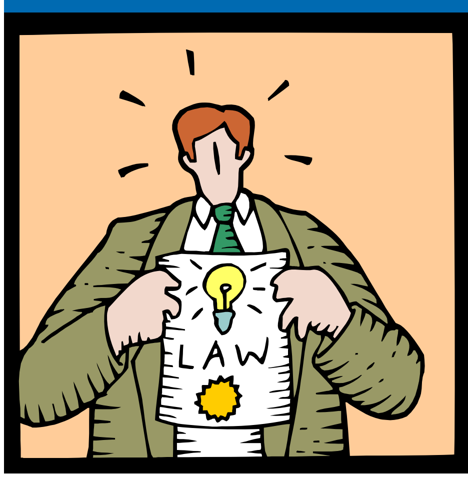
SINCE 1898

Milestones

- Initiative Passed 2006
- Permits Issued March 2008 w/ interim limits for Cu, Zn, Ni and ammonia
- Data Collection 2008
- Feasibility Assessment (2009)
- Deadline for Compliance Established (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

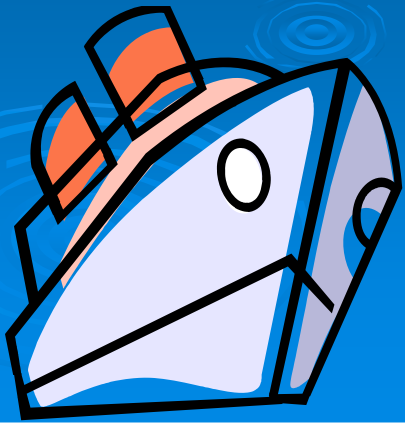
2008 Sampling Results

	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

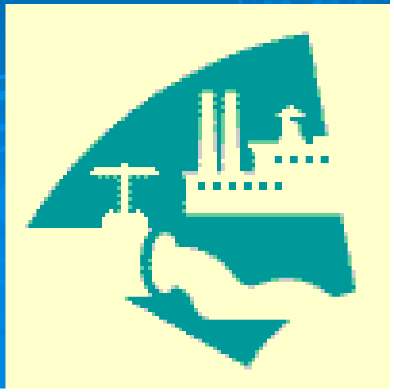
- Contacted more than 45 vendors, academics, or consultants
- Internet Search
- E-mail Solicitations, thousands of contacts
- Web-site

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)

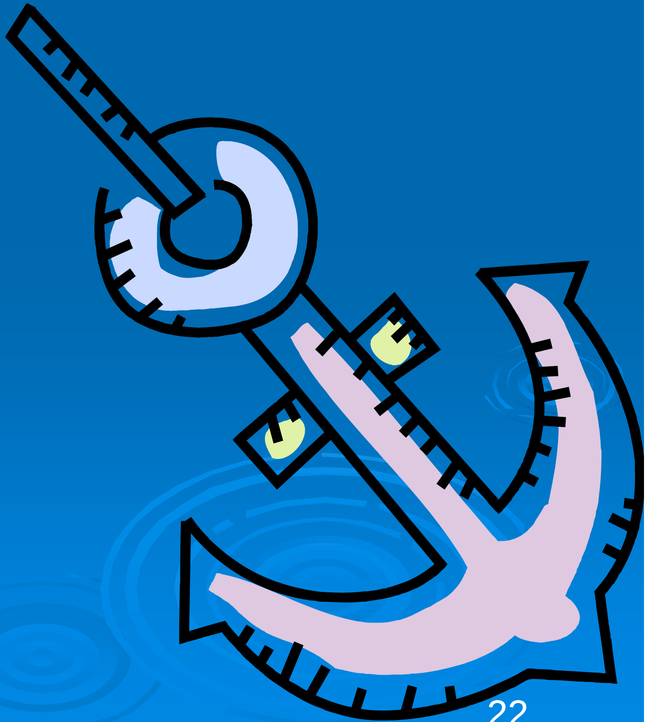
- Metals Only
  - Surface Clay Filtration
  - Electrowinning
  - Chemical Precipitation

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

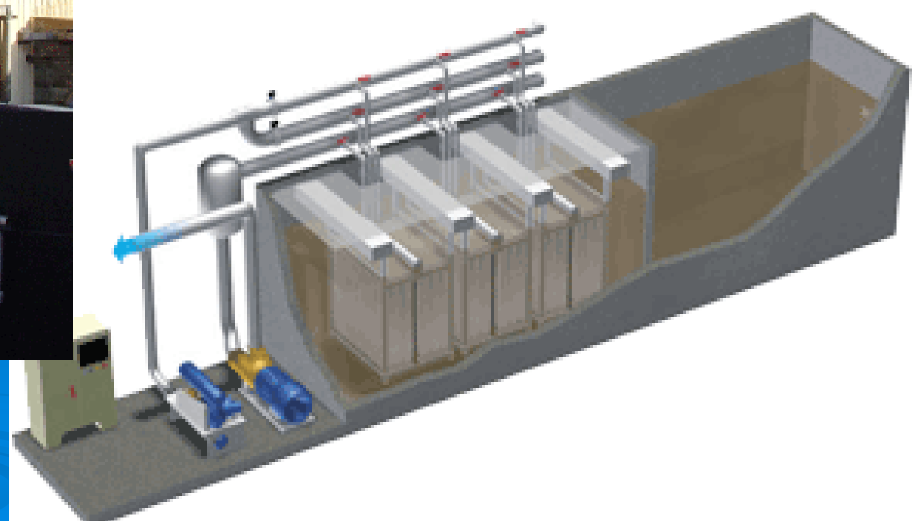
Air/Steam Stripping (Cont)

- 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)

- <u>Effluent Quality</u>
  - Capable of meeting permit limits for ammonia
- <u>Vessel Application</u>
  - 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

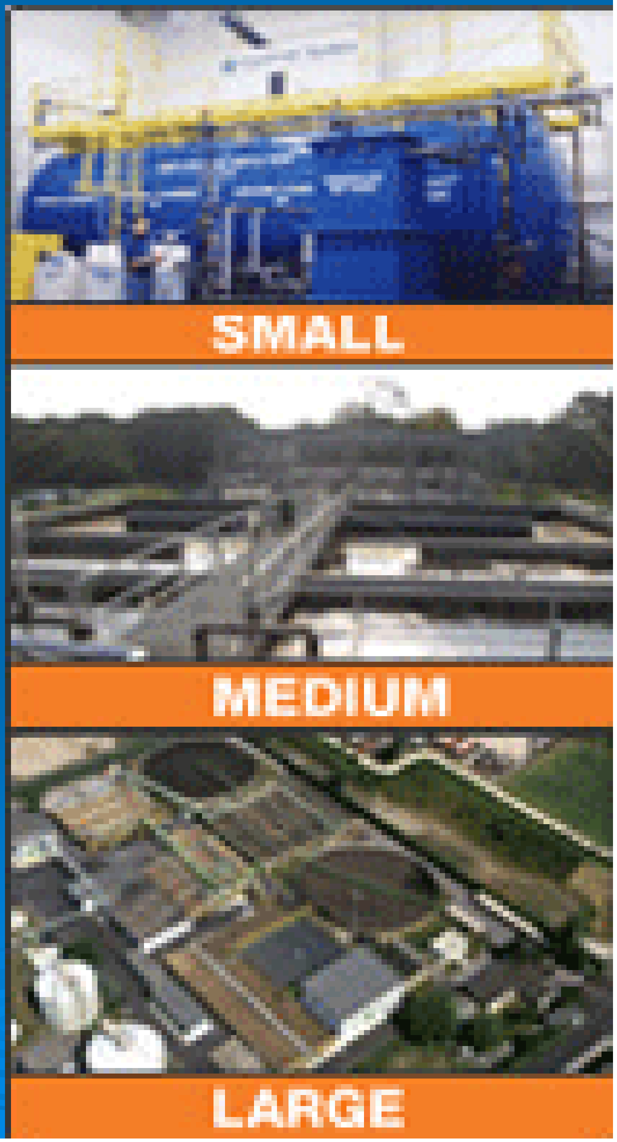
- Description
  - Removal of ammonia by microorganisms
  - Conversion to nitrate
- Where Used
  - This technology is widely used for ammonia removal in municipal and industrial wastewater applications

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)

- <u>Capabilities/Size</u>
  - 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)

- <u>Capabilities</u>
  - Treatment of ammonia only
  - Requires storage of chlorine or chlorine compounds
- <u>Waste Streams</u>
  - 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)

- <u>Effluent Quality</u>
  - Unlikely to meet permit standards consistently
- <u>Vessel Application</u>
  - 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)

- <u>Vessel Application</u>
  - Limited to pre-treatment or treatment of concentrated metals waste streams

Chemical Precipitation

- <u>Description</u>
  - pH, precipitate metal hydroxide, clarify, filter out metal waste
- <u>Where Used</u>
  - 90% of Metal Finishing processes use this for heavy metal removal including Cu, Ni, and Zn.
- <u>Capabilities</u>
  - 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)

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

Reverse Osmosis (Cont)

- Effluent Quality
  - 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)

- <u>Effluent Quality</u>
  - In land based systems nearly complete metals removal possible
  - Ammonia removal to meet limits.
- <u>Vessel Application</u>
  - 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)

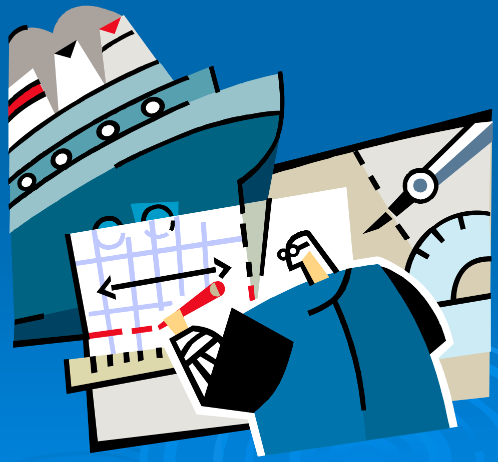
- Capabilities/size
  - Treats both metals and ammonia
  - Chlorine tolerant
- Waste Streams
  - Metals concentrated solution

Electrodialysis (Cont)

- <u>Effluent Quality</u>
  - Technology is capable meeting permit limits
- <u>Vessel Application</u>
  - 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)

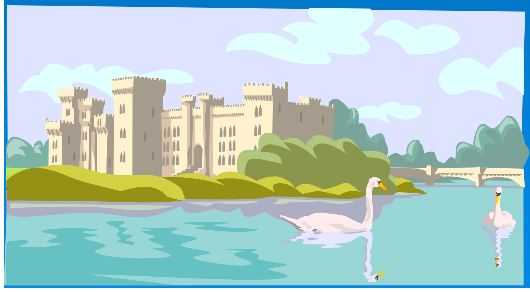
- Selection of Treatment Systems
  - Systematic Vessel Wastewater Evaluation
    - System Balance and Source Evaluation
    - Source Substitution/optimization
    - Pre and post treatment options

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