Metals and Ammonia Removal from Wastewaters

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Outline

- Background
- Ammonia removal technologies
- Metals removal technologies
- Proposed treatment methodology

Interim Limits

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.

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Background

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

Feasibility Assessment

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

- *Burns & McDonnell retained as waste treatment experts for land based systems*

Ammonia Sources

- Main Sources of Ammonia:
  - Domestic wastewater (typical 15 to 50 mg/L)
  - Fertilizers
  - Industrial contributions

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Ammonia Sources

- Main sources of Ammonia in Cruise Ships:
  - Domestic wastewater (black water)
  - Some cleaning agents

Ammonia Removal

- Why to remove ammonia?
  - Nutrient that impact environmental equilibrium when present in excess in receiving waters

Ammonia Removal

- Cause acute toxicity to aquatic life in receiving waters

Ammonia Treatment Technologies

- Most commonly used:
  - Biological nitrification-denitrification
  - Breakpoint chlorination
  - Selective ion exchange
  - Air stripping
- Less commonly used:
  - Electrodialysis
  - Reverse osmosis (RO)
  - Emerging technologies

Nitrification

- Reactions:
  - $2NH_4^+ + 3O_2 = 2NO_2^- + 4H^+ + 2H_2O$
  - $2NO_2^- + O_2 = 2NO_3^-$
  - Overall Reaction:
    - $NH_4^+ + 2O_2 = NO_3^- + 2N^+ + H_2O$

Nitrification

- 1 mg/L of ammonia requires 4.6 mg/L of O_2 for conversion to NO_3^-
- 7.14 mg of alkalinity as $CaCO_3$ are destroyed per mg of ammonia oxidized

Nitrification

- As temperature decreases the rate of nitrification also decreases

- As sludge age (SRT) increases the rate of nitrification also increases. Min SRT = 5 d for domestic wastewater at 20 ^{o}C

Nitrification

- Typical treatment systems:
  - Plug-Flow activated sludge
  - Complete mixed activated sludge
  - Extended aeration
  - Oxidation ditch systems
  - Sequencing batch reactor (SBR)
  - Membrane bio-reactors (MBR)
  - Fixed-film systems (biotowers, rotating biological contactors – RBC, moving bed bio-reactors – MBBR)

BMcD Experience
Municipal Wastewater

- Type: Activated Sludge
- Flow: 3,800 to 720,000 m^3/day
- Wastewater NH_3-N: 10 to 50 mg/L
- Effluent NH_3-N: < 3.0 mg/L
- 2010 Permit: 2.9 mg/L

BMcD Experience
Commercial Wastewater

- Type: MBR
- Flow: 40 to 80 m^3/day
- Wastewater NH_3-N: 90 to 110 mg/L
- Effluent NH_3-N: < 3.0 mg/L
- 2010 Permit: 2.9 mg/L

BMcD Experience
Grey Water Reuse

- Type: MBR and UF/RO
- Flow: 10 to 18 m^3/day
- Wastewater TKN: 20 mg/L
- Effluent TKN: <10 mg/L
- Effluent NH_3-N: <1. 0 mg/L
- 2010 Permit: 2.9 mg/L

BMcD Experience Refinery Wastewater

- Type: Fixed Film
- Flow: 3,000 m^3/day
- Wastewater TKN: 50 mg/L
- Effluent TKN: <5.0 mg/L
- Effluent NH_3-N: 1.0 mg/L
- 2010 Permit: 2.9 mg/L

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BMcD Experience
Beef Processing Wastewater

- Type: Activated Sludge
- Wastewater NH_3-N: 90 to 260 mg/L
- Effluent NH_3-N: <1.0 mg/L
- 2010 Permit: 2.9 mg/L

BMcD Experience
Pork Processing Wastewater

- Type: Activated Sludge
- Wastewater NH_3-N: 90 to 180 mg/L
- Effluent NH_3-N: <1.0 mg/L
- 2010 Permit: 2.9 mg/L

Breakpoint Chlorination

- Ammonia removal by addition of chlorine
- Can achieve 95% to 99% removal efficiency
- Ratio chlorine to ammonia of 7.6 to 1
- Chlorine handling may be an issue

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Breakpoint Chlorination

- Reactions:
  - $NH_4^+ + HOCl = NH_2Cl$ (monochloramine)
  - $NH_2Cl + HOCl = NHCl_2$ (dichloramine)
  - $NH_4^+ + 1.5\ HOCl = 0.5\ N_2 + 1.5\ H_2O + 2.5\ H^+ + 1.5\ Cl^-$

Air Stripping

- Conversion of ammonium to NH_3 gas by increasing pH to 10.5 – 11.5
  - $NH4^+ \rightarrow NH_3$ gas + H^+
- Removal of NH_3 gas by stripping

Air Stripping

- Countercurrent flow of air and water containing ammonia
- Resemble conventional cooling tower
- Odor threshold of ammonia is 35 mg/m^3
- Consider air pollution regulations

Metals Removal

- Technologies
  - Chemical Precipitation
  - Ion Exchange
  - Reverse Osmosis
  - Electrowinning
  - Electrodialysis

Metals Removal

- Treatment Methodology
  - Source Water
    - High background levels of metals
  - Wastewater
    - Evaporators
    - Leaching or impingement from pipes and fixtures
    - Chemical use

Metals Removal

SAMPLING RESULTS BY PORTS OF CONCERN FOR CONTAMINANTS OF CONCERN

Port	Contaminant	Average (µg/L)	Maximum (µg/L)	Exceedance Rate (% of Samples)
Vancouver	Copper	20	120	77
	Zinc	-	280	-
Juneau	Copper	54	280	83
Victoria	Copper	4	7	100
Seattle	Zinc	499	1500	63
Skagway	Nickel	28	470	29

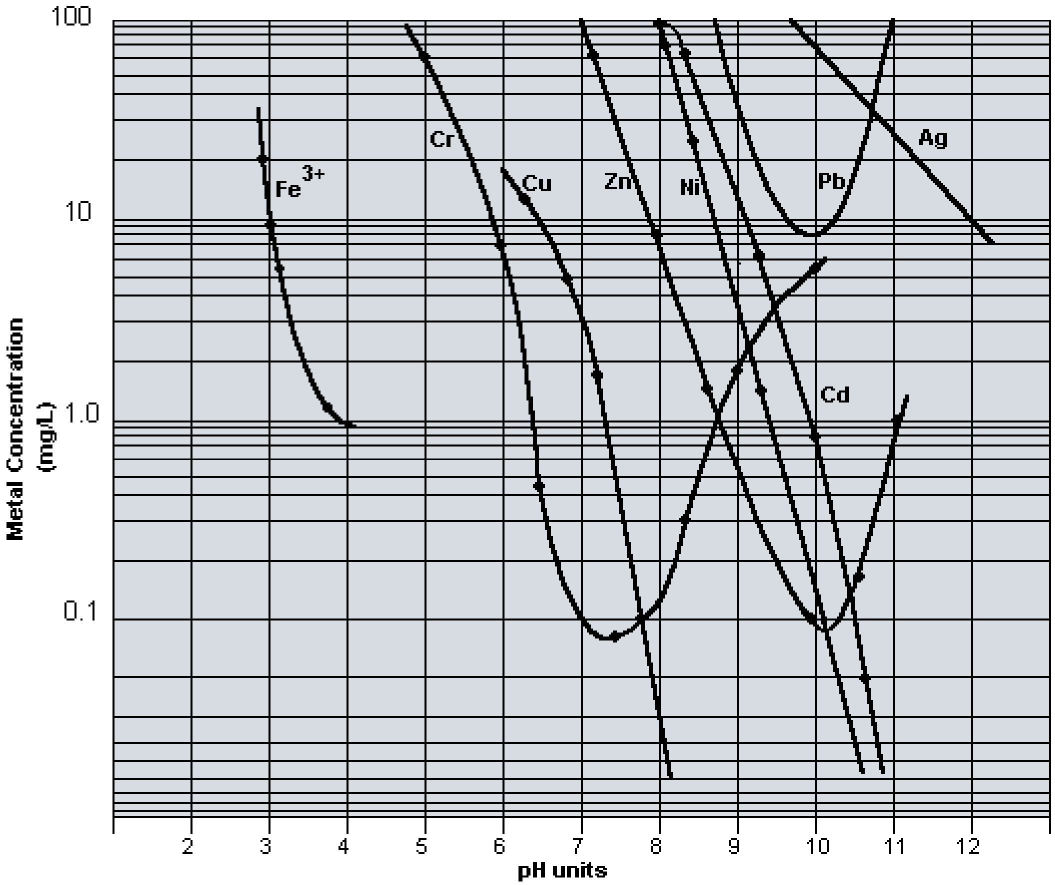
Chemical Precipitation

- Addition of Alkaline Hydroxide to adjust pH
- Addition of Sulfur compounds
- Formation of insoluble metal hydroxide or sulfide compounds

Chemical Precipitation

- Precipitation and clarification or filtration
- Solids separation to form sludge or cake
- Effluent quality dependent upon Metal
- Potential inhibition of chelating compounds

Metal Hydroxide Solubility Curves



Chemical Precipitation

- Effluent could reduce metals to ppm levels
- Process alone may not meet proposed levels
- Identified for use on wastewater only

Ion Exchange

- Use of Cation or Ion Selective resins to adsorb soluble metals
- Release of sodium, hydrogen, or chlorides into solution

Ion Exchange

- Regeneration concentrates adsorbed metals for storage or treatment
- Can be used on source water or wastewater
- Effluent can produce metal levels to ppb or non-detectable levels

Ion Exchange

- Influent Quality
  - No Suspended Solids
  - No Oil or Grease
  - Need to know all ions
- Use as Polishing Step
- Equipment can be Port or Ship side

Reverse Osmosis

- Use of Membranes under pressure to physically separate compounds and ions
- Technology can be used on source or wastewater
- Application can require a single or multiple pass setup of equipment
- Depending on influent qualities, ppm or ppb levels can be achieved

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Reverse Osmosis

- Process could be 85-99% efficient in removal/pass
- Variety of configurations
- Influent Quality
  - No Suspended Solids
  - No Oil or Grease
  - No Particles
  - Sensitive to Scaling

Reverse Osmosis

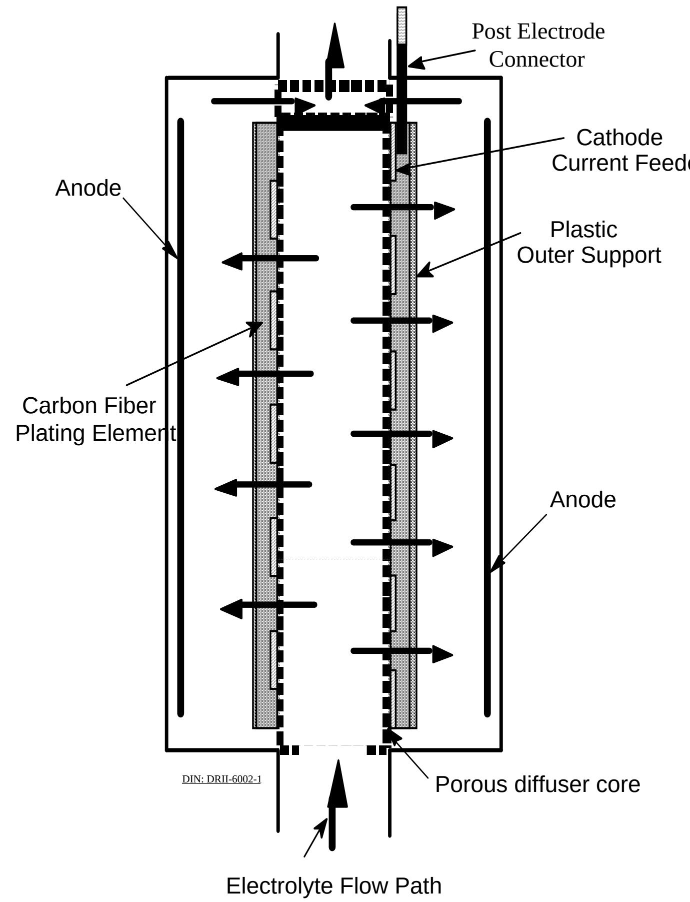
- Equipment can be installed port or ship side
- Variety of configurations
- Equipment utilizes electrical loads

Electrowinning

- Application of direct electrical current to deposit metal on a cathode
- Used in mining and metal finishing industries extensively
- Technology requires retention time
- Effluent can effectively/efficiently remove metals to the ppm level
- Competing reaction with hydrolysis

Electrowinning

- Use on source water
- Use on concentrates
  - RO reject
  - IX regenerant
  - ED reject
- Equipment compact



Electrodialysis

- Application of direct current across a semi-permeable membrane to concentrate ions
- Potential use on source or wastewater
- Effluent quality can achieve ppm or ppb levels
- Requires time retention or multiple passes

Electrodialysis

- Could be used on concentrates
  - RO Reject
  - IX Regenerant
- Equipment size to be determined by influent water

Treatment Methodology

Source or Bunkered Water

- Treat water prior to acceptance or use
- It is easier to remove metals in uncontaminated water
- Use of Port or Ship side equipment
- Reverse Osmosis and Ion Exchange independently or in conjunction with each other are viable opportunities

Treatment Methodology

Wastewater

- Recommend treating water after MBR unit
- Any Ammonia may complex copper
- Chemical Precipitation is viable initial treatment, but needs further steps
- Reverse Osmosis and Ion Exchange are viable as initial or polishing treatments
- ED and Electrowinning may have opportunities for treatment
- Additional information needed and treatability studies should be conducted

Questions

Thank you!