



21th ANNUAL BRITISH COLUMBIA-MEND ML/ARD WORKSHOP

“Challenges and Best Practices in Metal Leaching and Acid Rock Drainage”

December 4, 2014

Established and Innovative Sulfate Removal Treatment Processes





Outline of Presentation

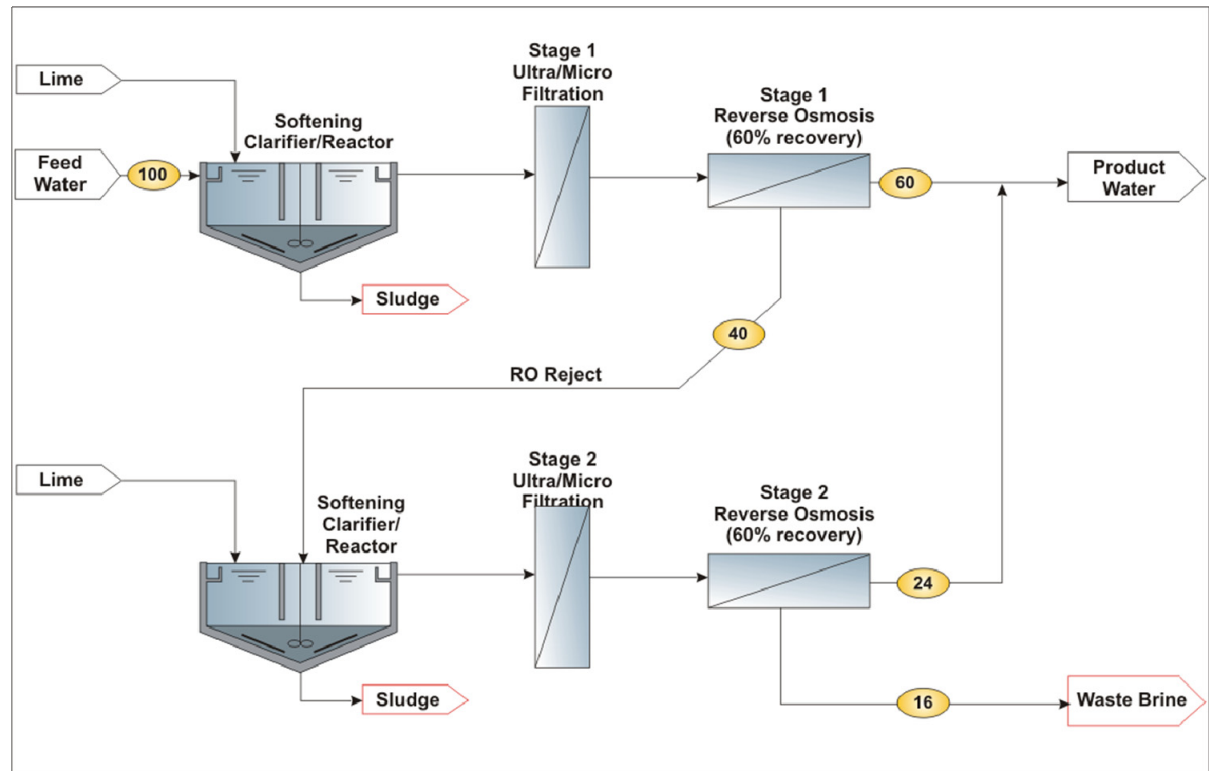
- Precipitation Based Processes
- Membrane Process Brine Management
- Ion Exchange Processes
- Biological Sulfate Removal
- Concluding comments on the evaluation of emerging sulfate treatment technology



Precipitation Based Processes

Established Multistage Membrane Processes

- UF/RO membrane processes with interstage gypsum precipitation are considered technically feasible and commercially proven for large scale sulfate removal to product water $\text{SO}_4 < 200 \text{ mg/L}$
- HiPRO Process has been operating since 2005 (eMalahleni) and 2009 (Optimum)
- More refinements to come





Multistage Membrane Processes

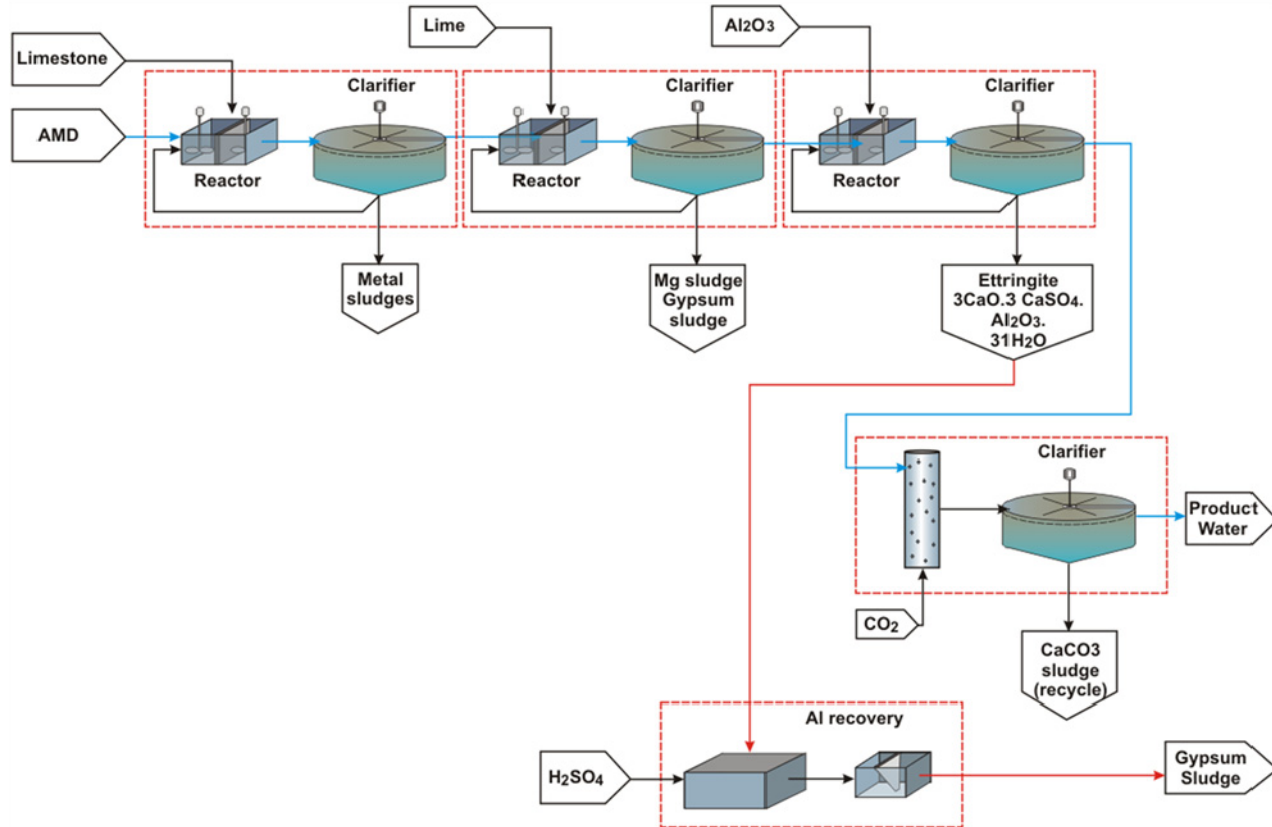
- eMalahleni > 98% recovery: 100 t/d of gypsum, 150 m³/d brine currently disposed to evaporation ponds
- Costs based on proprietary technology, however our independent observations and estimates
 - OPEX: \$0.60 to \$0.80/m³
 - CAPEX (24,000 m³/day facility): \$60M+
- Operations experience is published
 - Complex operations, labor intensive
 - High capital cost, scaling management
- Emerging trend in South Africa
 - Consider two stages of UF/RO process with eutectic freezing to further concentrate the residual brine steam





Ettringite Precipitation

- Variation on conventional gypsum precipitation
- Uses aluminum-based reagents to precipitate residual sulfate as ettringite

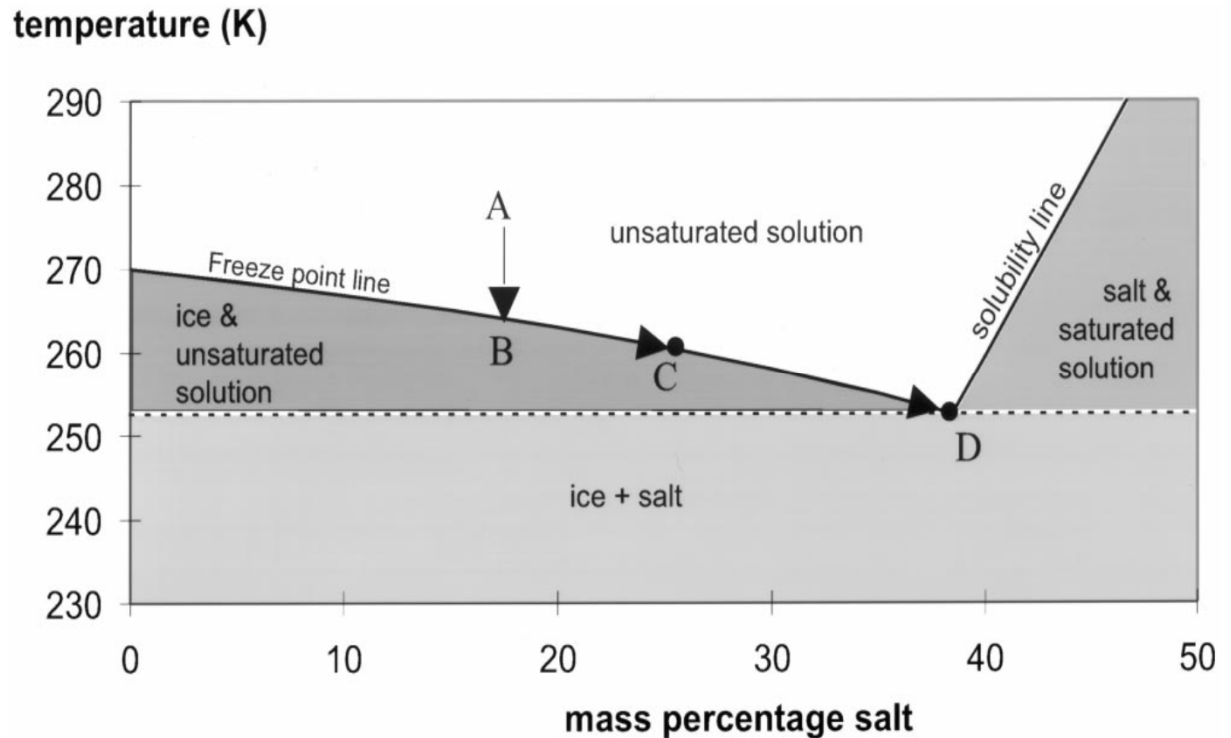




Membrane Process Brine Management

What is Eutectic Freezing?

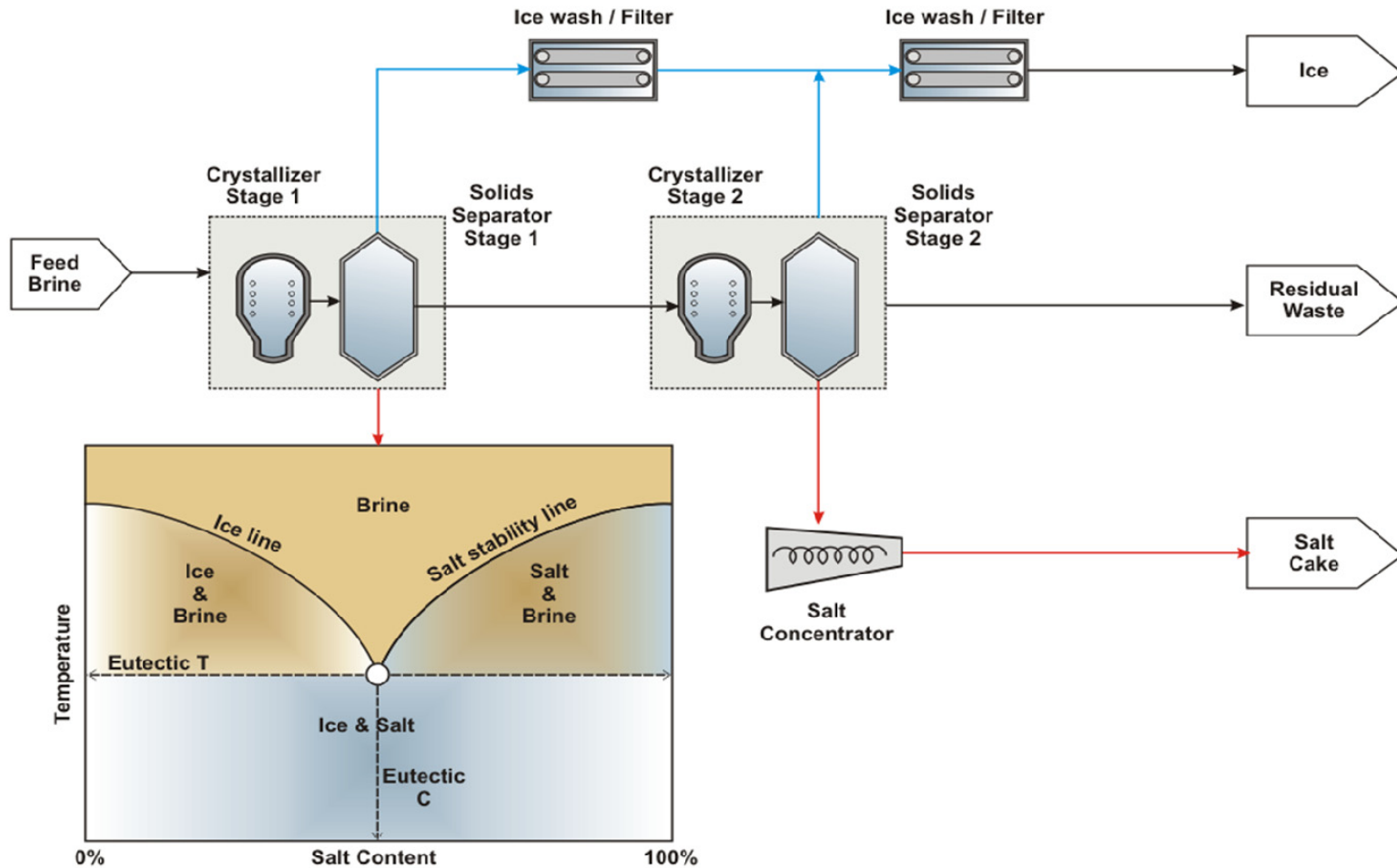
- Solution is cooled from A-B
- Ice forms from unsaturated brine from B to eutectic point D
- At D, crystals of both ice and salt form
- Ice, salt and brine can be easily separated by gravity
- Potential to also produce separate precipitated salt products



Source: F. Van der Ham et al. : *Chemical Engineering and Processing* 37 (1998) 207–213



Eutectic Freeze Flowsheet





Freeze Concentration – Cost Analysis

- Latent heat of fusion for water is 1/5 the latent heat of vaporization
- Example cost estimate based on published values for brine from a hypothetical membrane plant (from Oil Sands prefeasibility work)
 - Brine flow: 150m³/day case study (Na₂SO₄/CaSO₄ mixture)
 - Energy cost: \$9.00/m³ at \$0.10/kWhr
 - Compare to a similar MVR evaporation system: \$25/m³
 - Analysis is sensitive to efficiency of the cooling system



Brine/Paste Co-Disposal

- Combining brine (salts) and fly ash (silicate) results in pozzolanic reactions and geopolymerization, solidifying the highly concentrated brine
- Creates paste, a value-added beneficial product that has many uses including grouting, road base construction, and mine backfilling
- Salts and other contaminants in the brine are either bound or trapped within voids in the paste
- Reduces or eliminates the disposal cost of the highly concentrated brine and salt residuals without ponds

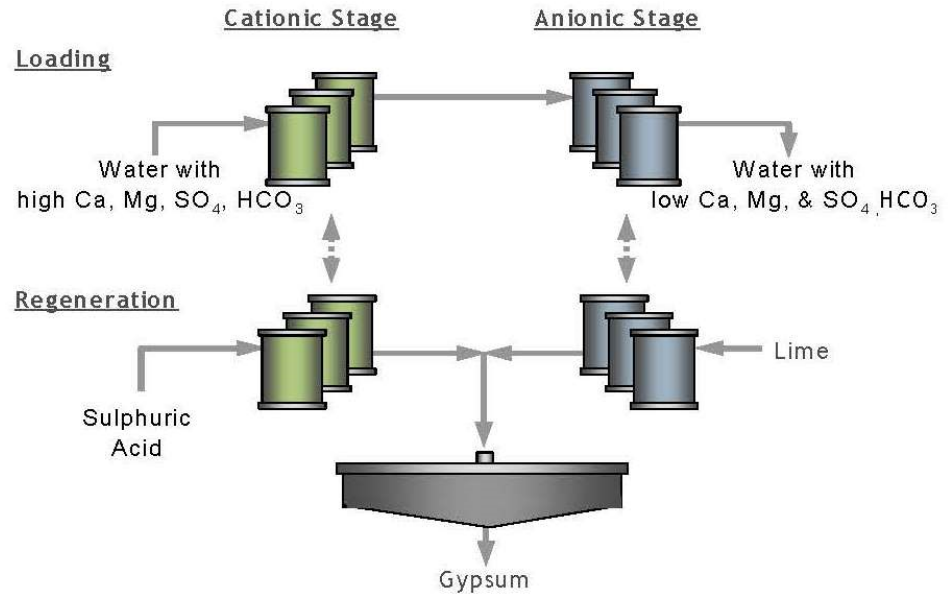




Ion Exchange Advances

Ion Exchange Processes

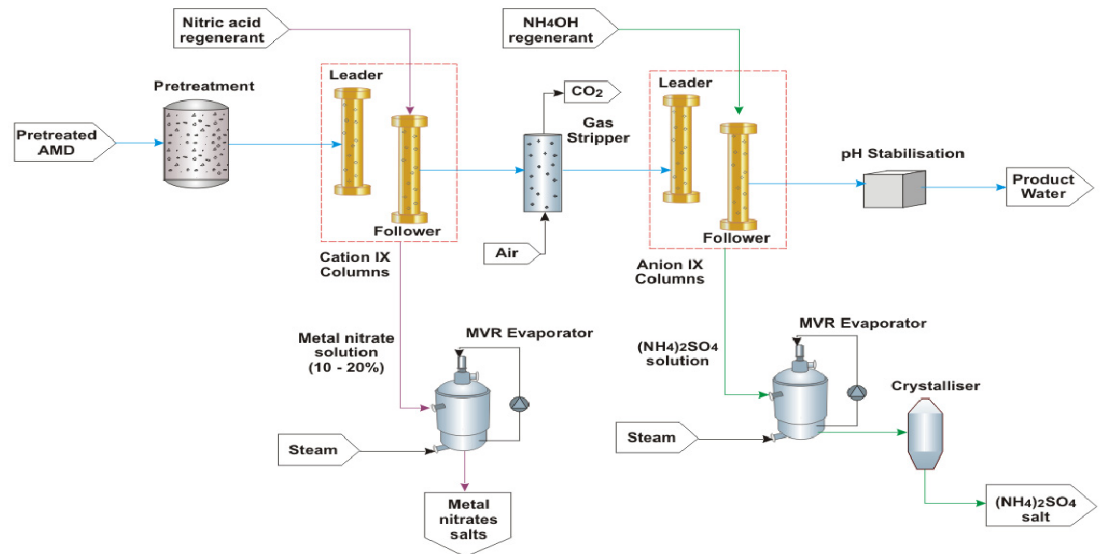
- BioteQ Sulf-IX™ process
 - Sequential removal of calcium and sulphate
 - Regenerated with sulphuric acid and lime with resulting formation of a potentially saleable gypsum product
 - BioteQ reports \$0.98-\$1.33/m³ total operating cost





Ion Exchange Processes

- Earth Technologies – selective / sequential recovery of saleable salts
- Cations report as nitrate salts, sulphate as ammonium sulphate
- 20,000 m³/day costs
- 2009 inflated to 2014
 - CAPEX – \$15,000,000
 - OPEX – \$1.33/m³





Biological Sulfate Removal

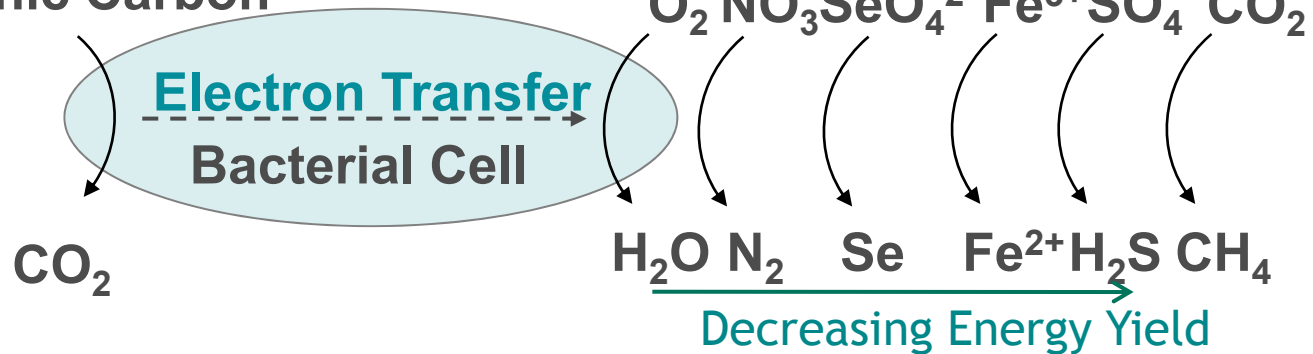


Biological Treatment Highlights

- Active treatment has seen limited use despite years of research
 - Cost of electron donor, capital cost of large reactors, solid/liquid separation stage have been limitations in the past
- Hydrogen cost, produced onsite with steam reforming
 - Our observation, recent price only, based on state-of-the-art technology = \$0.31/m³ (assuming 1 g/L sulfate reduction)
 - At 2008 North American gas prices, reagent cost alone is \$0.94/kg

Electron Donor

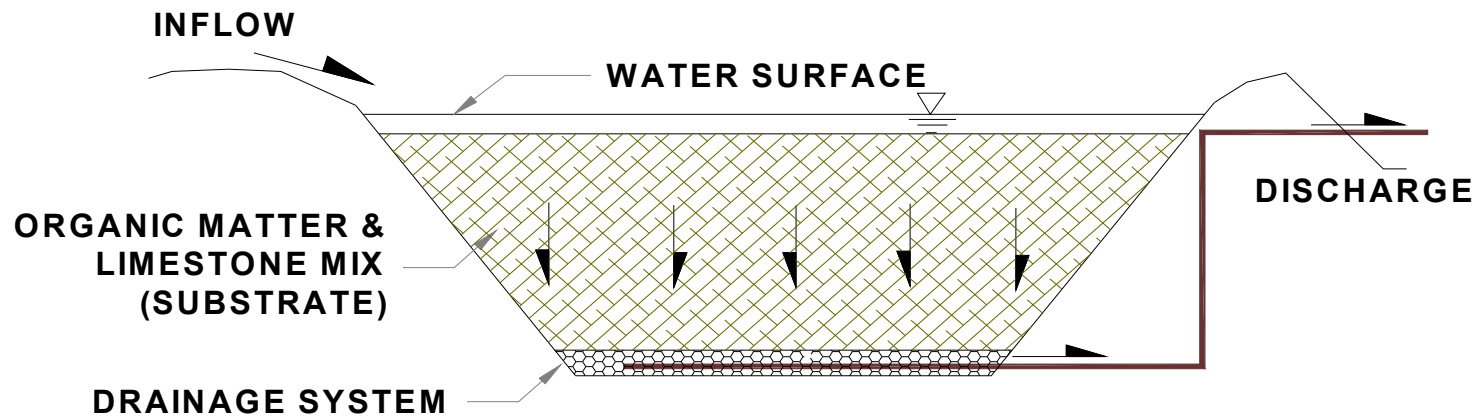
Organic Carbon





Biological Treatment Highlights

- Passive treatment has seen recent success, but on a smaller scale
 - Proven at a number of sites
 - Currently under construction in South Africa at large flow rates
 - Large land area and leakage of nutrients have been limitations
 - Theoretically uses low cost electron donor (site specific)





Passive Sulfate Removal Technology

- Biochemical reactors (BCR)
 - Also known as sulfate reducing bioreactors (SRBR)
 - Innovation with respect to the packing of bioreactors using a range of carbon sources (wood chips, manure, hay, etc.)
- Limitations
 - Sulfate reduction is limited by carbon availability
 - Need to sequester reduced sulfate (sulfide)





Passive Treatment Case Study

- Case Study – Sulfate removal at a coal mine
 - 70 to 75 gpm commercial demonstration (one quarter full scale)
 - Currently operating
- Reduces sulfate from 600 mg/L to approximately 300 mg/L target, consisting of:
 - BCR utilizes woodchips, hay, manure, and limestone
 - Anaerobic magnetite cell which sequesters bisulfide to a fraction of ppm
 - Aerobic polishing cell
- Total land area 0.8 ha
- Predicted life: BCR 10 to 15 years, magnetite cell 3 to 5 years



BCR Construction for sulfate removal in Canada (2012)

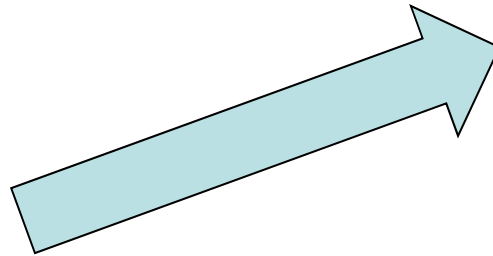
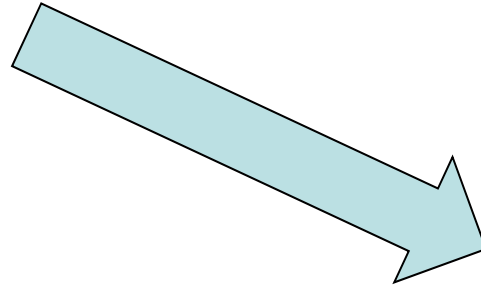


Hybrid Biological Sulfate Removal



Active Treatment

Large flow rates



Hybrid Treatment



*Cost effective for larger flow rates?
Commercially proven for Selenium
removal*



Passive Treatment

*Advantage of unattended operation, inexpensive carbon
source*



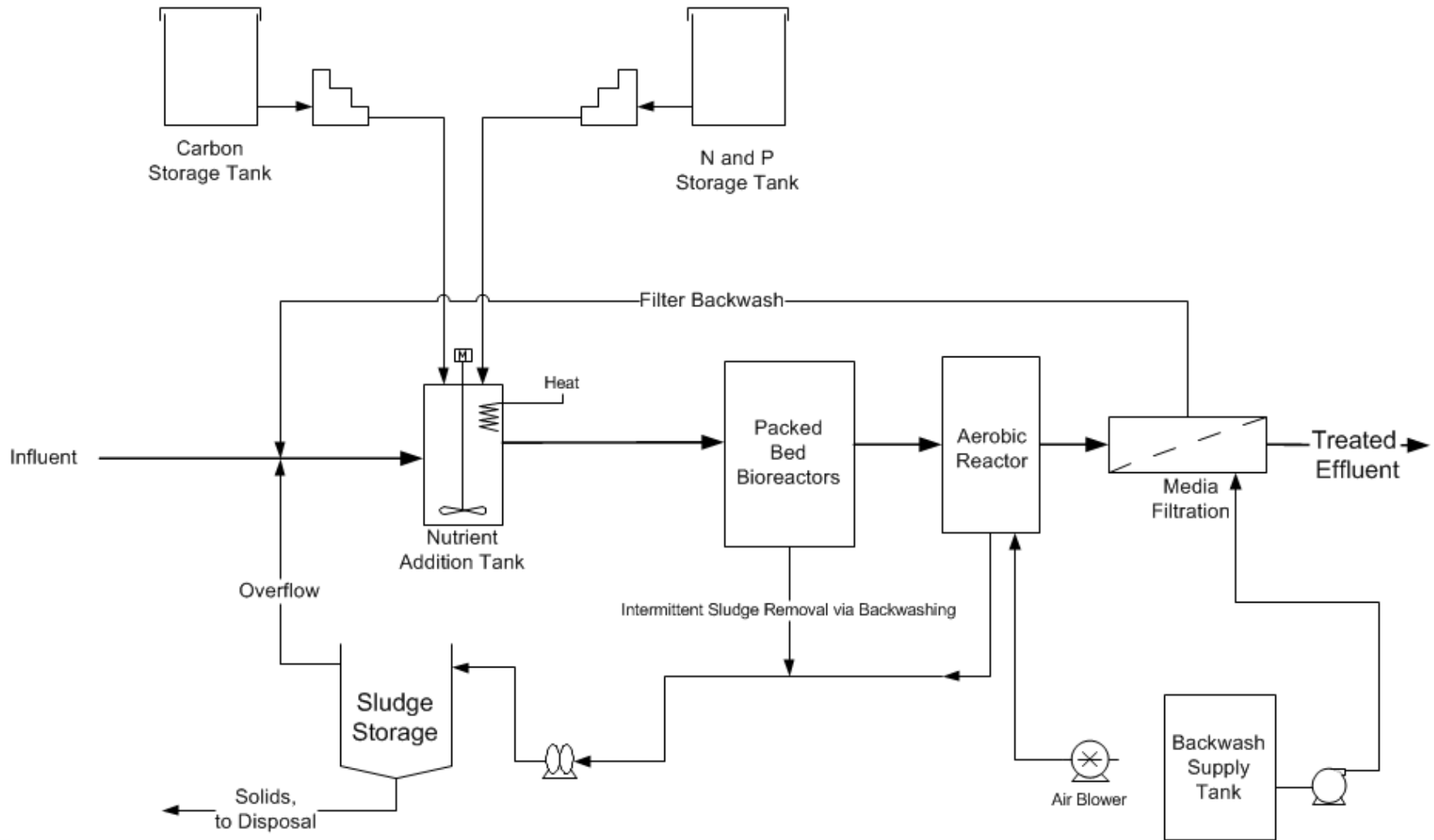
Hybrid Treatment for Selenium or Sulfate

- Consists of a passive bioreactor with inert media, with actively fed soluble electron donor
- Potentially makes use of mine wastes as media and for berm construction (i.e. CCR)
- Lower cost per unit volume but larger “reactors”
- Improved process control to reduce nutrient losses
- Reduced capital costs for mechanical, electrical, structural compared to active biological treatment and therefore reduced engineering cost
- May use a variety of locally available organic materials as base carbon source
- Isolates the SRB unit process from the conventional passive BCR microbial consortium
- Successful demonstration units constructed at two sites for selenium removal since 2010; but sulfate systems had limited success





Flowsheet for Hybrid Treatment





General Observations and Conclusions



Sulfate Removal – General Comments

Advanced sulfate removal technology is costly and justifies careful due diligence

- Have all other options been exhausted: optimized lime treatment, assimilative capacity of the environment, site specific targets for sulfate, seasonal discharge?

Is a technology and implementation risk management program in place?

- Identified all the drivers for the implementation schedule?
- Identified qualified external peer reviewers (both for technology and the planning process) without commercial or internal bias?
- Identified the cost/benefits of a pilot plant?
- Provided a thorough sensitivity analysis (reagent price, utilization, back-flush water consumption, process failure modes etc.)?



Bias in Technology Evaluation

- Engineers (and vendors) can be biased towards a specific technology
- Thorough planning and implementation processes are sometimes short-circuited due to internal bias or compressed schedule
- Technology comparisons are not always done on a consistent basis
- Emerging technology needs to be evaluated according to sensitivity of failure modes
- A process warranty is rarely sufficient to protect owners interests
- All decision making is subject to tradeoffs, and each one has biases

Mechanical Plant ↔ Land Area

Established ↔ Emerging Technologies

Capital ↔ Operation Costs

Quick ↔ Cheap

Power Input ↔ Reagent Input



Conclusions

- Membrane technologies for sulfate removal below gypsum saturation levels are commercially demonstrated and have achieved acceptance
- Membrane technologies are being optimized
- Brine management is the subject of intensive R&D in oil & gas
- Eutectic freezing is an emerging lower energy alternative to MVR
- Brine-ash paste sequestration has been demonstrated (oil & gas)
- Ion exchange technologies are available, but not in widespread use
- Active biological treatment has never taken off despite extensive R&D
- Passive treatment has advanced; we await published life cycle costings
- Hybrid biological treatment has been successful in the case of selenium removal with potential applicability to sulfate treatment
- Cost and complexity of advanced sulfate removal projects warrants independent peer review



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