Metals Precipitation

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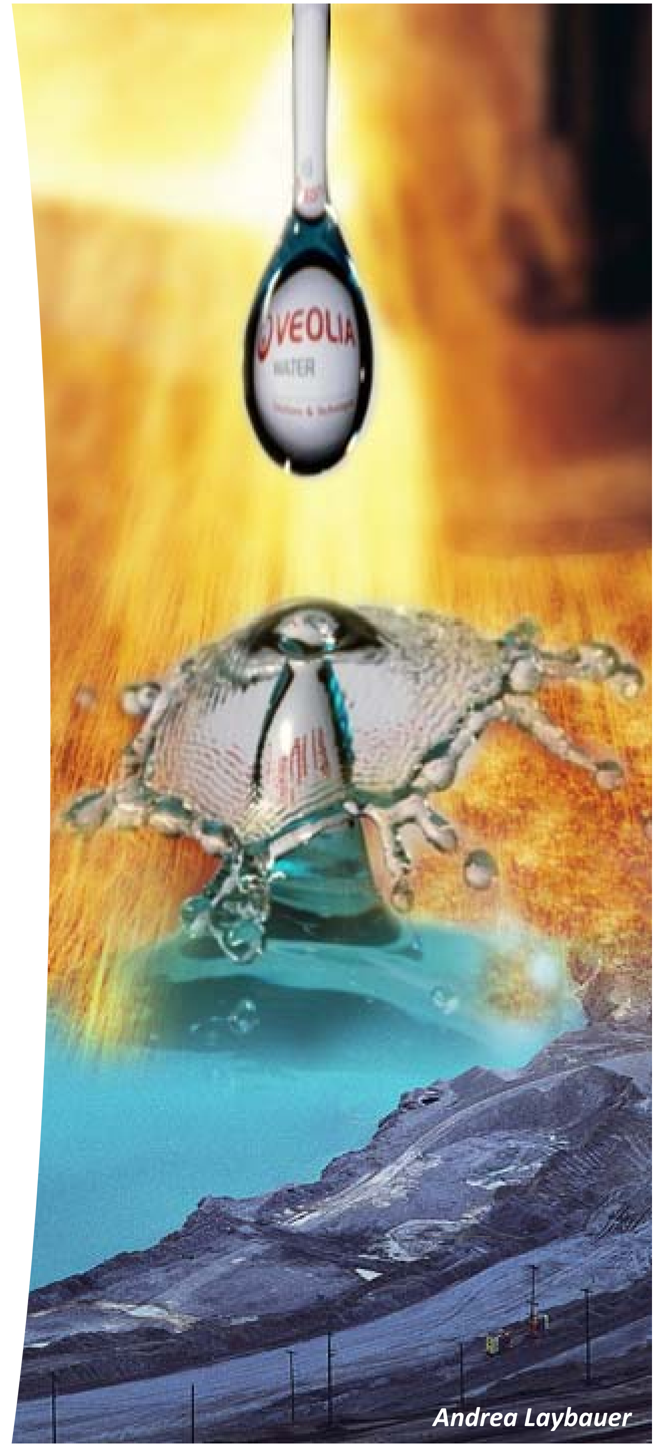


Introduction

- Metals in Mining Wastes
  - Type of Mines and Ore Characteristics
- Fe, Mn, Al, Cu, Pb, Zn, Cd, As, Mo, Sb, etc.
- Separated into three groups
  - Iron/Manganese/Aluminum
  - Heavy Metals (Cu, Pb, Zn, Cd)
  - Oxyanions of Metals (As, Mo, Sb)

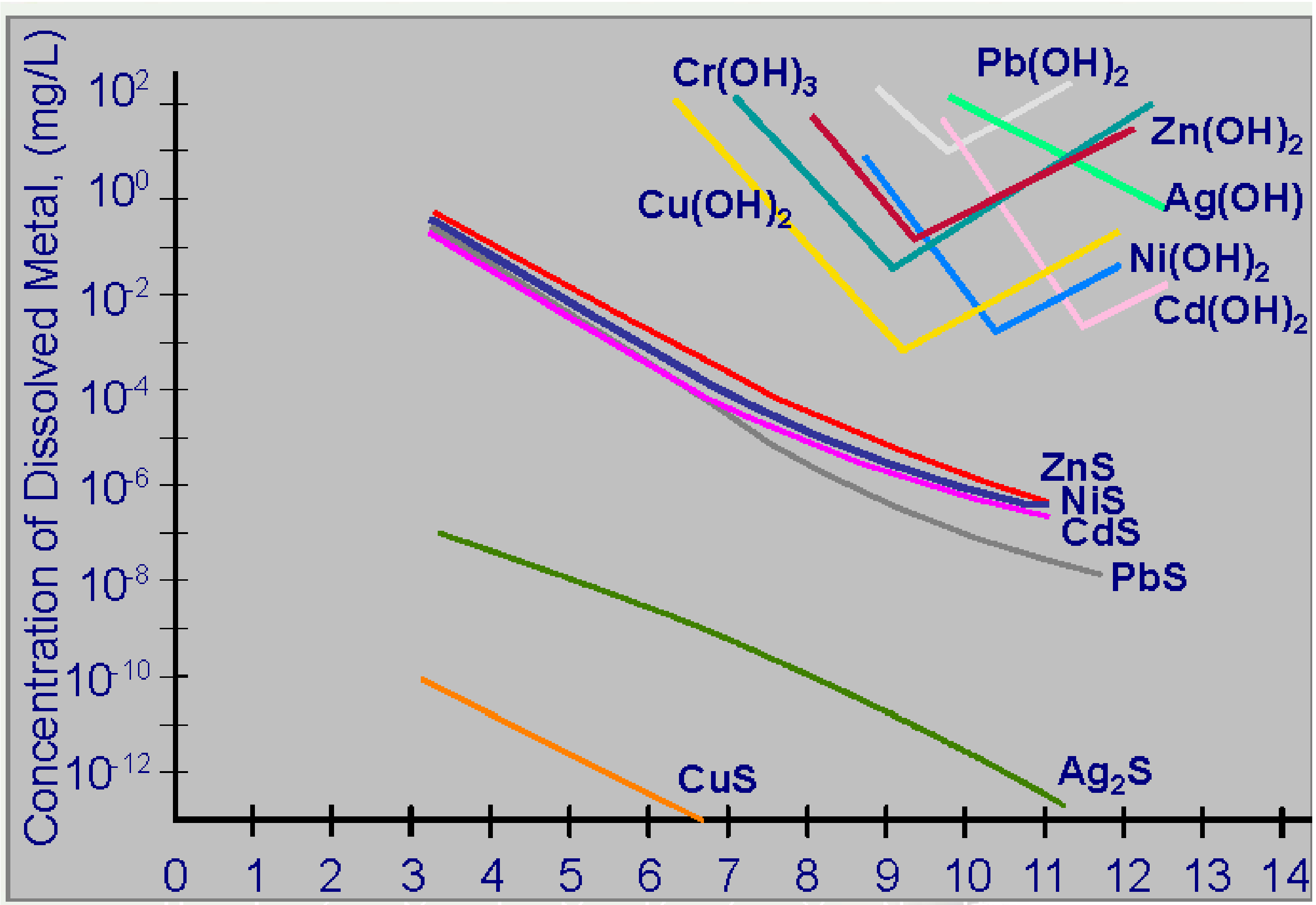
Iron and Manganese Removal

- Oxidation Process (Aeration)
- Fe^{2+} to Fe^{3+} at pH > 6.0 (fast reaction ≤ 10 min)
  - Precipitate Fe^{3+} as $Fe(OH)_3$ at pH 7.0 – 7.5
- Oxidize Mn^{2+} to Mn^{4+} by Air at pH > 9.5 (Reaction time: 20 to 30 min)
  - Precipitate Mn^{4+} as MnO_2
- Other Oxidants: $KMNO_4$, chlorine, Ozone, etc
- Oxidation Reaction Generates Acid, needs alkali to maintain pH
- Aluminum is precipitated as $Al(OH)_3$
- Optimum pH for Aluminum precipitation 7.2 (Minimum Solubility & best Settling)

Heavy Metals Treatment by Chemical Precipitation, and coprecipitation/adsorption

- Need to form a precipitate (crystal) or adsorb the metal onto a matrix/solid surface.
- This can be accomplished by:
  - adjusting the pH
  - adding sulfide (sodium hydrosulfide or organic sulfide)
  - adding carbonate
  - adding iron or aluminum salts
  - Some times Redox Treatment may be required prior to Chemical Precipitation

Solubility of Metal Hydroxides and Sulfides as a Function of pH



Iron Co-Precipitation and Adsorption

- $2Fe^{+3} + 4H_2O \rightarrow Fe_2O_3 \bullet H_2O + 6H^+$

- $Fe_2O_3 \bullet H_2O$ has high binding capacity for heavy metals as well as for oxyanions of metals
- Depending on the pH, the oxide surface acts as an adsorbent for heavy metals and for oxyanions of metals
- Removes heavy metals (Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}, etc) at $pH > 7.5$
- Removes Oxyanions of metals (As, Mo, Sb, V) at $pH < 7.5$
- Process focuses on pH and iron dosages rather than the solubility of each metals

VWS Cutting Edge Technologies For Metal Treatment

- TURBOMIX Reactor
- High Rate Settling Technology
  - ACTIFLO & MULTIFLO Systems
- HDS Technology
- Low pH RO
- VWS Proprietary Chemicals (HYDREX Products)
- MetClean Technology

MetClean™ Technology

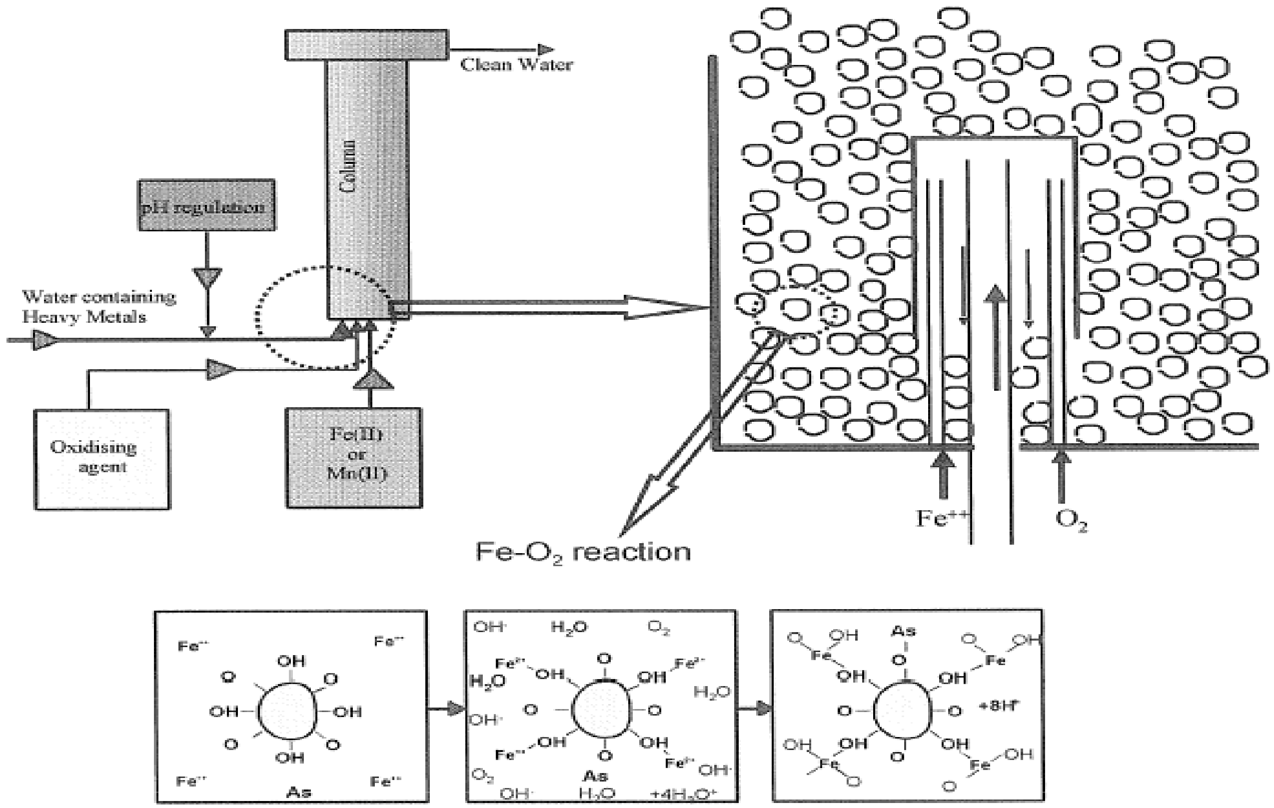


Figure 1. Principe the MetClean™ process

MetClean™ Technology

- Removes heavy metals (Cu, Pb, Zn, Cd, Cr, Ni, Mn, etc.) as well as oxyanions (As, Cr, Se [IV], Mo, V, etc.)
- Mechanism: Adsorption onto ferric oxyhydroxide (FOOH) or MnO_2
- Forms thick coating of FOOH or MnO_2 onto which adsorption of the heavy metals and oxyanions take place
- Contaminant Removal depends on pH, water quality, presence of co-occurring contaminants
- Popular technology in Europe and Australia

Case History: Heavy Metals Treatment

Raw Water Characteristics:

Flow:	- Process Range:	2,300 – 5,700 m3/h
	- With Stormwater:	Up to 34,000 m3/h
pH:	1.5 – 5.0	
TSS:	200 – 2,500 mg/l	
Total Cu:	0 – 140 µg/l	
Total Ni:	0 – 140 µg/l	
Total Zn:	0 – 5 mg/l	

Treated Water Requirements:

pH:	6 – 9
TSS:	< 20 mg/l
Total Cu:	< 5 µg/l
Total Ni:	< 20 µg/l

Case History: Heavy Metals Treatment (Contd.)

- Process: Sulfide Precipitation in Presence of Iron.
- Reaction pH: 9.5 – 10.0
- Reaction Time: 10 Min.
- NaHS dosage: 1 – 5 mg/L as S
- Settling Rate: 100 – 180 m/h

	Raw Water	Clarified Water
Ni (µg/l)	10 – 110	4 – 20
Zn (µg/l)	250 – 1,800	10 – 40
Cu (µg/l)	30 – 100	2 – 5
Pb (µg/l)	< 5 – 14	< 5
TSS (mg/L)	200 – 1,500	<20

Case History: Heavy Metals Treatment (Contd.)

- Start-Up: 2004
- Installed Capacity:
- - Storm Weather: 2 x 17,000 m3/h (at 185 m/h)
- - Dry Weather: 5,700 m3/h (1 Unit at 60 m/h)

- Actual Performance:

	Raw Water	Limit Req.	Effluent
TSS (mg/l)	405	< 19	4.7
Total Cu (µg/l)	0 – 140	< 6.1	2
Total Ni (µg/l)	0 – 140	< 20	8

Case History: Heavy Metals Treatment (Contd.)

Neutralization with Lime prior to Treatment

Case History: Heavy Metals Treatment (Contd.)

General View of 2 x 17,000 m3/h Actiflo Trains

Case History: Heavy Metals Treatment (Contd.)

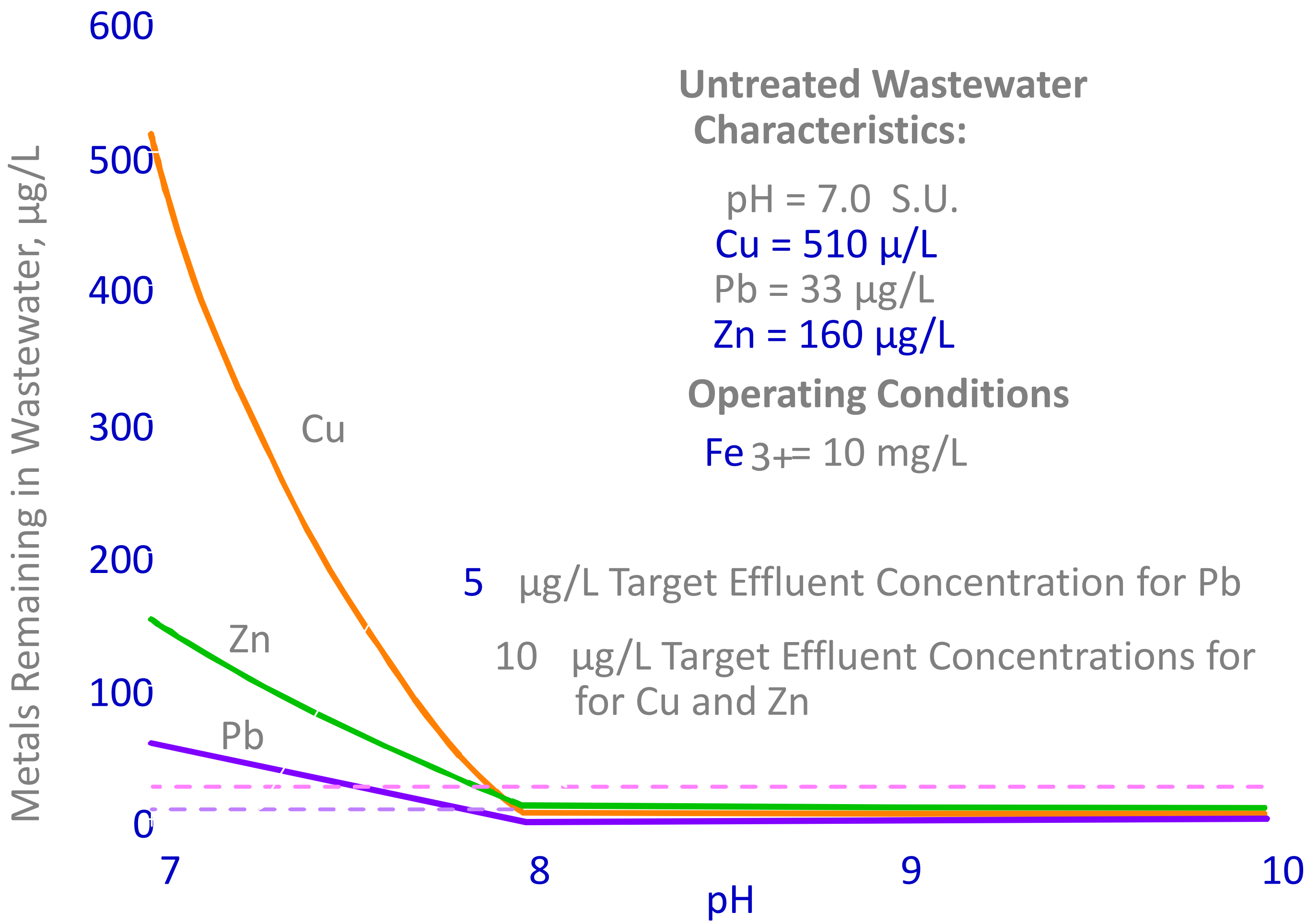
Hydrocyclone Battery per 17,000 m3/h Train

Case History: Heavy Metals Treatment (Contd.)

Clarified Water Discharge from Treatment Plant

Heavy Metals Treatment with Coprecipitation & Adsorption

- Effect of pH on Metal Removal



Case History: Heavy Metals Treatment with Coprecipitation & Adsorption

- Iron Coprecipitation/Adsorption Process is capable of reducing Cu and Zinc concentrations below 10 ppb and Pb below 5 ppb.
- Cd can be reduced to less than 5 ppb.
- Concentrations of Metals in the Treated Wastewater decreases with an increasing Iron Dosage. To achieve less than 10 ppb of Zinc and less than 5 ppb of lead, an Iron to metal weight ratio between 20 to 1 and 30 to 1 is recommended
- Desired pH Condition for the Process is between 8.0 and 8.5 S.U. for Zn, Cu, and Pb
- Higher pH is required for Cadmium (pH > 9.5)
- Fast Kinetics (10 – 15 minutes Reaction); Non-Hazardous Waste.

Case History: Heavy Metals Removal (contd.)

- Process: HDS [chemical precipitation and adsorption of dissolved metals onto Iron oxides/hydroxide surface]
- Plant: USA, MT
- Flow: 1100 m3/Hr. Two stg. HDS Process
- Final Design Contract Was Awarded to VWS in March 2001
- Start up and Commissioning began in Nov. 2003
- Performance Test: December 2003

Case History: Heavy Metals Removal (contd.)

Parameters	Influent	Effluent	Limit
Al	100	<0.5	1.0
Cd	1.0	0.002	0.005
Cu	50	0.01	0.05
Zn	158	0.06	0.50
Fe	153	0.05	1.0
SO4	4665	2500	NA
TSS	60	<4	<10

- All values are in mg/L

Case History: Heavy Metals Removal (contd.)

- Site: South America
- AMD Mine Tunnel: Copper and coal Mines
- Single Stage HDS ; Start-up & Commissioning : Mid 2010
- Design Flow: 5000 m3/Hr
- Average Flow: 4000 m3/Hr

Parameters	Influent	Effluent	Design
Cd	0.12	<0.003	0.005
Fe	70	0.20	2.0
Pb	0.25	0.02	0.05
Zn	40	0.07	1.0
Mn	36	0.05	3.0

All values are in mg/L

Technology for Arsenic Removal

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Arsenic in Mine Water

- Principal Aqueous Forms of Inorganic Arsenic
  - Arsenite (As III)
  - Arsenate (As V)

- Arsenite (As III)
  - **Predominant Under Moderately Reducing Condition**

- $H_3AsO_3^0$ $H_2AsO_3^-$ $HAsO_3^{2-}$ AsO_3^{3-}

  pK=9.22 *pK=12.13* *pK=13.40*

- Arsenate (As V)
  - **Predominant Under Moderately Reducing Condition**

- $H_3AsO_4^0$ $H_2AsO_4^-$ $HAsO_4^{2-}$ AsO_4^{3-}

  pK=2.2 *pK=6.98* *pK = 11.55*

State-of-the-Art Arsenic Treatment Technologies

- Softening
- Coprecipitation and adsorption with Iron/Aluminum Salt
  - Clarification [VWS ACTIFLO System; must include sludge recirculation]
  - Clarification/Filtration
  - pH should be between 7.0 and 7.5
  - If As (III): oxidize to As (V), prior to adsorption
- Enhanced Coagulation/Filtration [two stage systems]
- Adsorption onto Iron Oxide based media
- Activated Alumina (AA)
- Ion Exchange (IX)
- Membrane Technology

Iron Coprecipitation and Adsorption

- Two Step Reaction Process
  - Formation of Iron Oxyhydroxide

    $2\,Fe^{3+} + 4\,H_2O \rightarrow Fe_2O_3 \,.\, H_2O + 6H^+$
  - Adsorption of Oxyanions of Arsenic onto Active Sites
- Important Parameters
  - pH: 7.0 – 8.0
  - Mixing Time: Fast Reaction (10 to 15 Min.)
  - Depends on Water Quality and Goal

    20 to 1 or More!

    Need Higher Ratio to Achieve Low Effluent Concentration.

  Co-occurring Contaminants Effect: Silica, PO_4, SO_4, Other Oxyanions, etc.

Iron Coprecipitation and Adsorption (Continued)

- Raw Water Contains Hi Dissolved Fe (> 1.00 mg/L)

  Oxidation of Fe^{2+} to Fe^{3+}

- Add More Fe^{3+} Externally to Maintain Desired Fe to As Ratio (In-Line, Small Mix Tank)
- Add Polymeric Flocculant
- Solid/Liquid Separation (Clarifier/Filter/MF) [Sand Ballasted Settling]
- Produces 2 lbs of Sludge per lb of Iron

Case History: Arsenic Treatment from Mine Water

- Site: USA, MT;
- Process: Two Stage HDS [adsorption of dissolved arsenic onto Iron oxides/hydroxide surface]
- Flow: 1100 m3/hr.
- Dissolved Iron in Raw Water = 153 mg/L
- Dissolved Arsenic in Raw Water = 0.03 mg/L
- Arsenic in Clarifier Effluent = 0.005 mg/L (limit ≤ 0.01 mg/L)
- Dissolved Iron in Effluent = 0.05 mg/L (limit 1 mg/L)

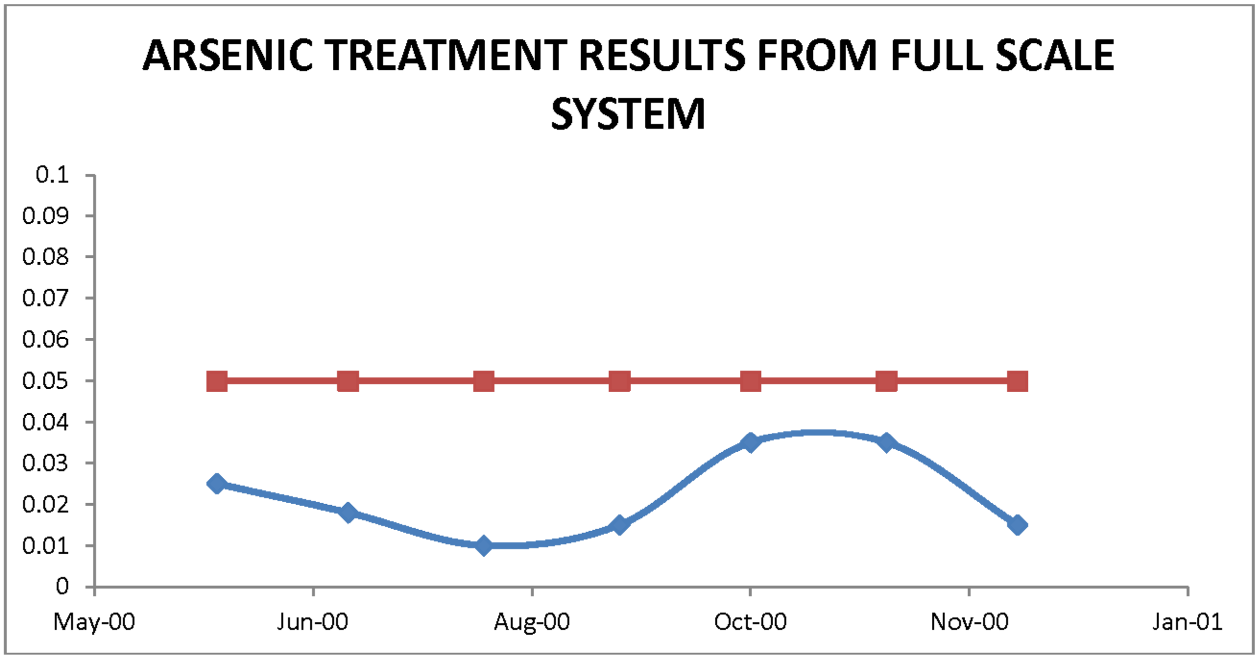
Case History: Arsenic Treatment from Mine Water (Contd.)

- Site: South America
- Process: Single Stage HDS [adsorption of dissolved metals onto Iron oxides/hydroxide surface]
- Design Flow: 5,000 m3/hr
- Average Flow: 4,000 m3/hr
- Dissolved Iron in Raw Water: 70 mg/L
- Dissolved Arsenic in Raw Water: 1.1 mg/L
- Arsenic in Clarifier Effluent: <0.005 mg/L (Design ≤0.01 mg/L)
- Dissolved Iron in Effluent: 0.20 mg/L (Design ≤ 2.0 mg/L)

Arsenic Treatment Case History (contd.)

- Site: Eastern USA
- Flow: 80 m3/hr
- Total As $_{sol}$: 30 mg/L [As (V) + As (III) + Organic As]
- Effluent Target : Total Arsenic < 0.05 mg/L
- 1ST DBO Project on Arsenic Treatment
- Process
  - **Oxidation with Fenton Reagent + Iron coprecipitation and adsorption at pH 7.5 and 8.0 + clarifier w/HDS process and MMF**
- Produces effluent Arsenic < 0.05 mg/L

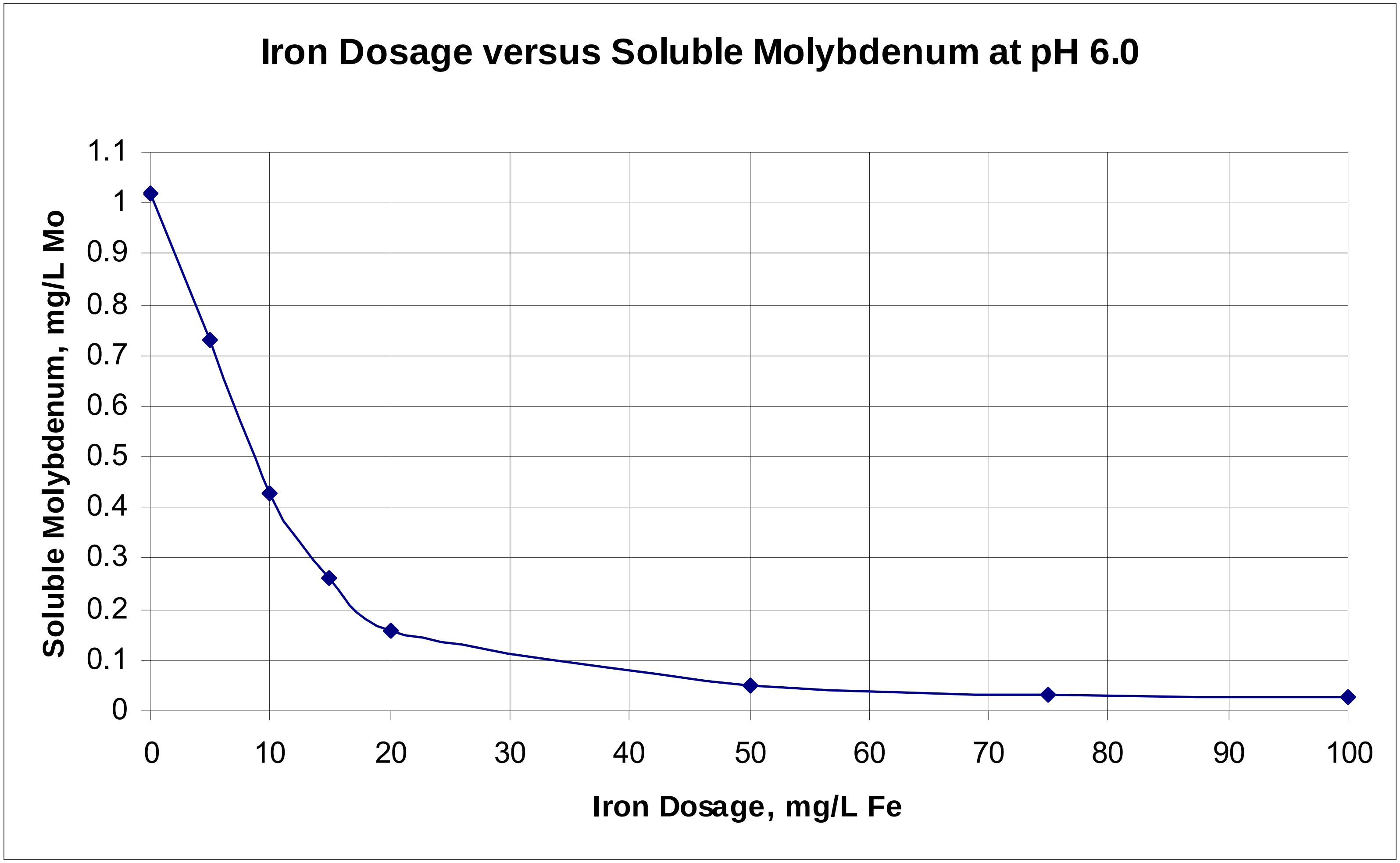
Arsenic Treatment Case History (contd.)



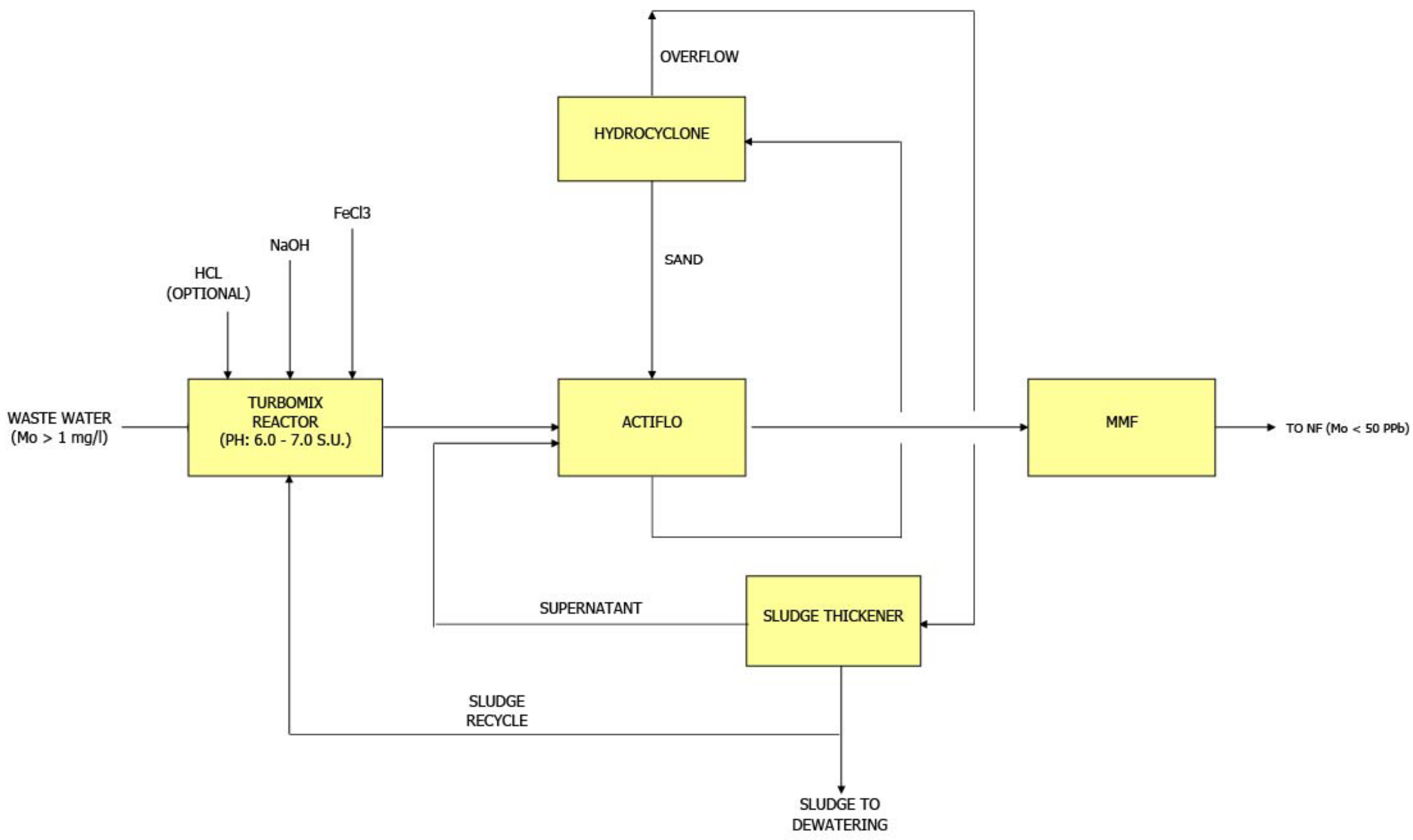
Molybdenum in Mine Water

- Dissolved Mo: exists as Molybdate ion Mo_4^{2-} [MO (VI)]
- Treatment Technologies: Similar to Arsenic
  - **Iron Coprecipitation/adsorption**
  - **HDS Process**
- Important process parameters:
- **pH, Iron dosage, reaction time, water quality, presence of phosphate, arsenic, selenite, etc.**
- Calcium Molybdate ($CaMoO_4$): Insoluble in water
- Forms Scale on Membrane Surface

Mo Removal Results for Sulfate Treatment Project



Mo Removal Pre/Treatment Concept Applied in Sulfate Treatment Project



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Questions?

Thank You!
¡Gracias!

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