Uranium Tailings Management at AREVA Resources Canada Inc.

Part 1: Design Confirmation and Geochemical Observations from the McClean Lake Operation in Northern Saskatchewan

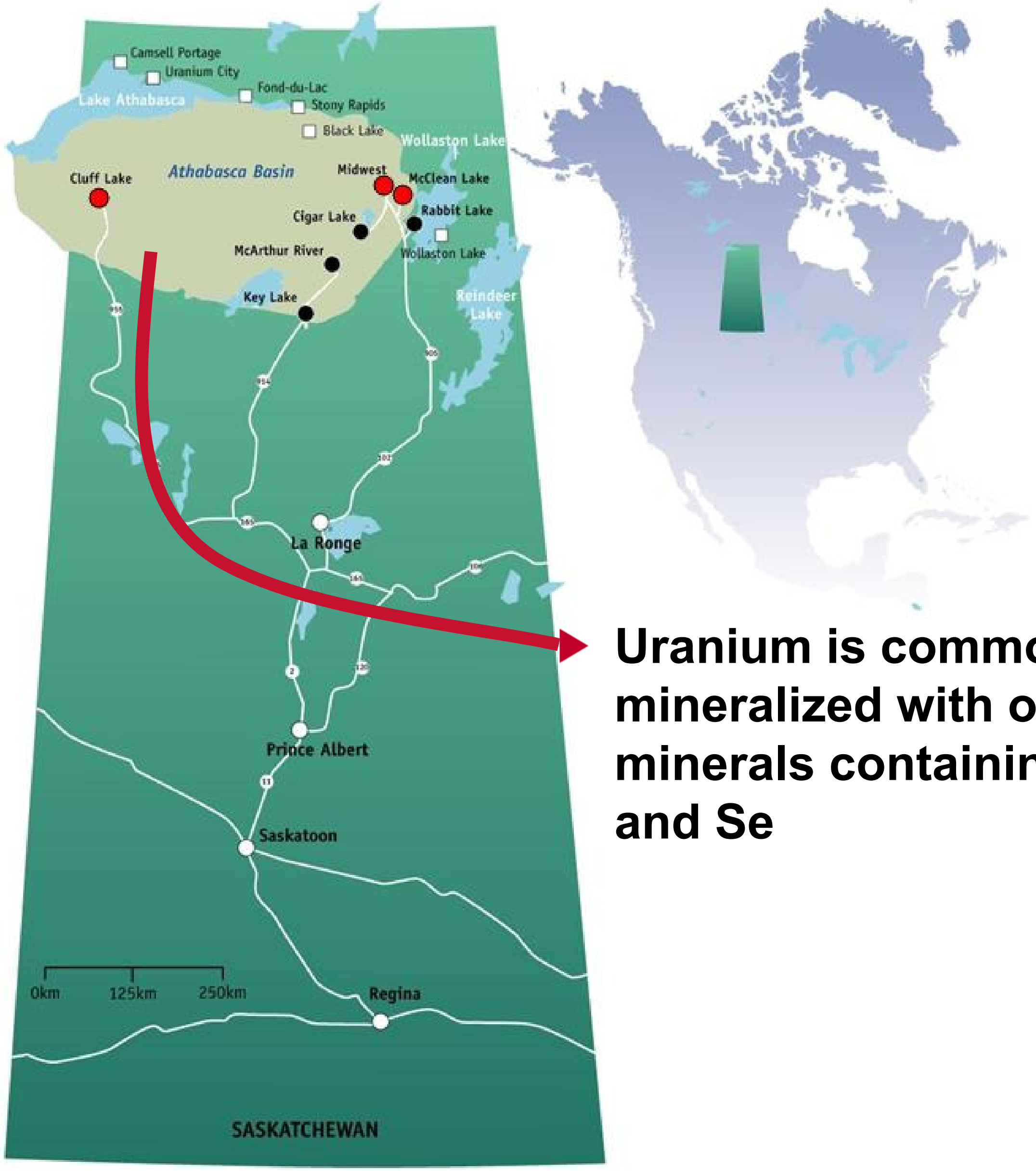
18th Annual BC/MEND Workshop

November 30 – December 2011
Vancouver

Contents of Presentation

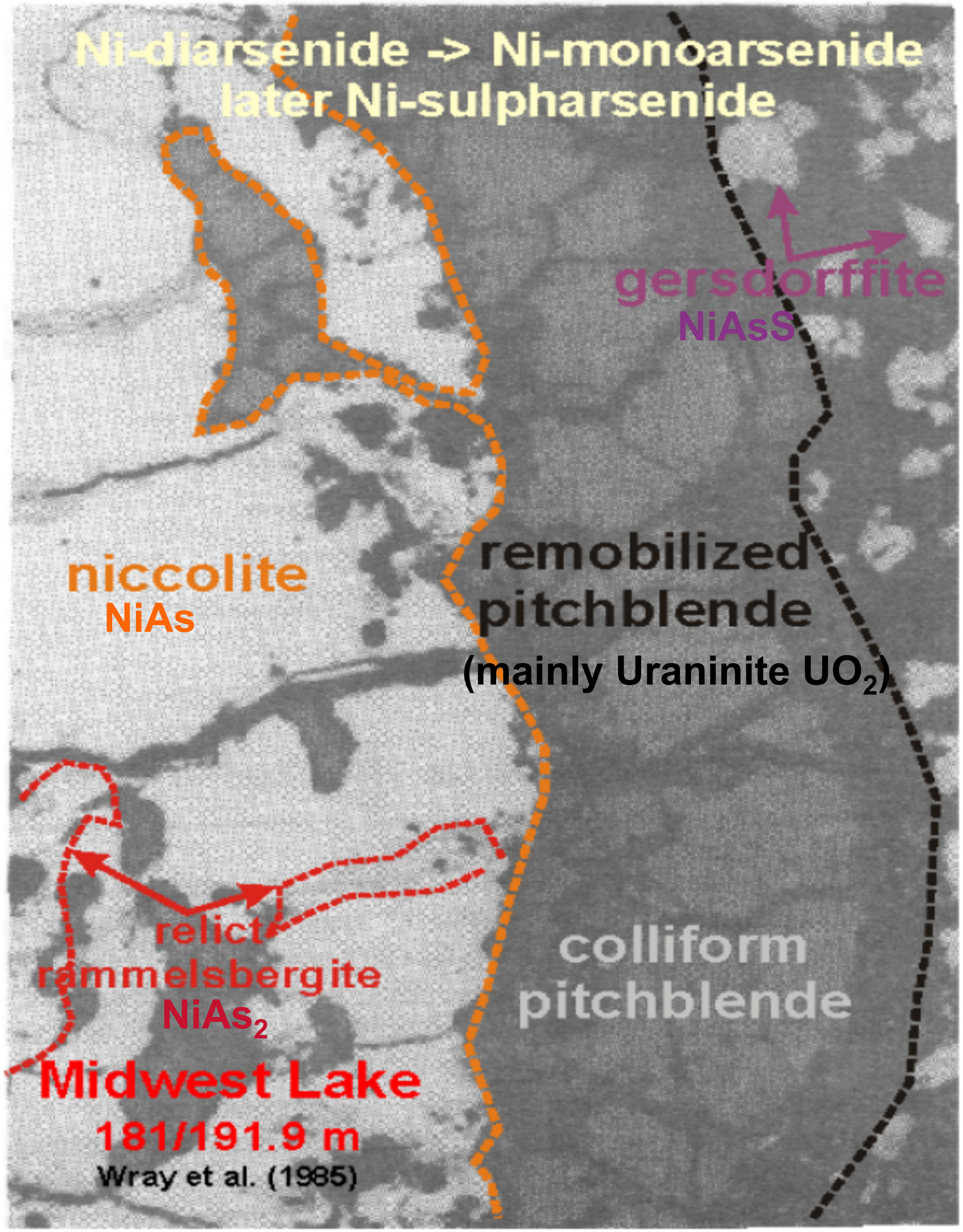
- Overview of Waste Water and Tailings Management Systems
- Tailings Management System Design
- Tailings Geochemical Performance
  - sampling
  - pore water observations
  - sediment observations
- COC Pore Water Controls
  - arsenic
  - bicarbonate ion (uranium)
  - molybdenum
- Case Studies – Effect of Grain Size Distribution
  - whole tailings
  - coarse tailings
  - fine tailings
- Conclusions

Overview



Uranium is commonly co-mineralized with other reduced minerals containing As, Ni, Mo and Se

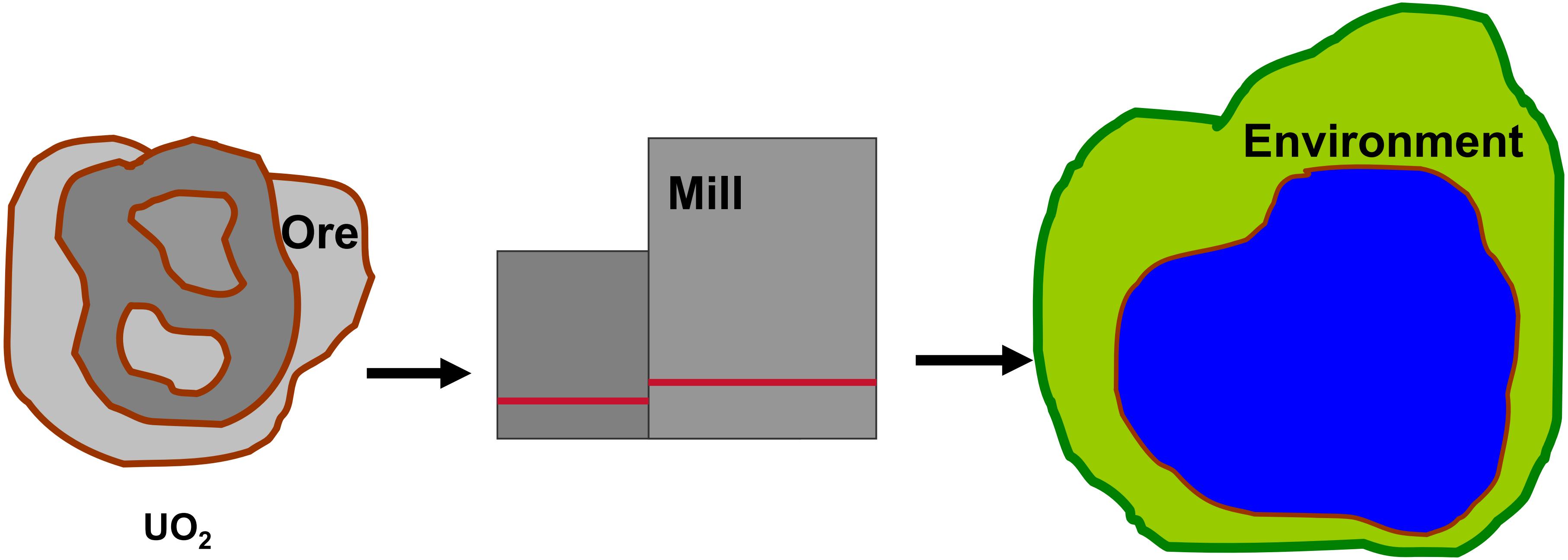
Overview



- Uraninite – UO_2
- Rammelsbergite – $NiAs_2$
- Niccolite – NiAs
- Gersdorfite – NiAsS
- Molybdenite – MoS_2
- Jolliffeite – (Ni,Co)AsSe

Overview

Uranium and reduced co-mineralized elements are oxidized to more soluble forms by the mill process



UO_2

$NiAs_2$

$NiAs$

$NiAsS$

MoS_2

$(Ni,Co)AsSe$

UO^{2+}

AsO_4^{3-}, AsO_3^{3-}

Ni^{2+}

MoO_4^{2-}

SeO_4^{2-}, SeO_3^{2-}

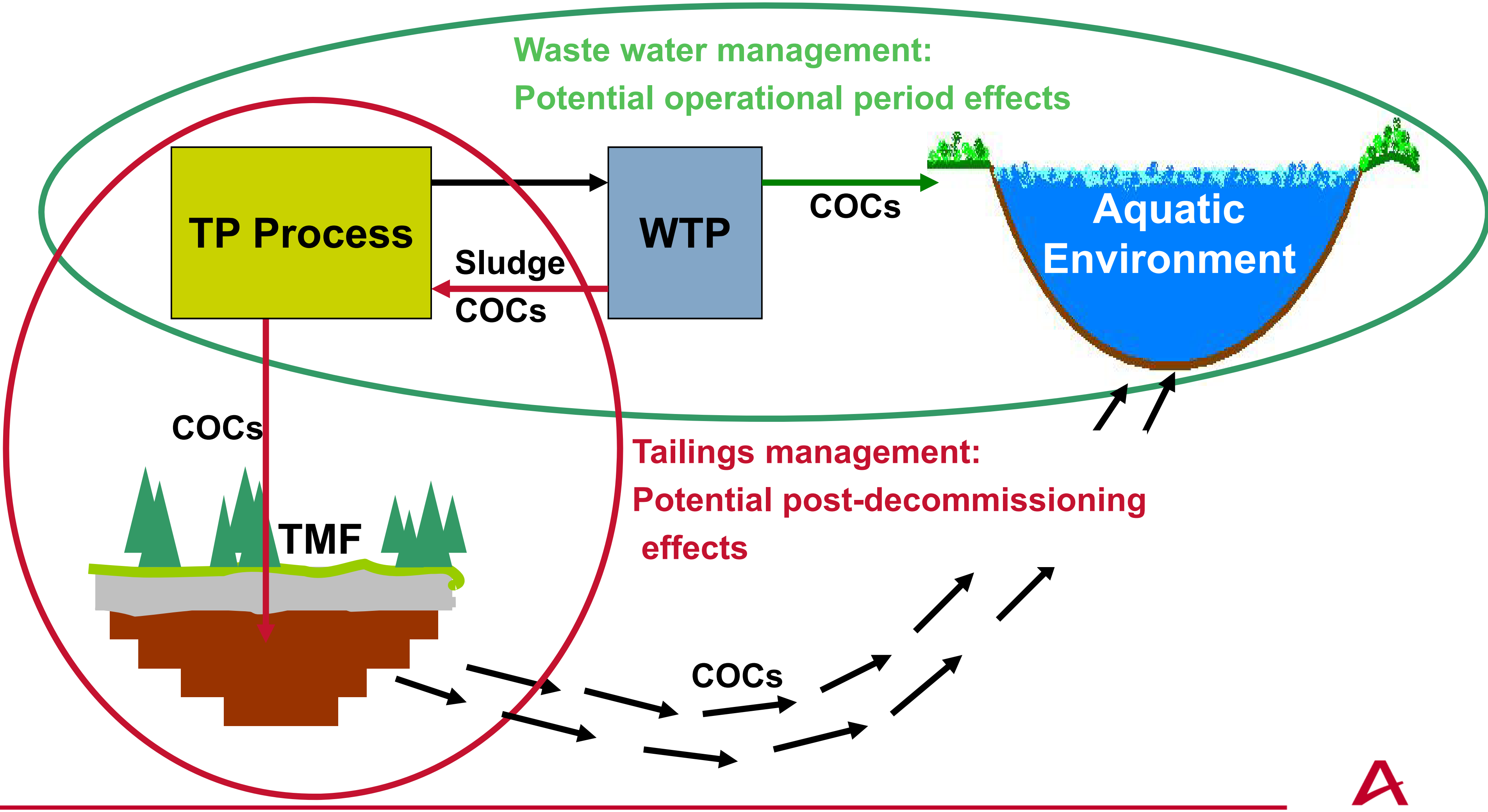
Constituents of Concern (COC)

Soluble forms of five elements are identified as COCs in the receiving aquatic environment

Overview

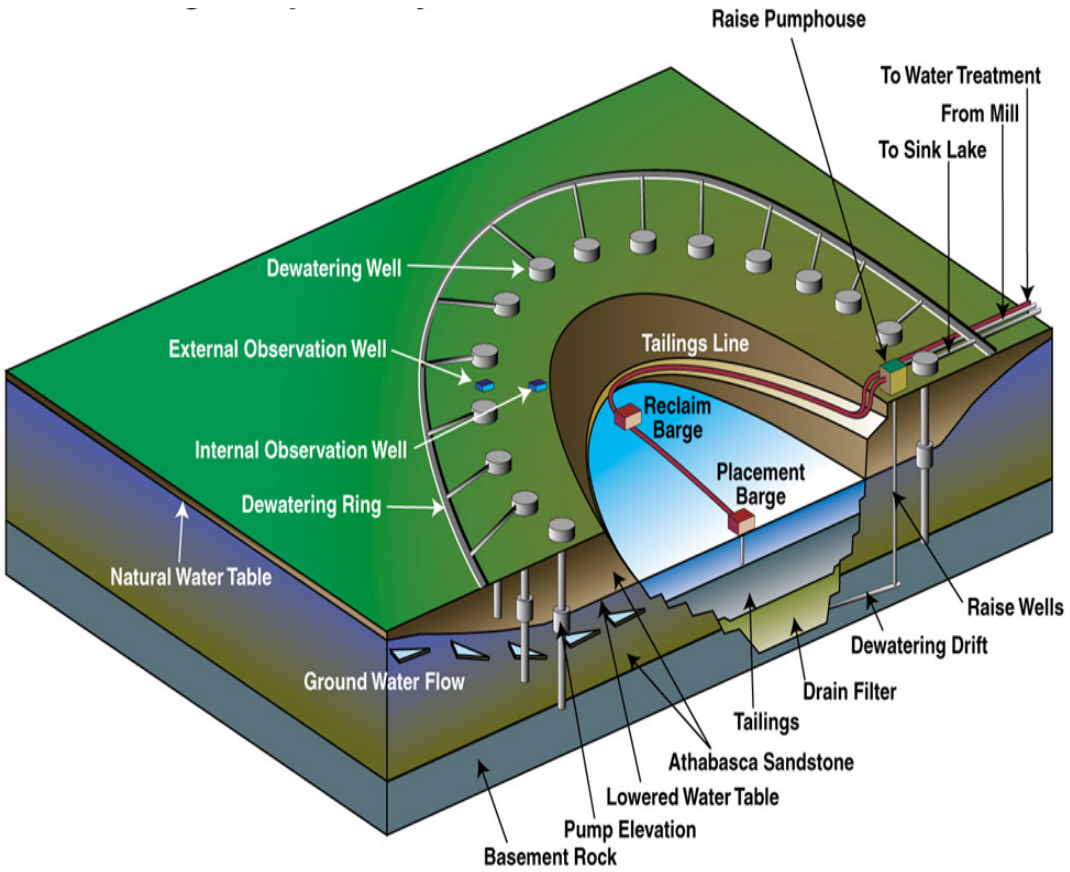
Waste Water and Tailings Management Systems

Require a Process Capable of Controlling these 5 COCs



Overview

Operational Features of the JEB Tailings Management Facility (TMF)



Overview

Arial Photo of JEB TMF

Arsenic Content of Ore Bodies to be Processed at the JEB Mill

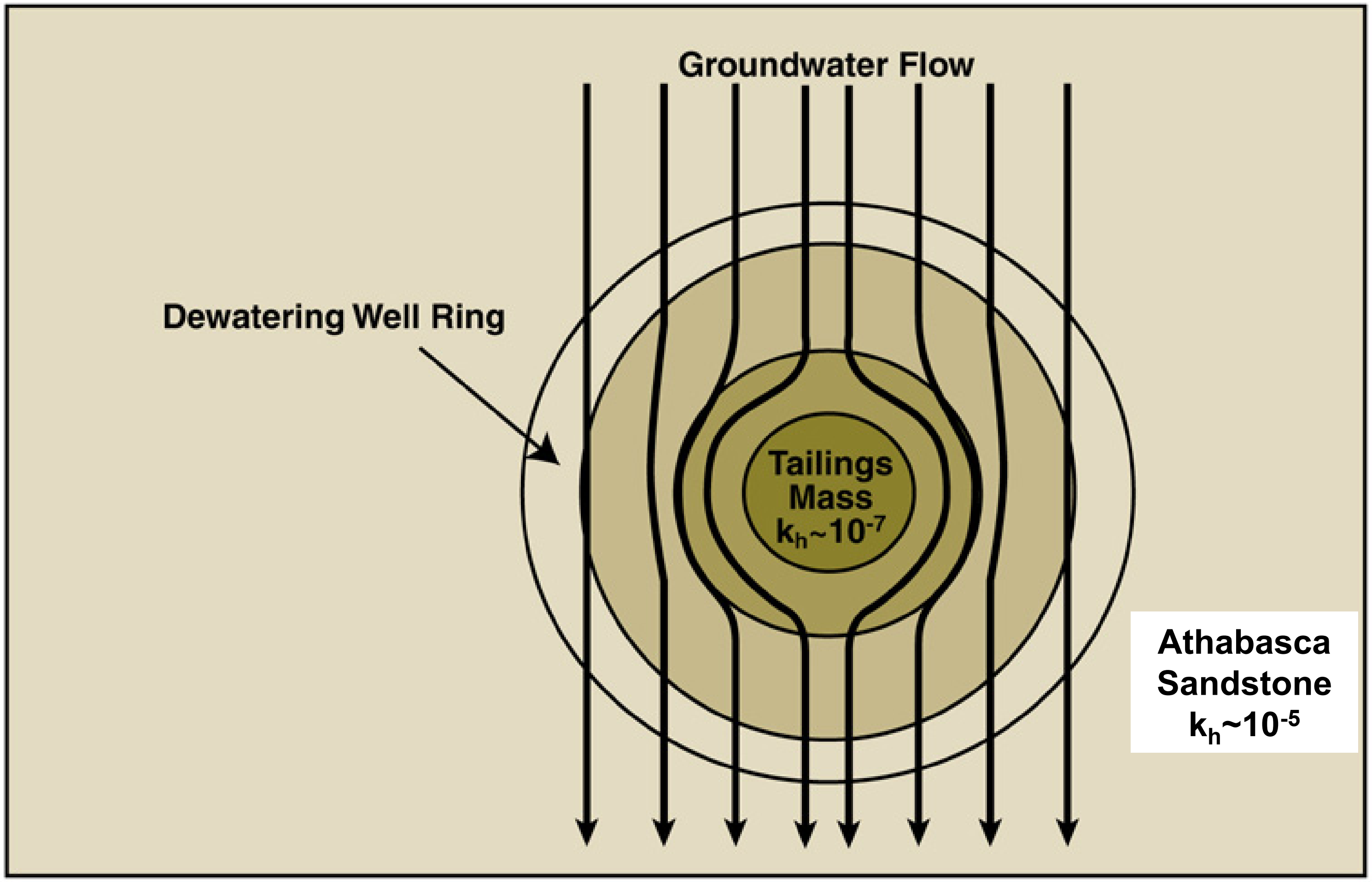
Ore Body	**As Content** (µg/g)
JEB	9,100
Sue C	300
Sue A	6,000
Sue E	2,500
Sue B	6,000
Caribou	5,000
Midwest	43,000
Cigar Lake	25,700
McClean u/g	2,000

Post-Decommissioning Control of Solute Release to Groundwater System

- Two Passive Techniques
  - geotechnical – natural surround design: physical control of groundwater flow path around tailings mass.
  - geochemical – engineered tailings geochemistry: minimize and stabilize COC pore water concentrations in tailings solids.

Geotechnical

Plan View Depicting the Natural Surround Concept

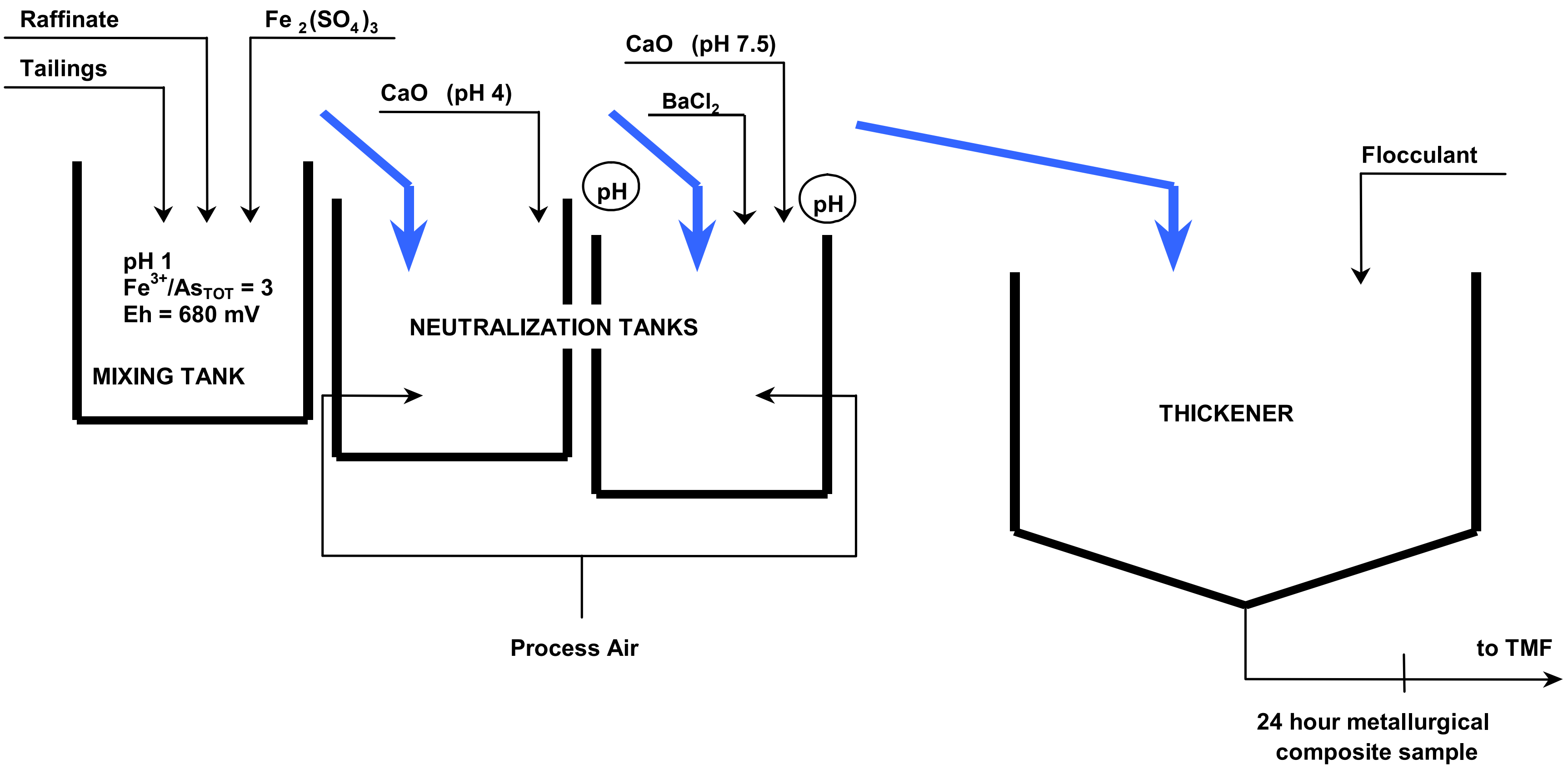


Geochemical

Engineered Tailings Geochemistry Concept

- Design
  - precipitate arsenic with ferric iron at low pH
  - the ferric arsenate precipitate produced is a poorly crystalline form of the mineral scorodite – $FeAsO_4 \cdot 2H_2O$
  - near neutral discharge pH from tailings preparation process
  - arsenic pore water concentration constant, controlled by K_{sp}, and independent of arsenic content in ore

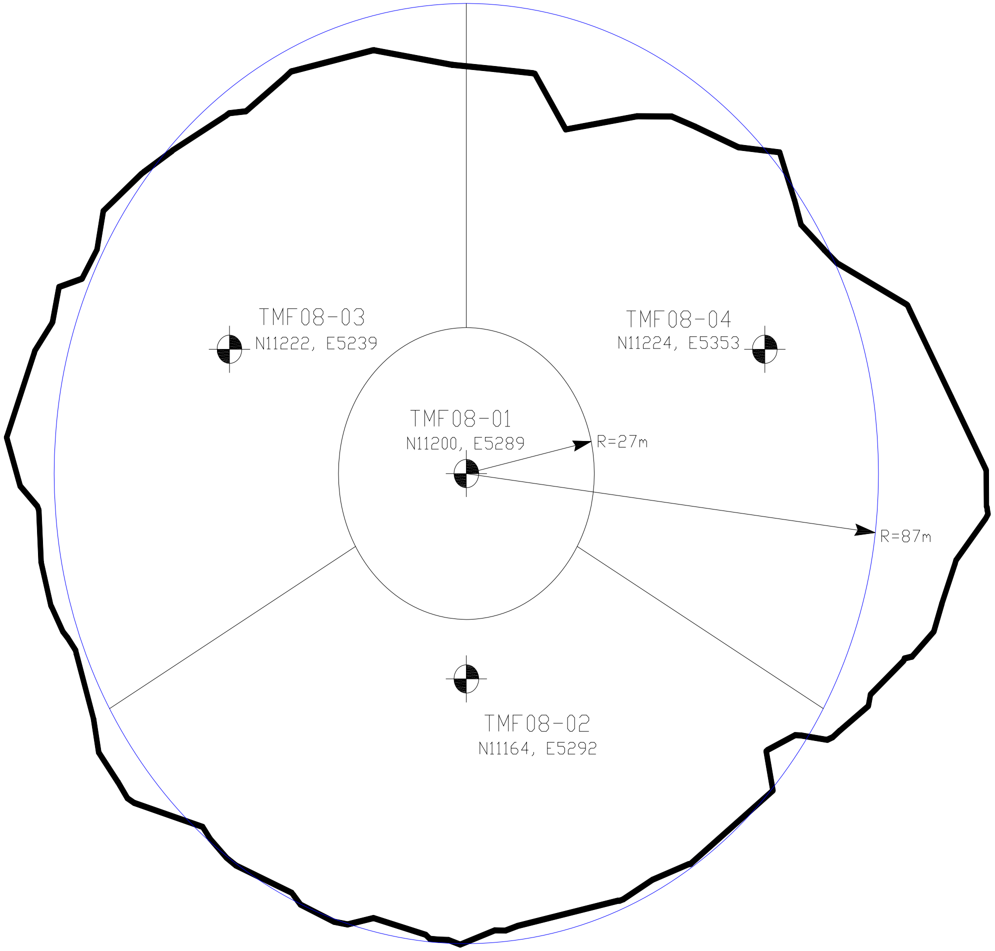
Tailings Preparation Process



TMF Performance

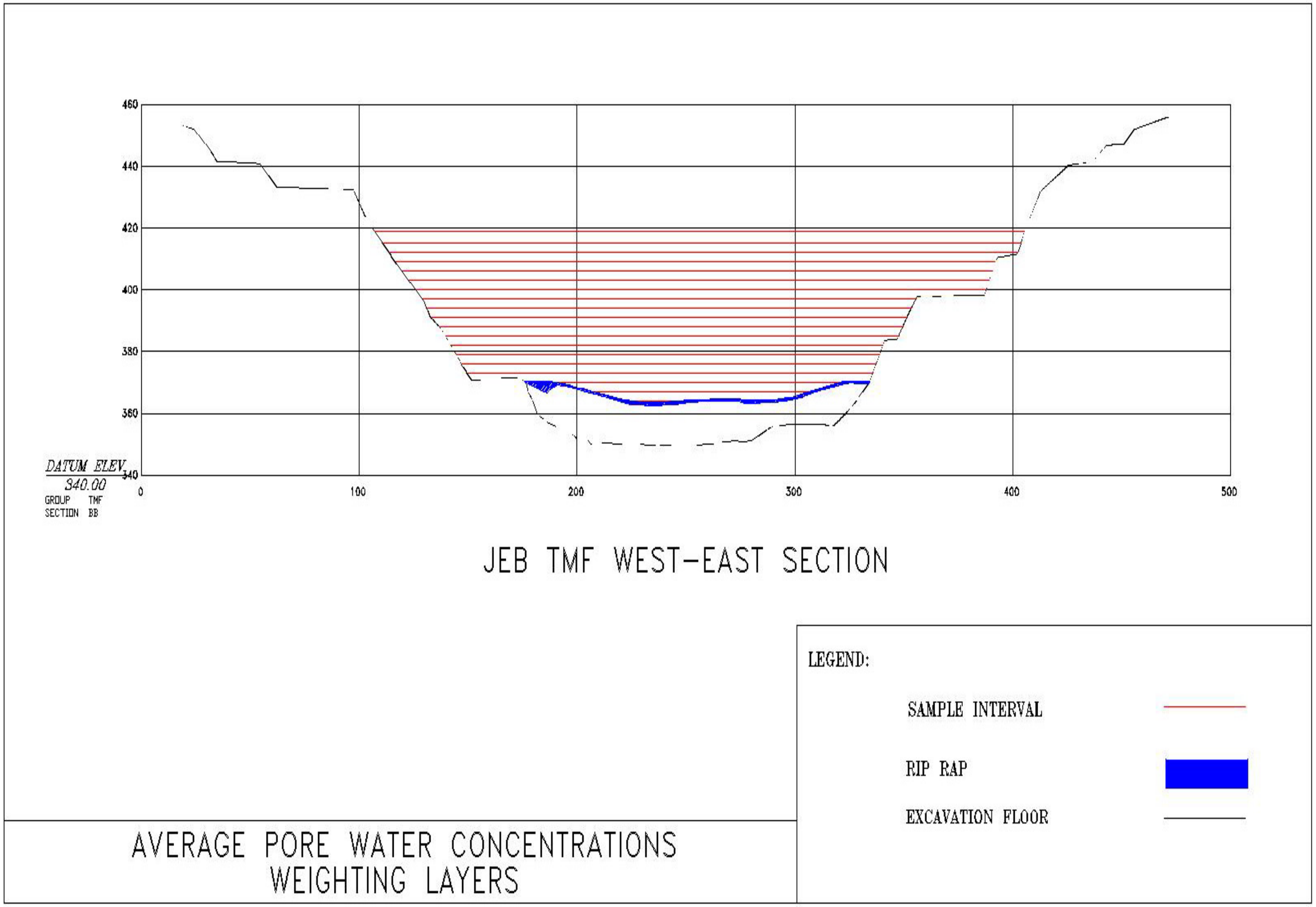
TMF Sampling

Average solute concentration volume weighting



TMF Sampling

Average Pore Water Solute Concentration



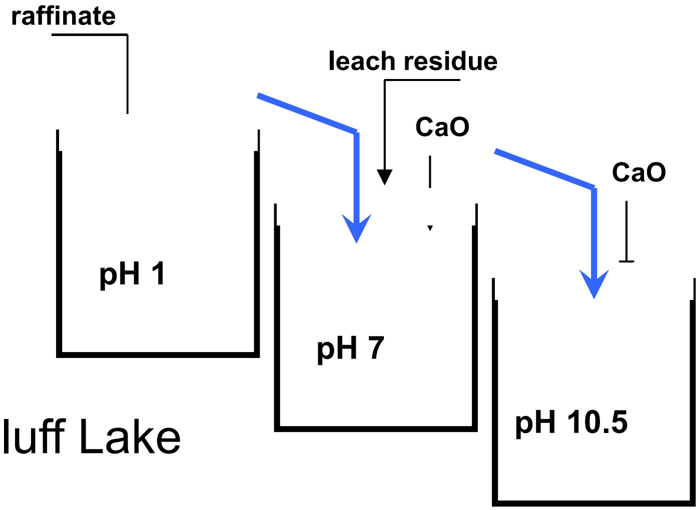
TMF Performance

TMF Sampling

TMF Performance

Control Mechanism

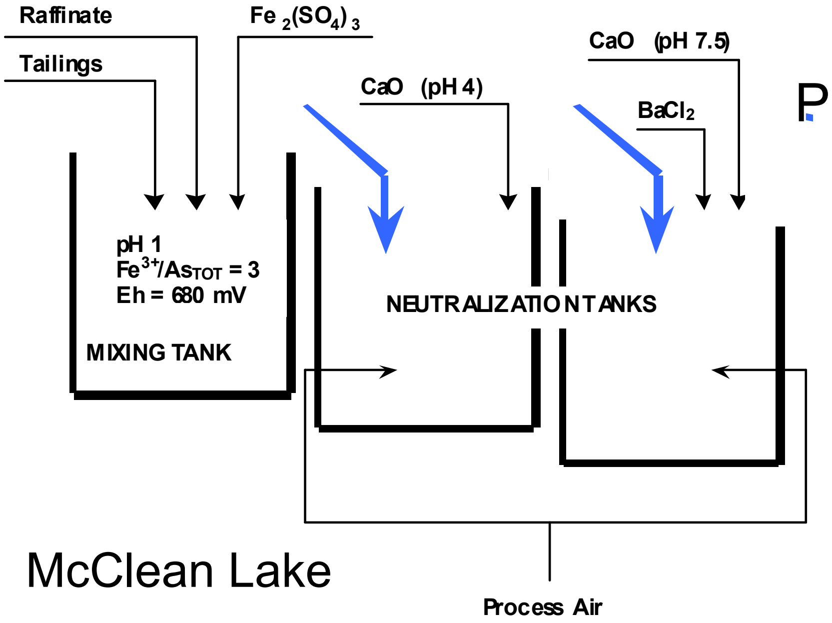
Precipitation VS Adsorption



Cluff Lake

Adsorption:

$$K_p \ \alpha \ \frac{[As]_{aq}}{[As]_{sed}}$$



McClean Lake

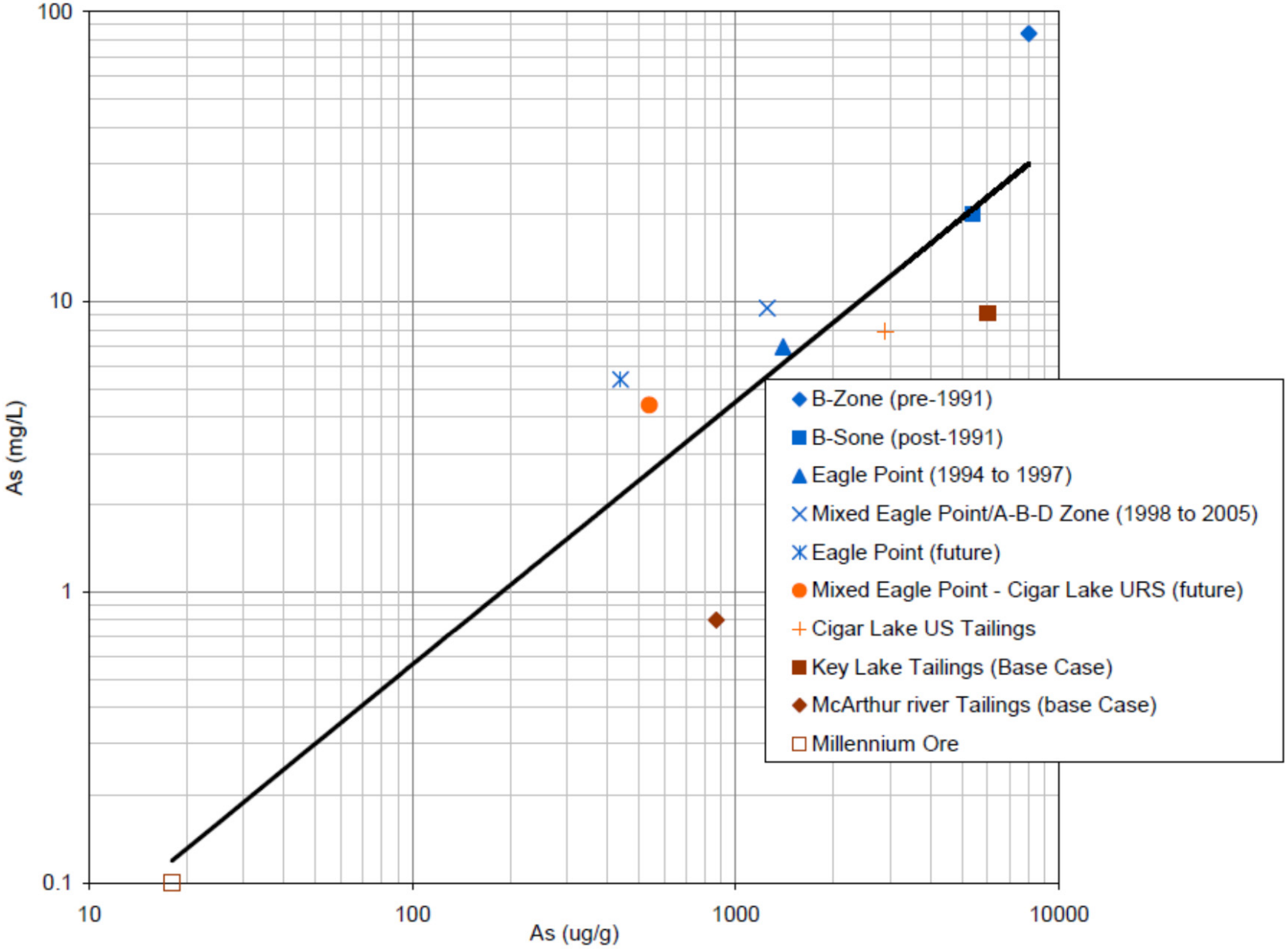
Precipitation:

(Scorodite)

$$K_{sp} \ \alpha \ [Fe^{3+}]_{aq} \, [AsO_4^{3-}]_{aq}$$

TMF Performance

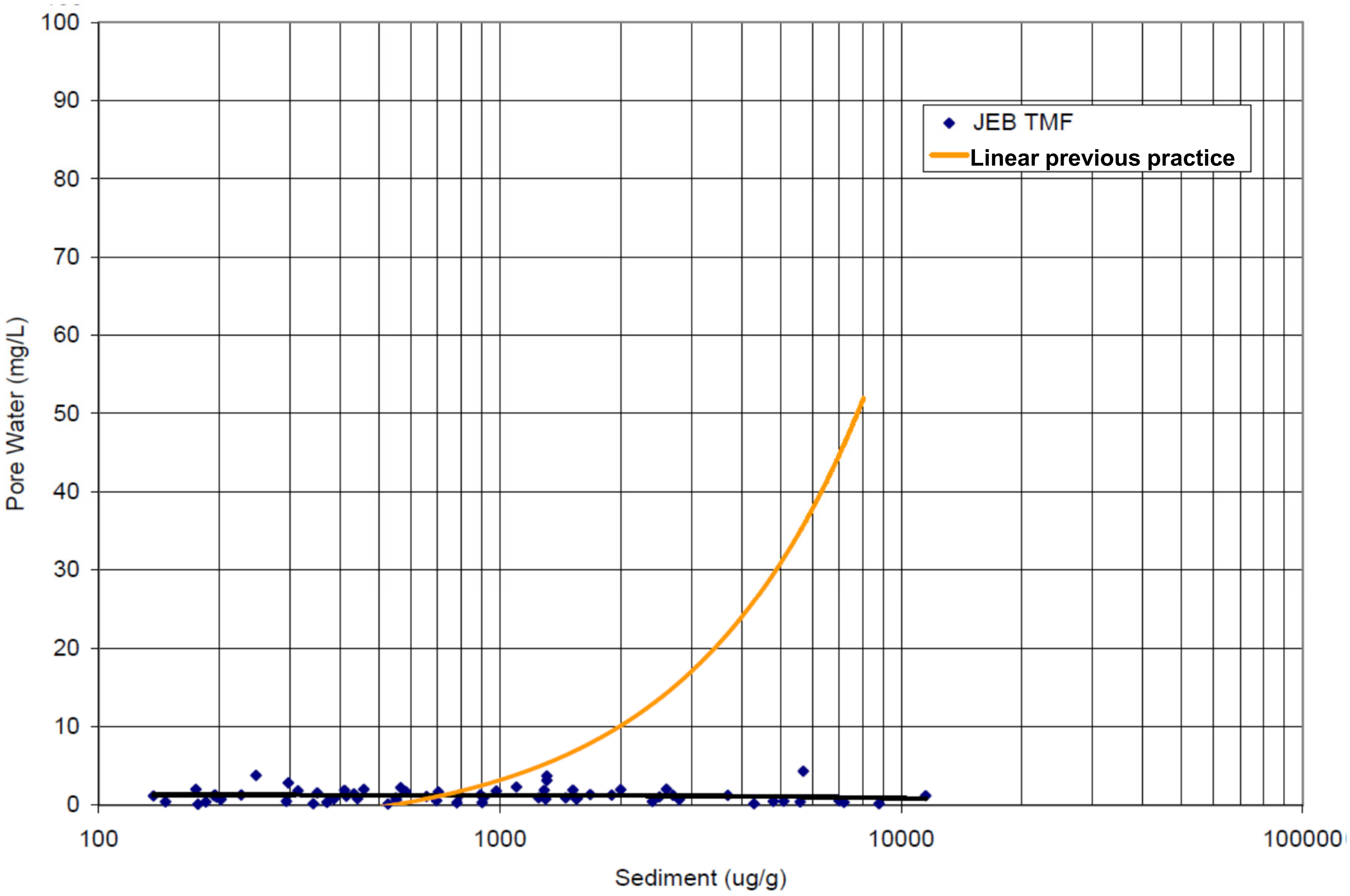
As in Tailings Pore Water vs Total As Content of Solids



TMF Performance

JEB TMF

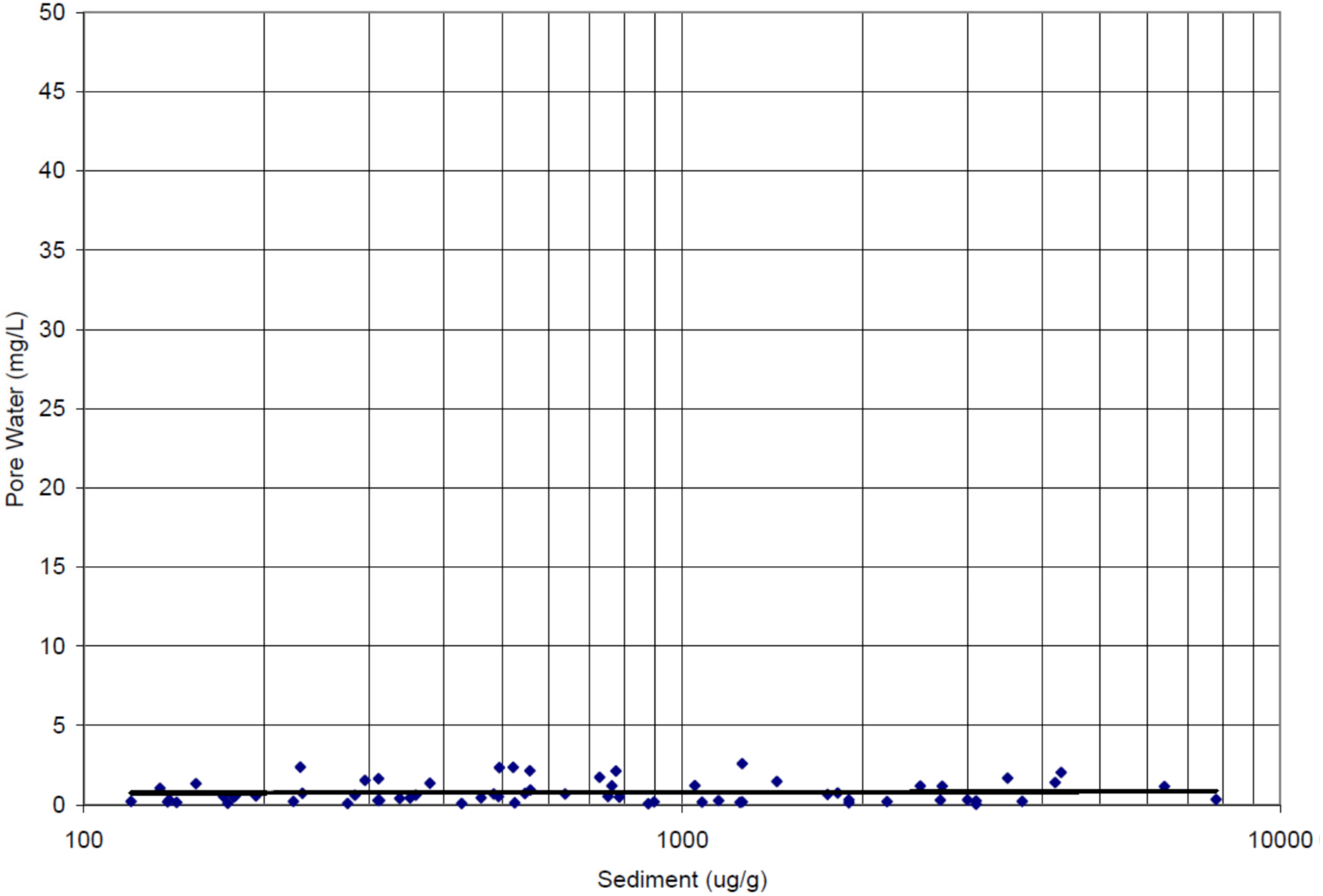
2008 JEB TMF Tailings Pore Water As^{5+} (mg/L) vs Sediment As (ug/g)



TMF Performance

JEB TMF

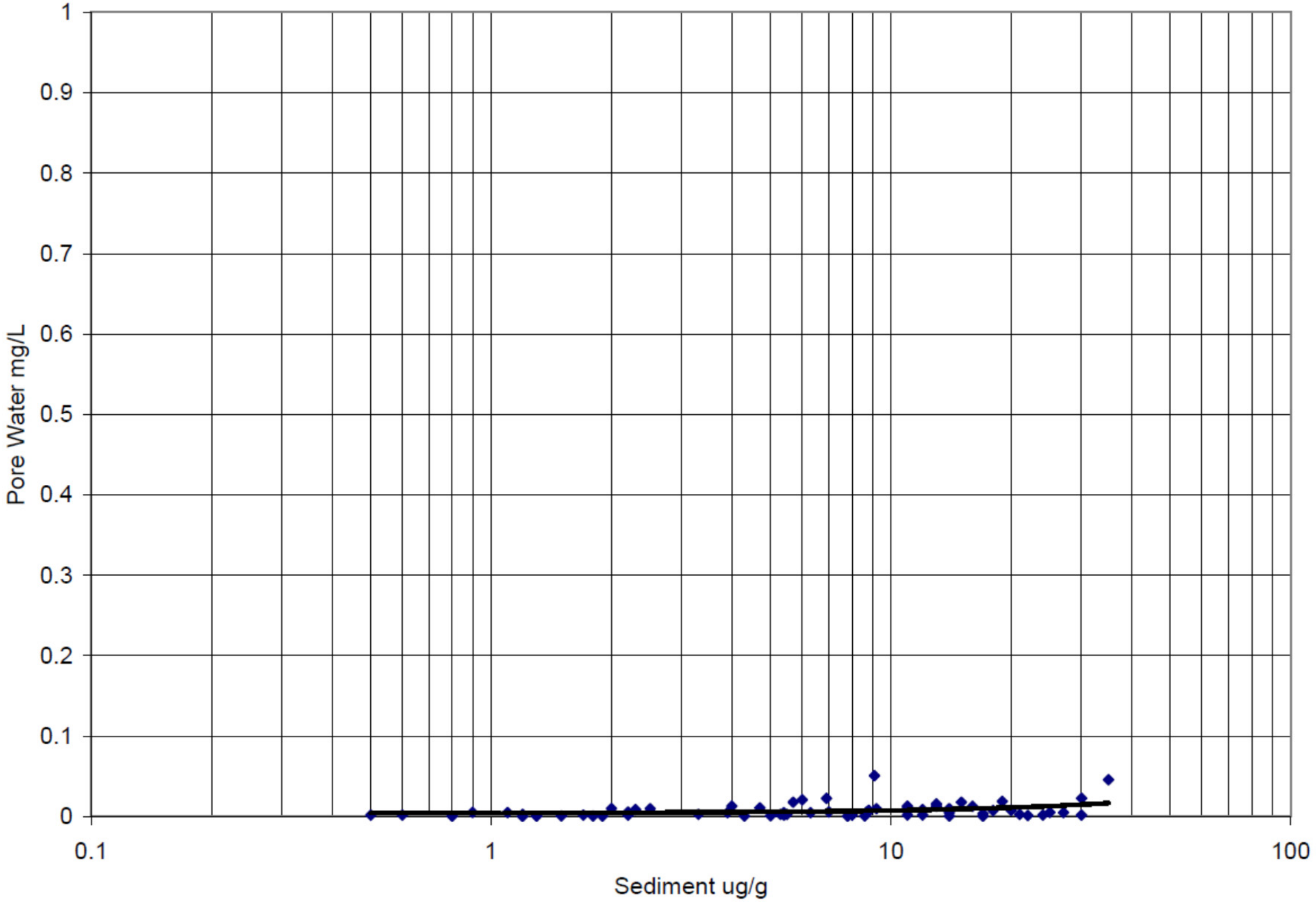
2008 JEB TMF Tailings Pore Water Ni (mg/L) vs Sediment Ni (ug/g)



TMF Performance

JEB TMF

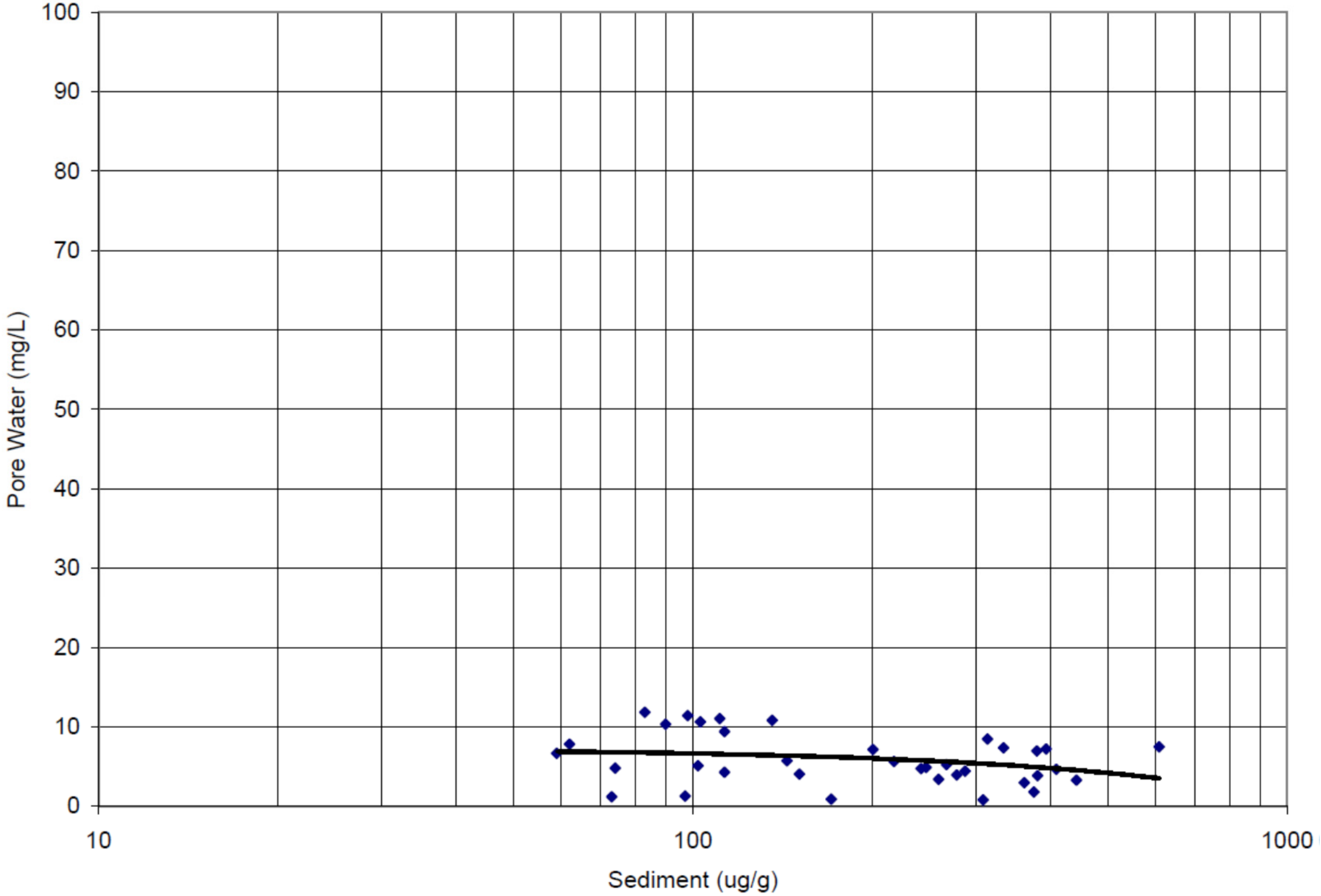
JEB TMF Tailings Pore Water Se (mg/L) vs Sediment Se (ug/g)



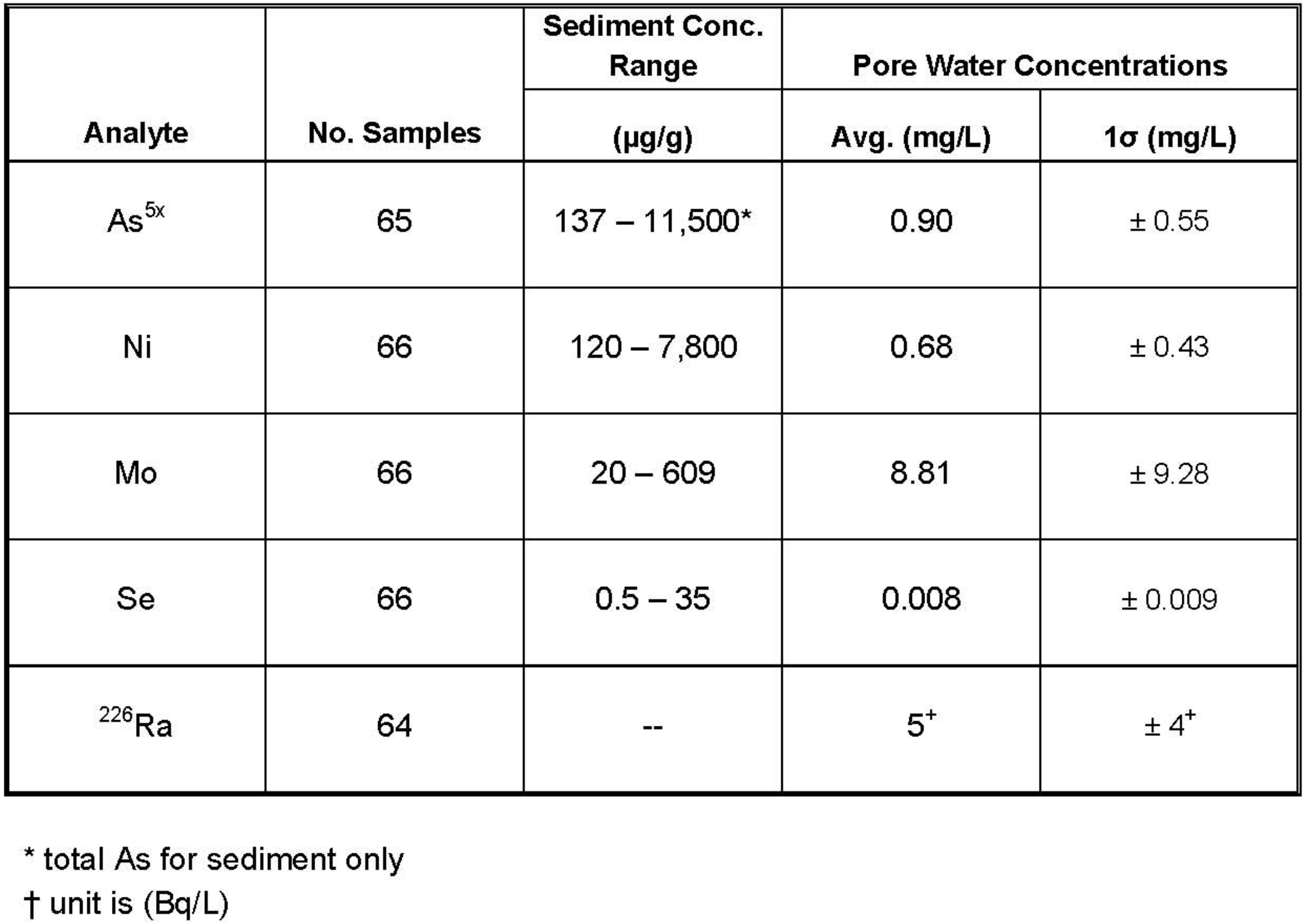
TMF Performance

JEB TMF

2008 JEB TMF Tailings Pore Water Mo (mg/L) vs Sediment Mo (ug/g)



JEB TMF
COC Pore Water Concentrations



Analyte	No. Samples	Sediment Conc. Range (µg/g)	Pore Water Concentrations Avg. (mg/L)	1σ (mg/L)
As^{5x}	65	137 – 11,500*	0.90	± 0.55
Ni	66	120 – 7,800	0.68	± 0.43
Mo	66	20 – 609	8.81	± 9.28
Se	66	0.5 – 35	0.008	± 0.009
^{226}Ra	64	--	5^{+}	± 4^{+}

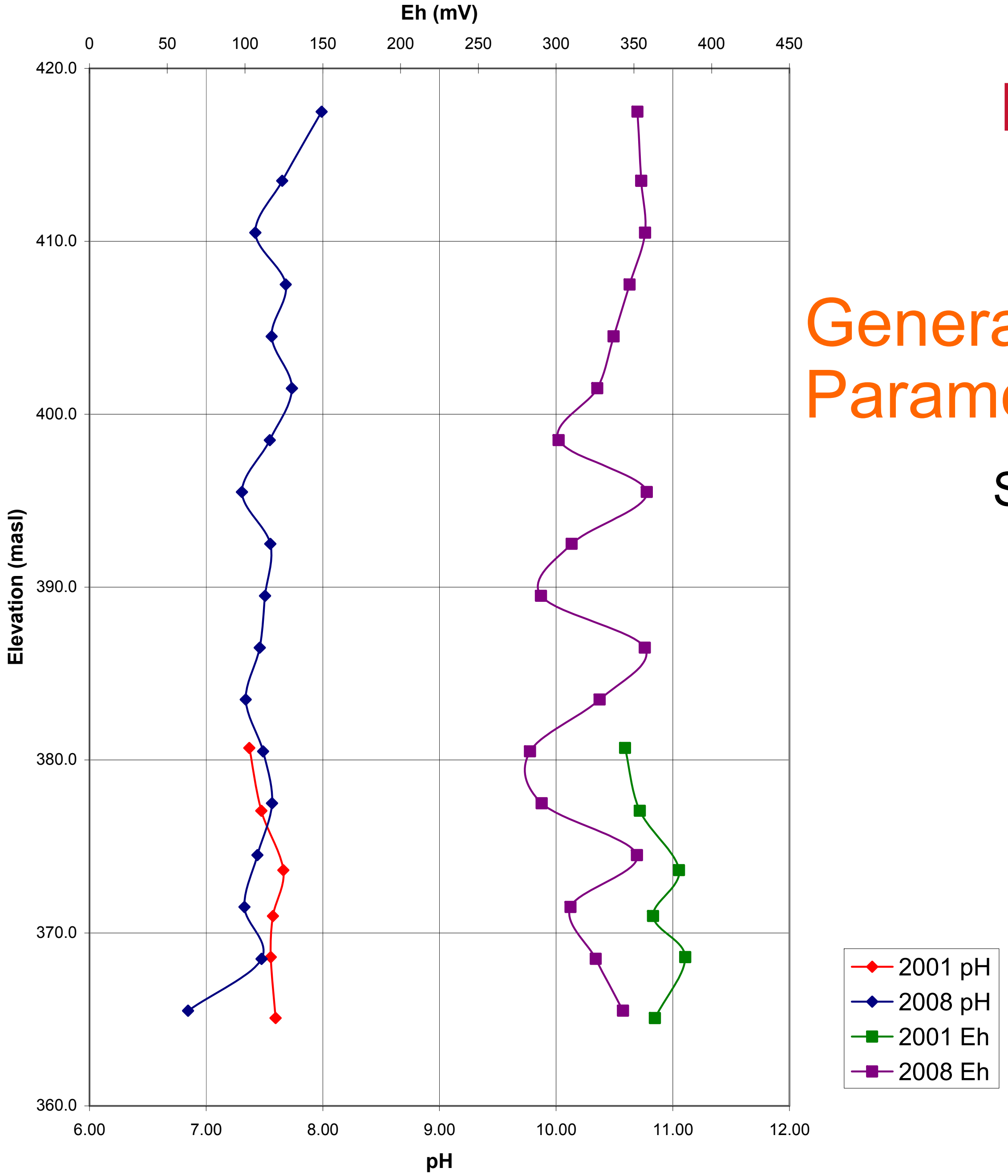
* total As for sediment only

† unit is (Bq/L)

TMF In Situ Monitoring and Sampling

General Water Quality Parameters

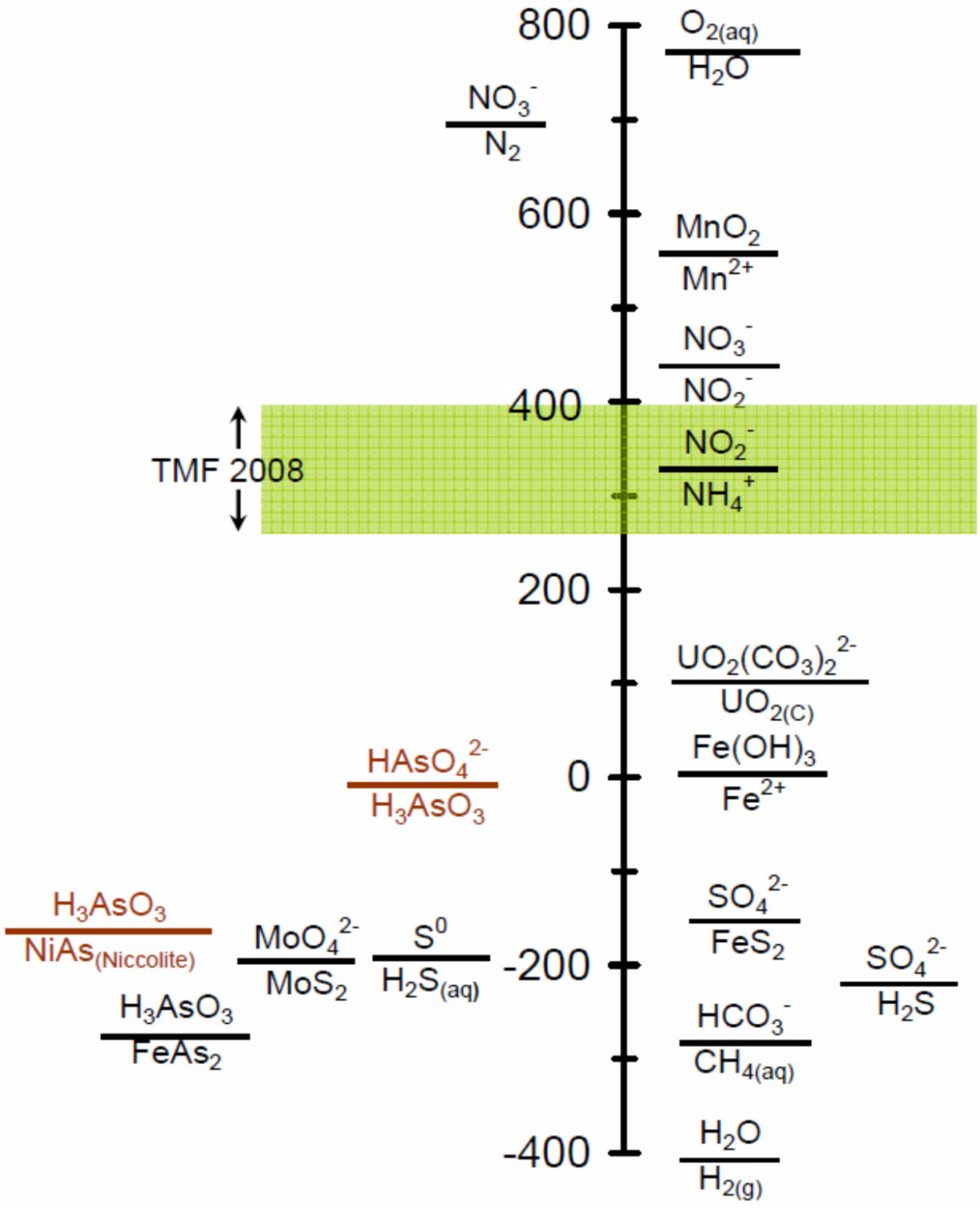
Sample Elevation vs pH and Eh



TMF In Situ Monitoring and Sampling

Current Redox Conditions

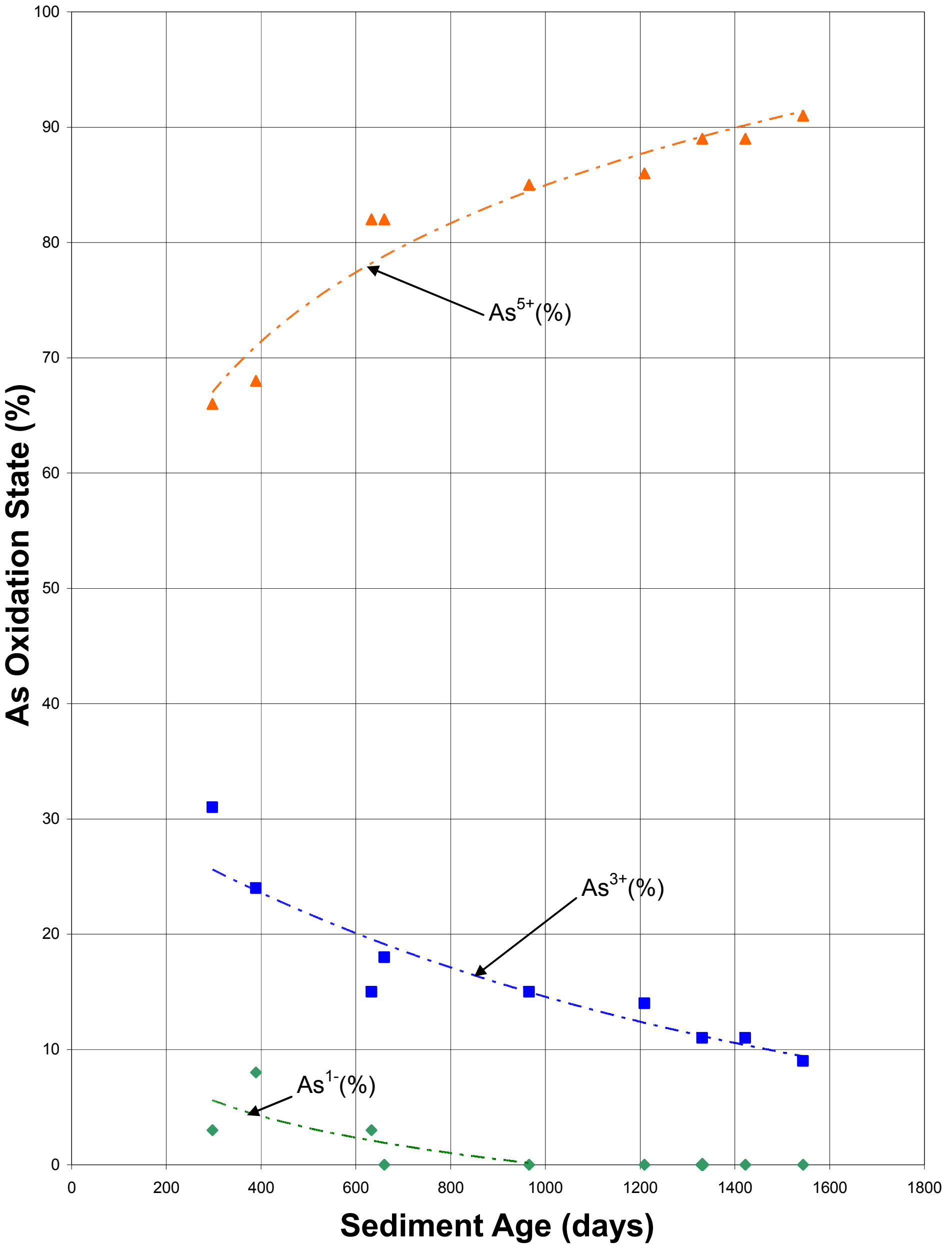
Eh Ladder



Laboratory Studies

Arsenic Geochemical Model

Relative As Oxidation State in Sediment vs Sediment Age



Laboratory Studies

Arsenic Geochemical Model

- Tailings sediments contain small residual amounts of primary arsenic bearing minerals – niccolite (NiAs) rammelsbergite ($NiAs_2$) and gersdorfite (NiAsS)
- These reduced minerals are not stable in the TMF and must oxidize
- Oxidation of arsenides to stable arsenates occurs through a two step process: As^{1-} to As^{3+} and As^{3+} to As^{5+}

AREVA

Arsenic Geochemical Model

First Oxidation Step

$$\overset{[As^{1-}]}{\underset{\text{(niccolite)}}{NiAs\downarrow}} + 5\,Fe^{3+} + 3H_2O \rightarrow \overset{[As^{3+}]}{H_3AsO_3^{o}} + Fe^{2+} + Ni^{2+} + 3H^+$$

$$H_3AsO_3^{o} \rightarrow \underset{\text{(claudite)}}{As_2O_3\downarrow} + 3H_2O$$

Arsenic Geochemical Model

Second Oxidation Step

$$\underset{[As^{3+}]}{H_3AsO_3^{o}} + 2Fe^{3+} + H_2O \rightarrow \underset{[As^{5+}]}{HAsO_4^{2-}} + 2Fe^{2+} + 4H^+$$

$$HAsO_4^{2-} + Fe^{3+} + 2H_2O \rightarrow \underset{\text{(scorodite)}}{FeAsO_4 \cdot 2H_2O} \downarrow + H^+$$

- Second oxidation step is rate limiting

Arsenic Geochemical Model

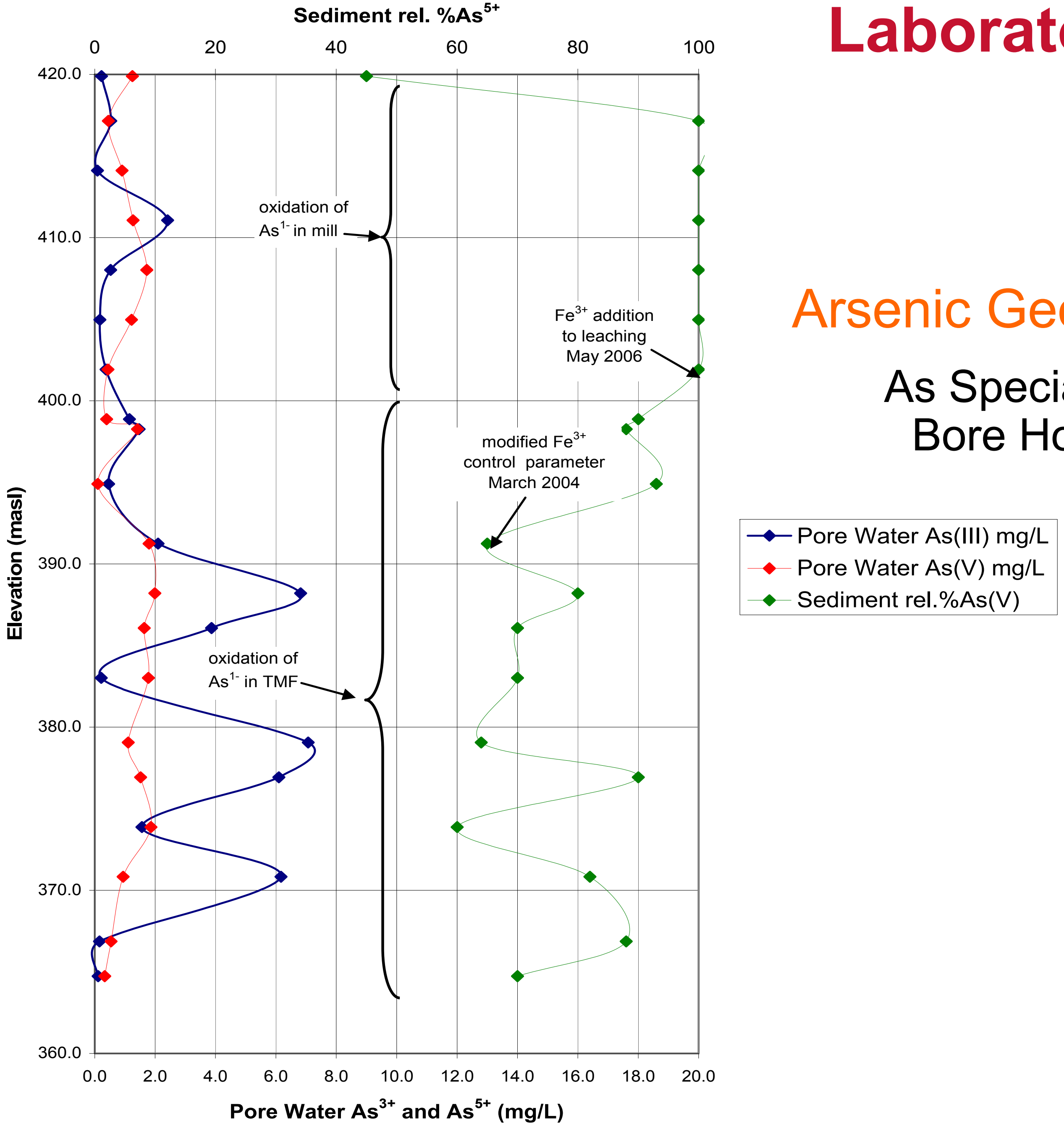
Overall Reaction

[As^{1-}] [As^{5+}]

$$\underset{\text{(niccolite)}}{NiAs} + 8Fe^{3+} + 6\ H_2O \rightarrow \underset{\text{(scorodite)}}{FeAsO_4 \cdot 2H_2O}\downarrow + 7Fe^{3+} + Ni^{2+} + 8H^+$$

- In the TMF, reactions occur very slowly (over 3 to 4 years) due to a lack of mixing and low L/S ratio
- Anticipate As^{3+} pore water concentrations to initially rise then fall to near zero after the As^{1-} content in the sediment is depleted
- As^{5+} pore water concentrations should remain constant

Laboratory Studies



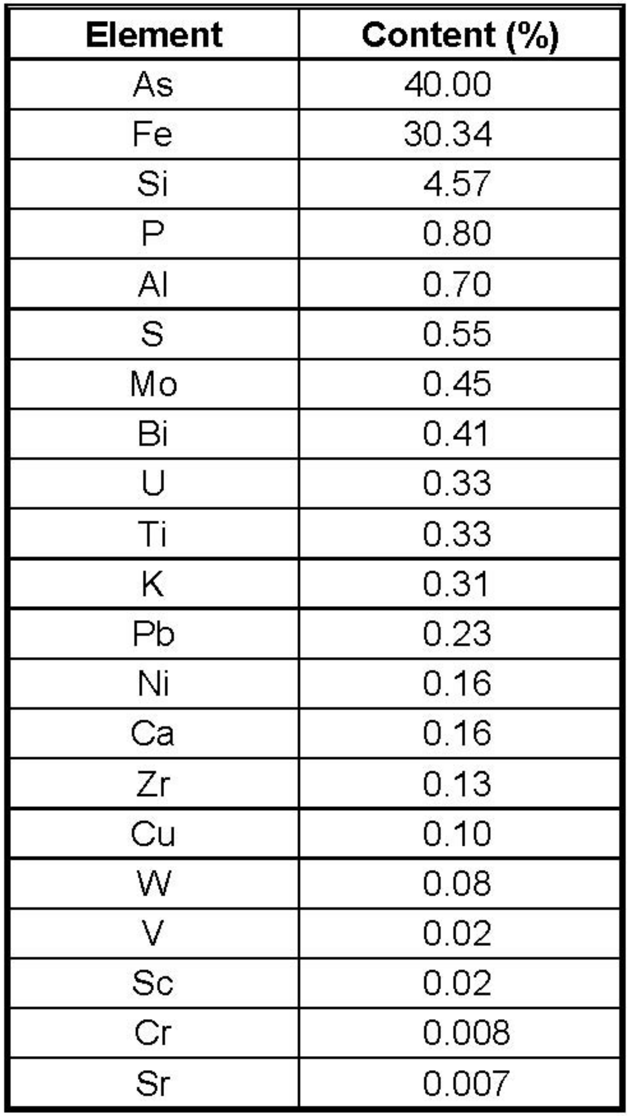
Arsenic Geochemical Model

As Speciation Data for Bore Hole TMF08-01

Laboratory Studies

Photograph of Scorodite Scale from Leaching Process Reactor Tank

Laboratory Studies

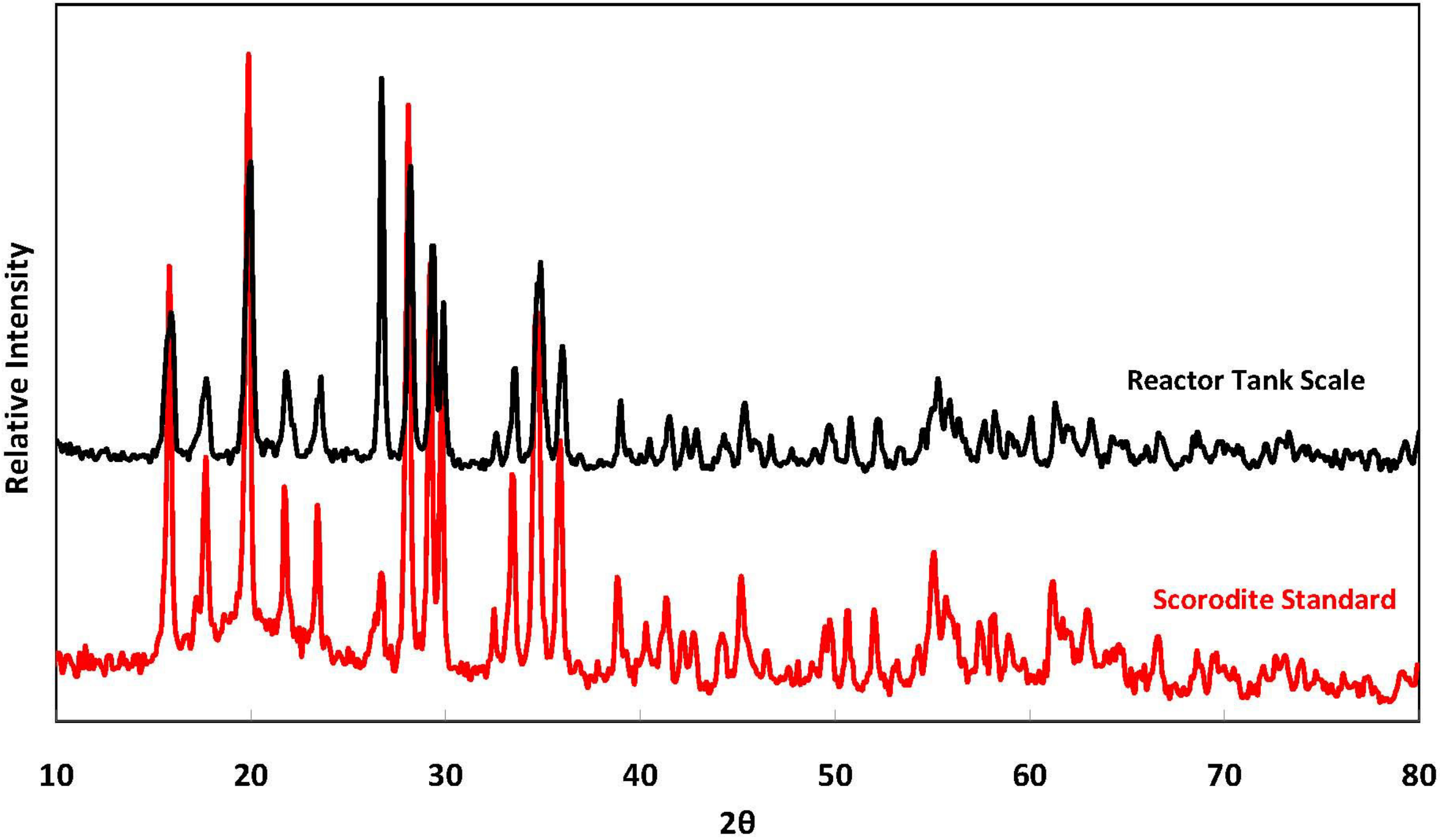


Element	Content (%)
As	40.00
Fe	30.34
Si	4.57
P	0.80
Al	0.70
S	0.55
Mo	0.45
Bi	0.41
U	0.33
Ti	0.33
K	0.31
Pb	0.23
Ni	0.16
Ca	0.16
Zr	0.13
Cu	0.10
W	0.08
V	0.02
Sc	0.02
Cr	0.008
Sr	0.007

Chemical Analysis of Scale from #5 Secondary Leach Vessel

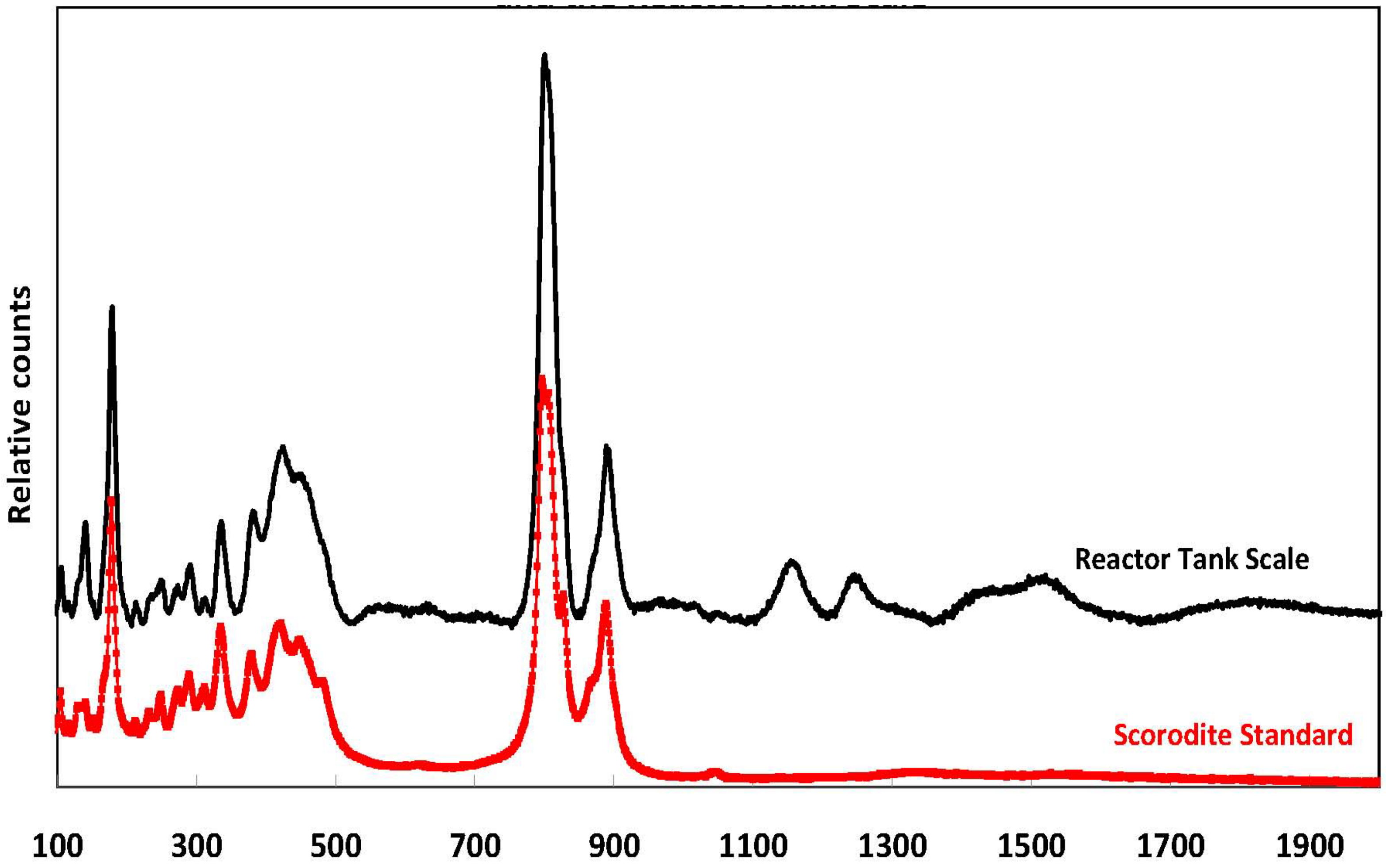
Laboratory Studies

Comparison of XRD patterns from Scorodite Standard and the Reactor Tank Scale



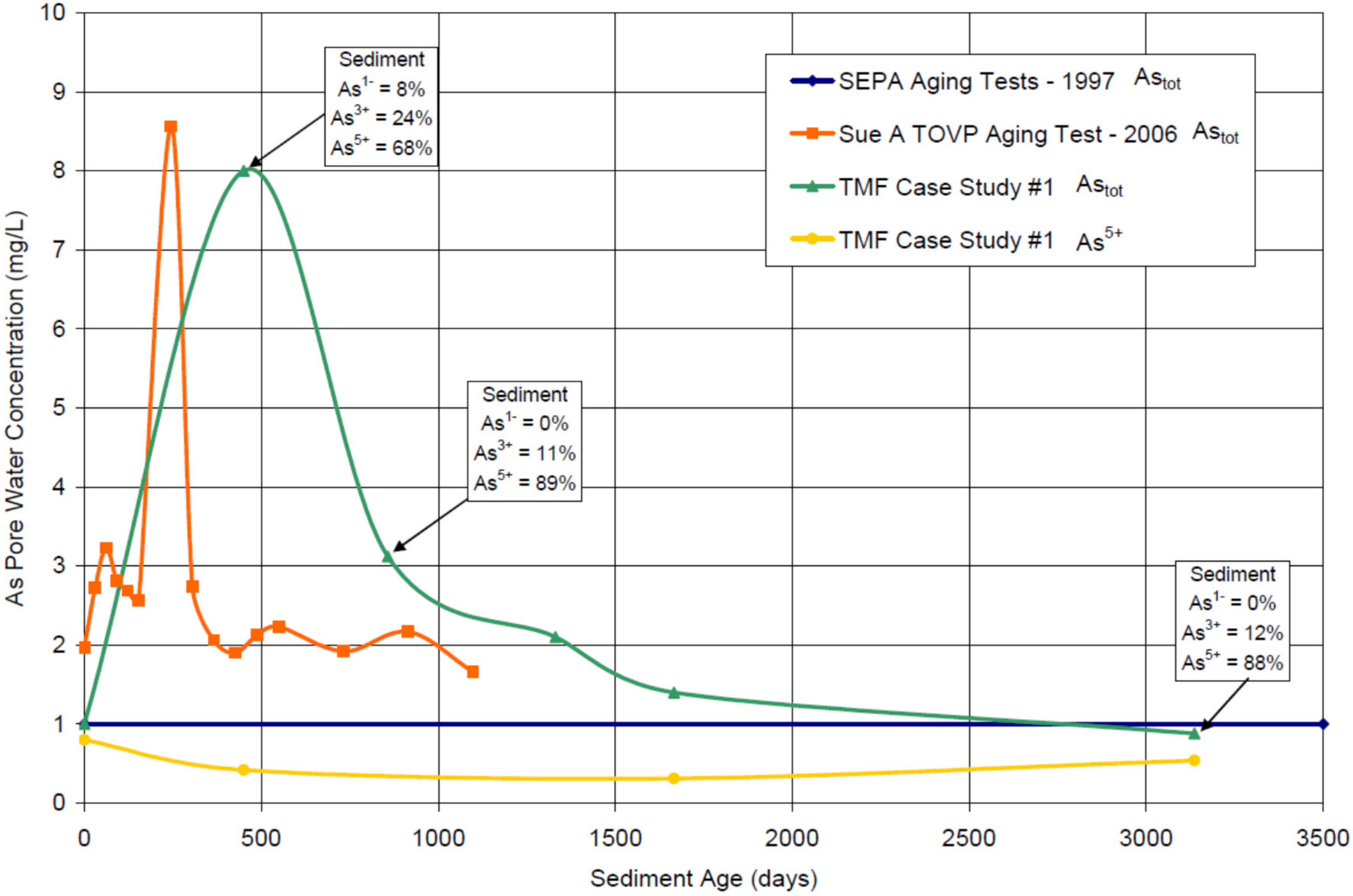
Laboratory Studies

Comparison of Raman Spectra from Scorodite Standard and the Reactor Tank Scale



Arsenic Geochemical Model

Comparison of [As] Observed in SEPA Aging, TOVP Aging and Actual Aging in the TMF



Sediment
As^{1-} = 8%
As^{3+} = 24%
As^{5+} = 68%

Sediment
As^{1-} = 0%
As^{3+} = 11%
As^{5+} = 89%

Sediment
As^{1-} = 0%
As^{3+} = 12%
As^{5+} = 88%

HC Geochemical Model

- Small amounts of $HC_{11\text{-}20}$ absorb onto the surface of tailings solids and are deposited in the TMF
- Bacterial communities oxidize HC to soluble HCO_3^- following placement in the TMF
- HCO_3^- concentrations may reach saturation with calcite providing an upper bound HCO_3^- value

HC Geochemical Model

$CH_2O + O_2 \xrightarrow[\text{(bacteria)}]{} HCO_3^- + H^+$

$CaSO_4 \cdot 2H_2O\downarrow \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

(gypsum)

$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3\downarrow + H_2O$

(calcite)

HC Geochemical Model

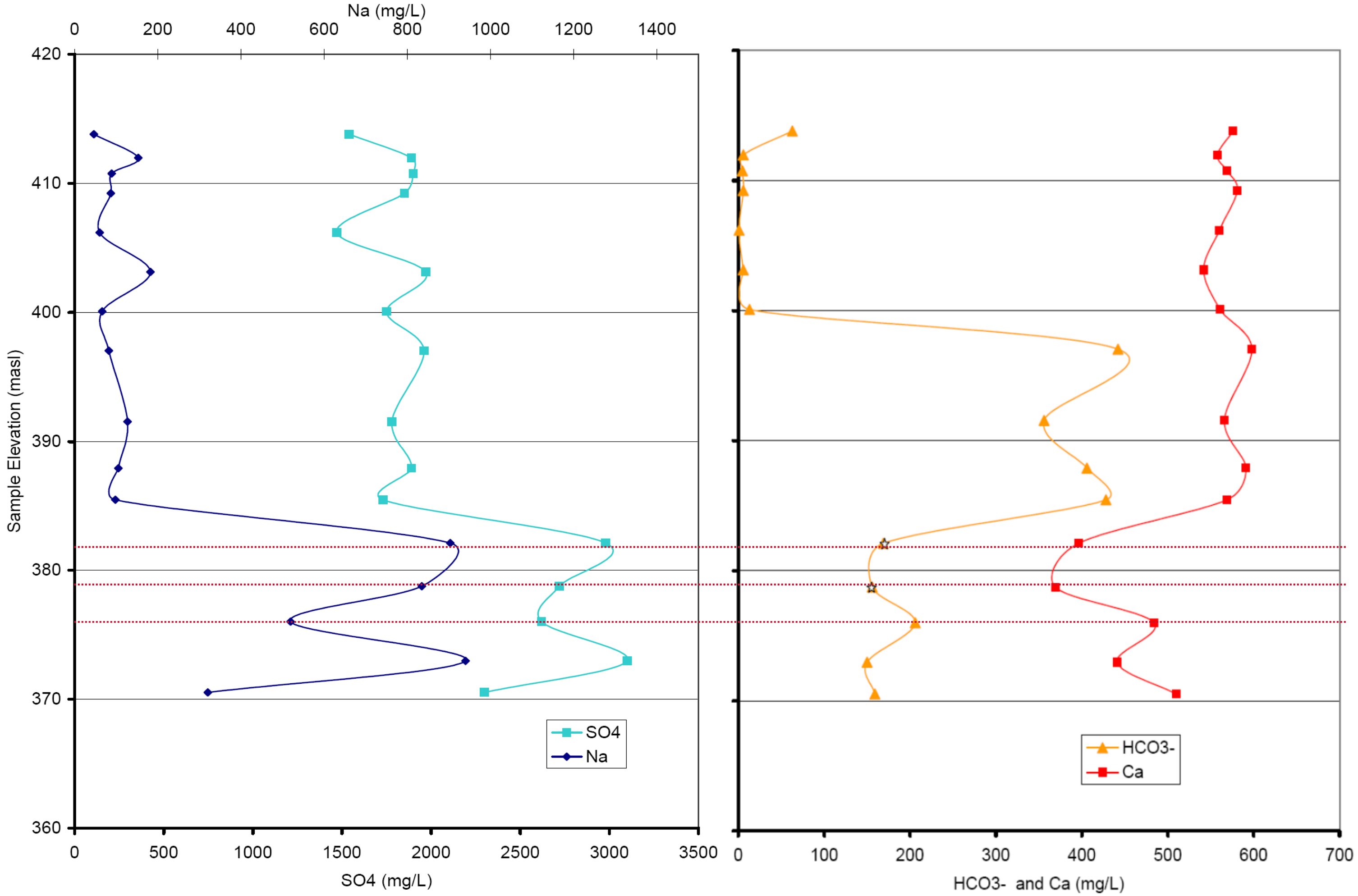
Overall Reaction

$$\underset{\text{(gypsum)}}{CaSO_4{\cdot}2H_2O\downarrow} + HCO_3^- + OH^- \rightarrow \underset{\text{(calcite)}}{CaCO_3\downarrow} + SO_4^{2-} + 3H_2O$$

- The reaction proceeds very slowly due to a lack of mixing and low L/S ratio
- HCO_3^- can accumulate prior to the precipitation of calcite
- Expected evidence of the occurrence of this reaction in the TMF includes controlled HCO_3^- concentrations, temporarily depressed Ca^{2+} concentrations, and rising SO_4^{2-} and Na^+ values

HC Geochemical Model

Major Ion Pore Water Concentrations in TMF08-03 Indicating Calcite Precipitation below 384 masl

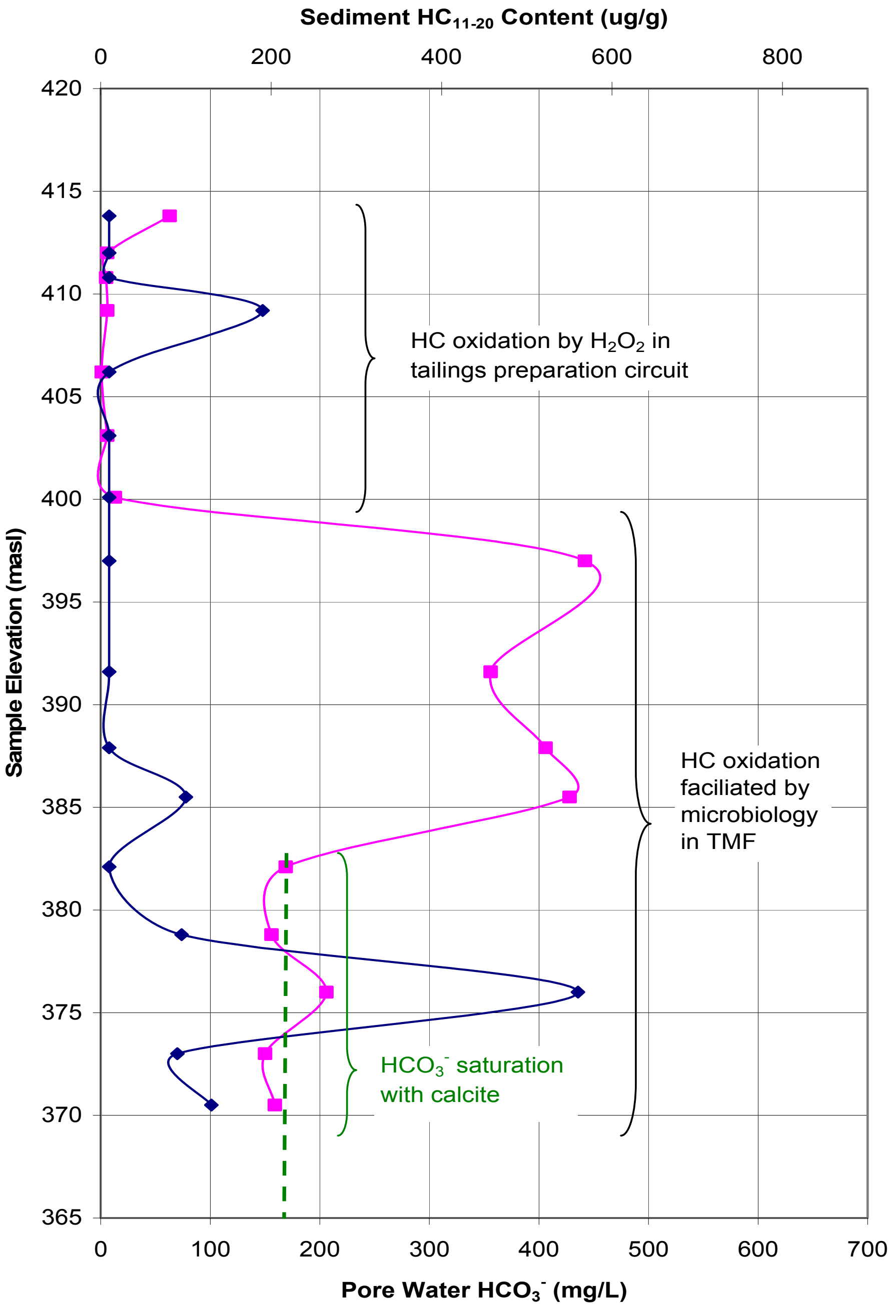


*** indicates values extrapolated from charge balances**

Laboratory Studies

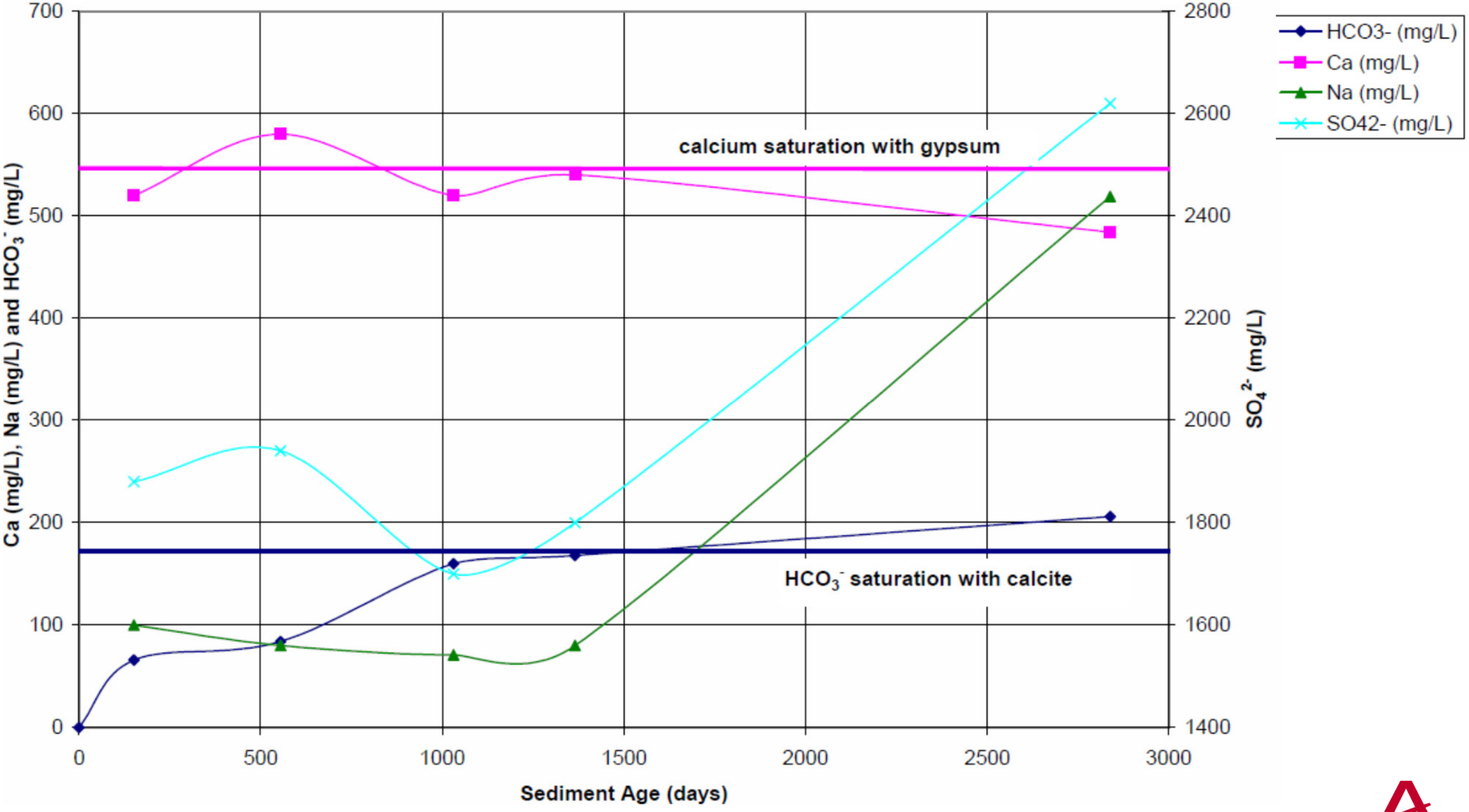
HC Geochemical Model

Sample Elevation vs Sediment $HC_{11\text{-}20}$ (ug/g) and Pore Water HCO_3^-(mg/L) for Bore Hole TMF08-03



HC Geochemical Model

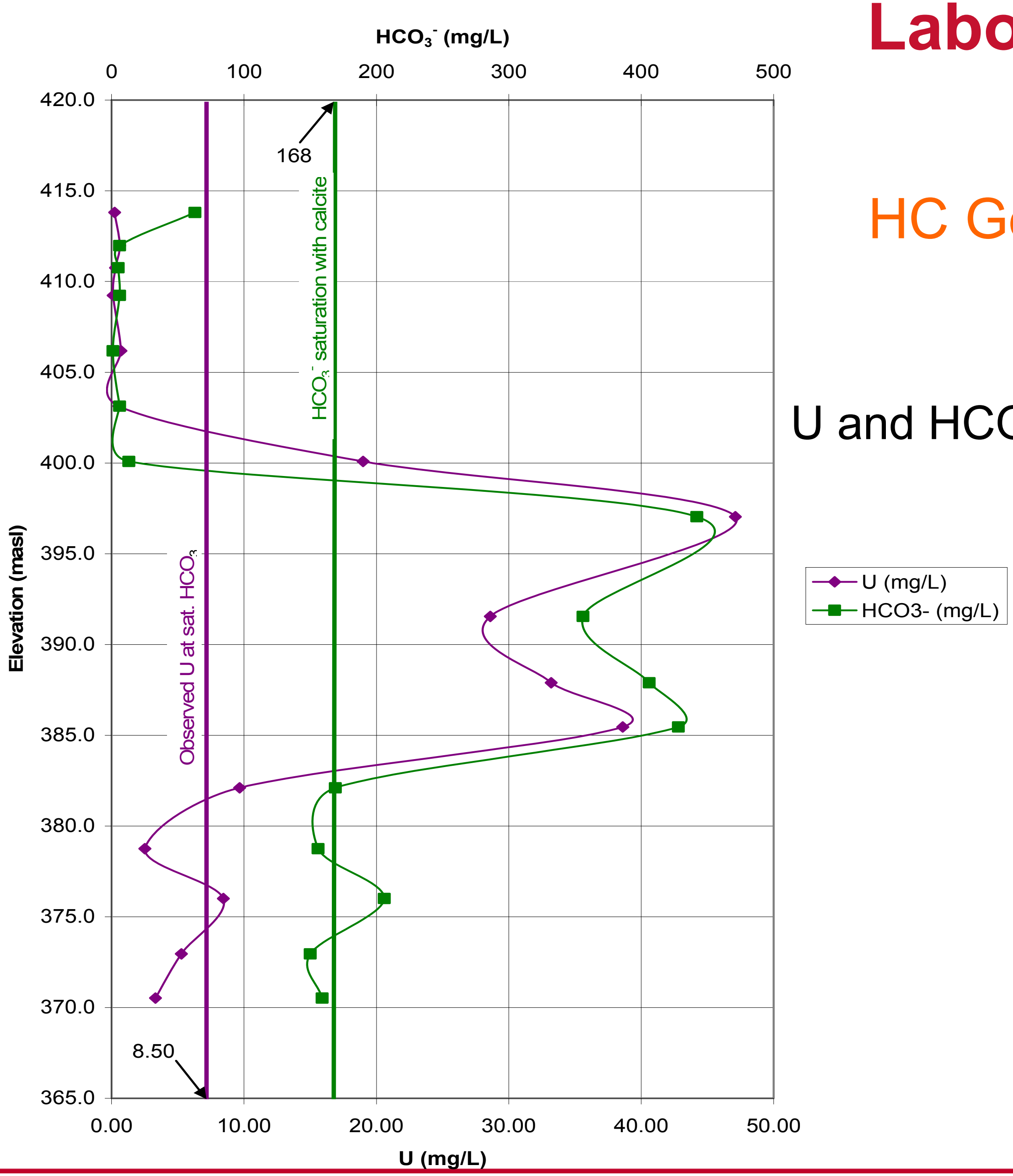
Calcite Formation in Lower Tailings Containing 560ug/g Residual HC, TMF08-03 SA-14 376.0 masl



Laboratory Studies

HC Geochemical Model

U and HCO_3^- in Bore Hole TMF08-03

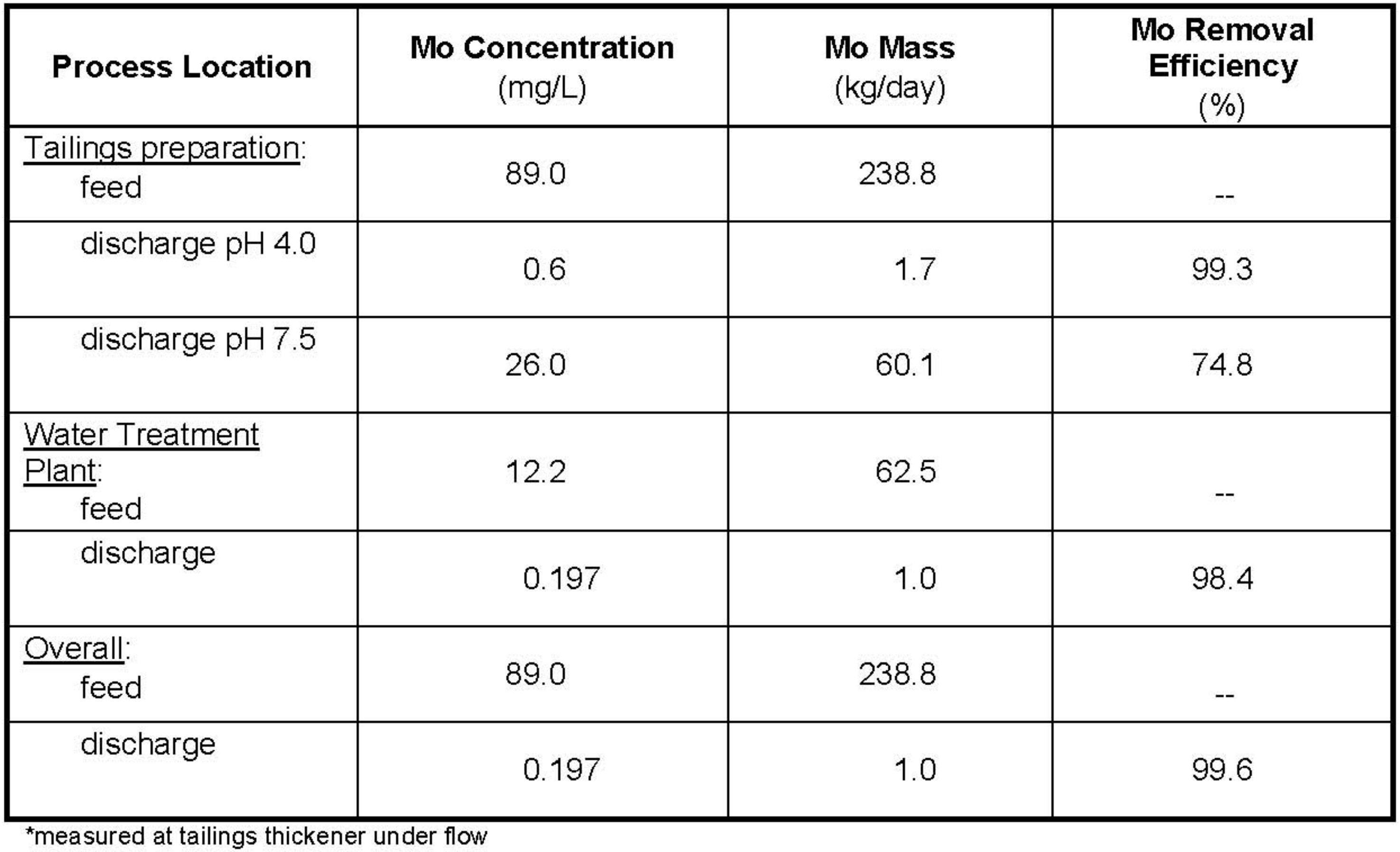


Mo Geochemical Model

- MoO_4^{2-} precipitates with Fe^{3+} at pH 4 potentially as the mineral ferrimolybdite in the tailings preparation process
- At the terminal pH of 7.5, ferrimolybdite begins to re-dissolve
- After disposal in the TMF the dissolution continues to completion
- Rising MoO_4^{2-} values reach saturation with powellite providing a long term Mo concentration upper bound

Mo Geochemical Model

Overall Waste Water Management Mo Mass Balance for McClean Lake Operation January to October 2004.



Process Location	**Mo Concentration** (mg/L)	**Mo Mass** (kg/day)	**Mo Removal Efficiency** (%)
Tailings preparation: feed	89.0	238.8	--
discharge pH 4.0	0.6	1.7	99.3
discharge pH 7.5	26.0	60.1	74.8
Water Treatment Plant: feed	12.2	62.5	--
discharge	0.197	1.0	98.4
Overall: feed	89.0	238.8	--
discharge	0.197	1.0	99.6

*measured at tailings thickener under flow

Mo Geochemical Model

$$Fe_2(MoO_4)_3 \cdot 6H_2O\downarrow \rightarrow 3MoO_4^{2-} + 2Fe(OH)_3\downarrow + 6H^+$$

(ferrimolybdenite) (ferrihydrite)

$$CaSO_4 \cdot 2H_2O\downarrow \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

(gypsum)

$$Ca^{2+} + MoO_4^{2-} \rightarrow CaMoO_4\downarrow$$

(powellite)

Overall:

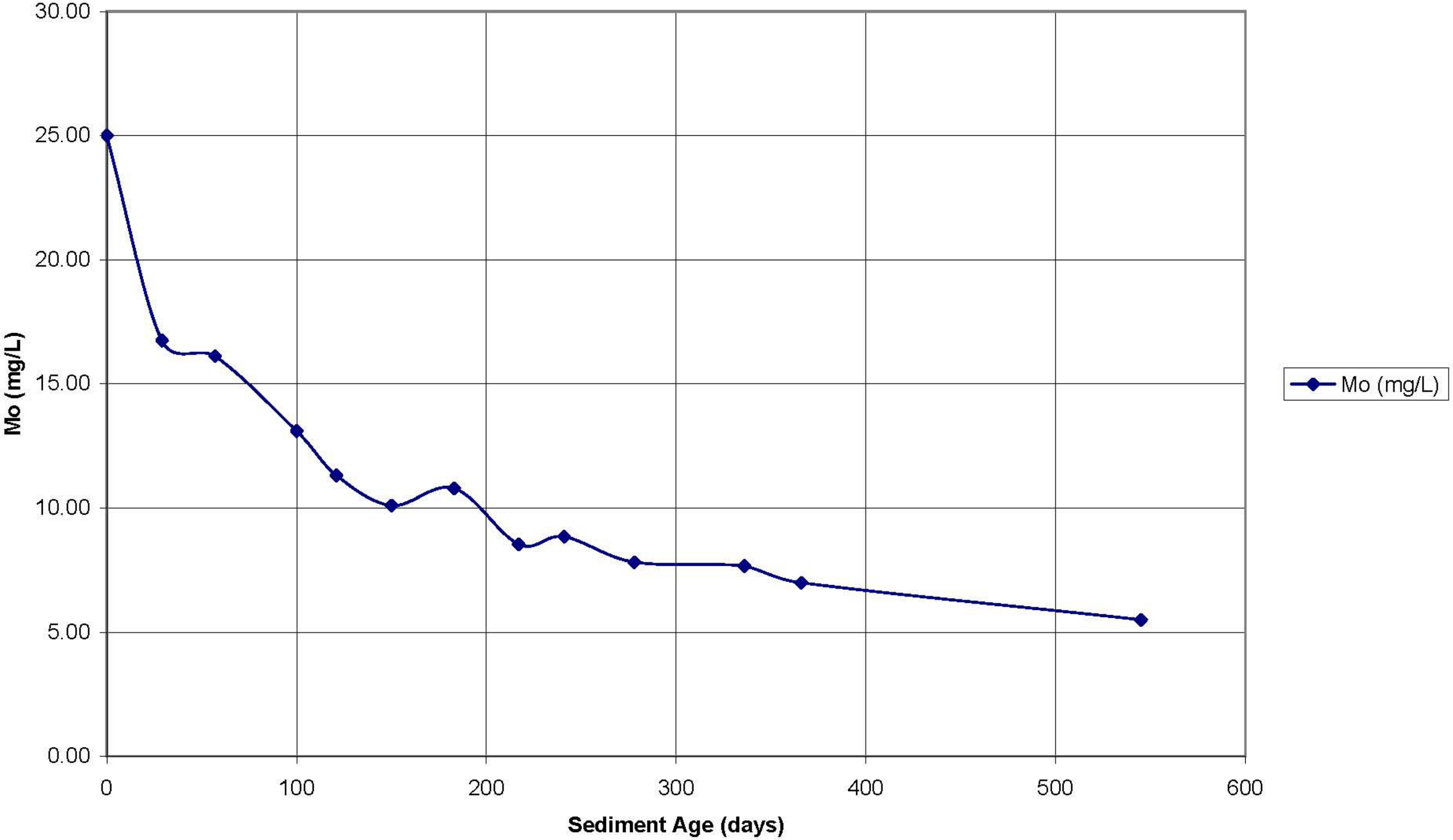
$$CaSO_4 \cdot 2H_2O\downarrow + MoO_4^{2-} \rightarrow CaMoO_4\downarrow + SO_4^{2-} + 2H_2O$$

(gypsum) (powellite)

Laboratory Studies

Mo TOVP Aging Test

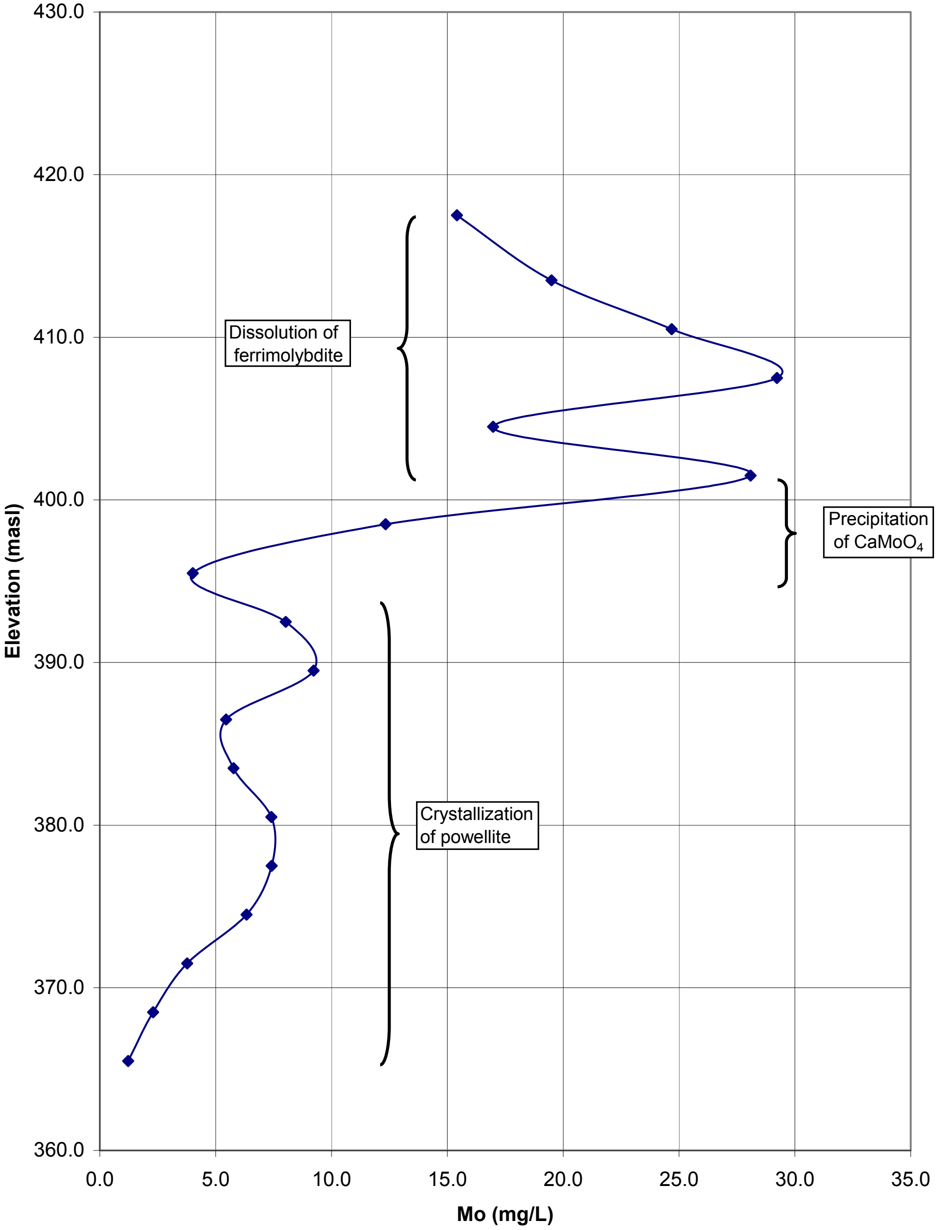
(Jan. 30, 2010 to July 29, 2011)



Laboratory Studies

Mo Geochemical Model

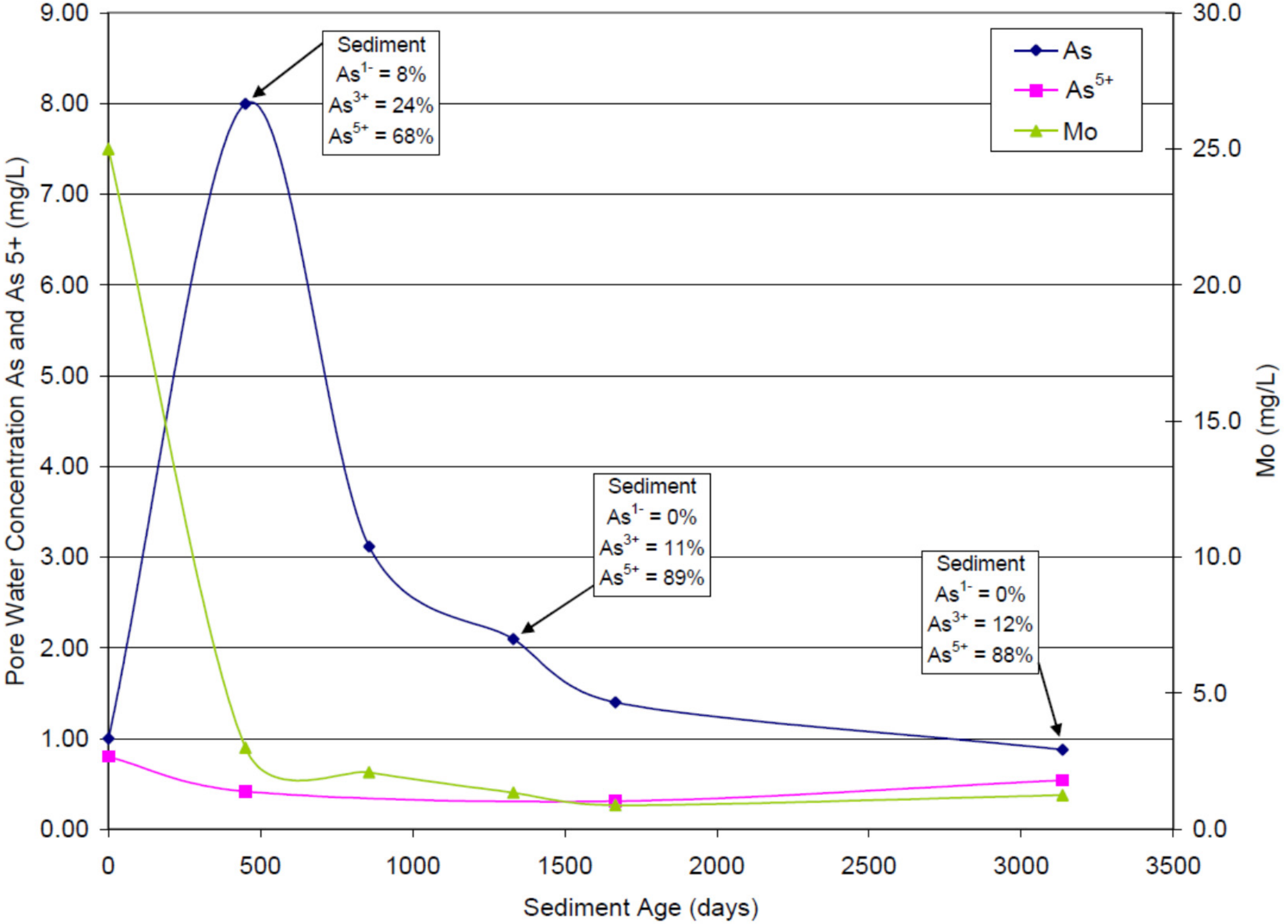
Sample Elevation vs 2008 Mo Pore Water Concentration



Effect of Particle Size Distribution

Case Study #1

Sediment Aging of Whole Tailings – As and Mo



Sediment
As^{1-} = 8%
As^{3+} = 24%
As^{5+} = 68%

Sediment
As^{1-} = 0%
As^{3+} = 11%
As^{5+} = 89%

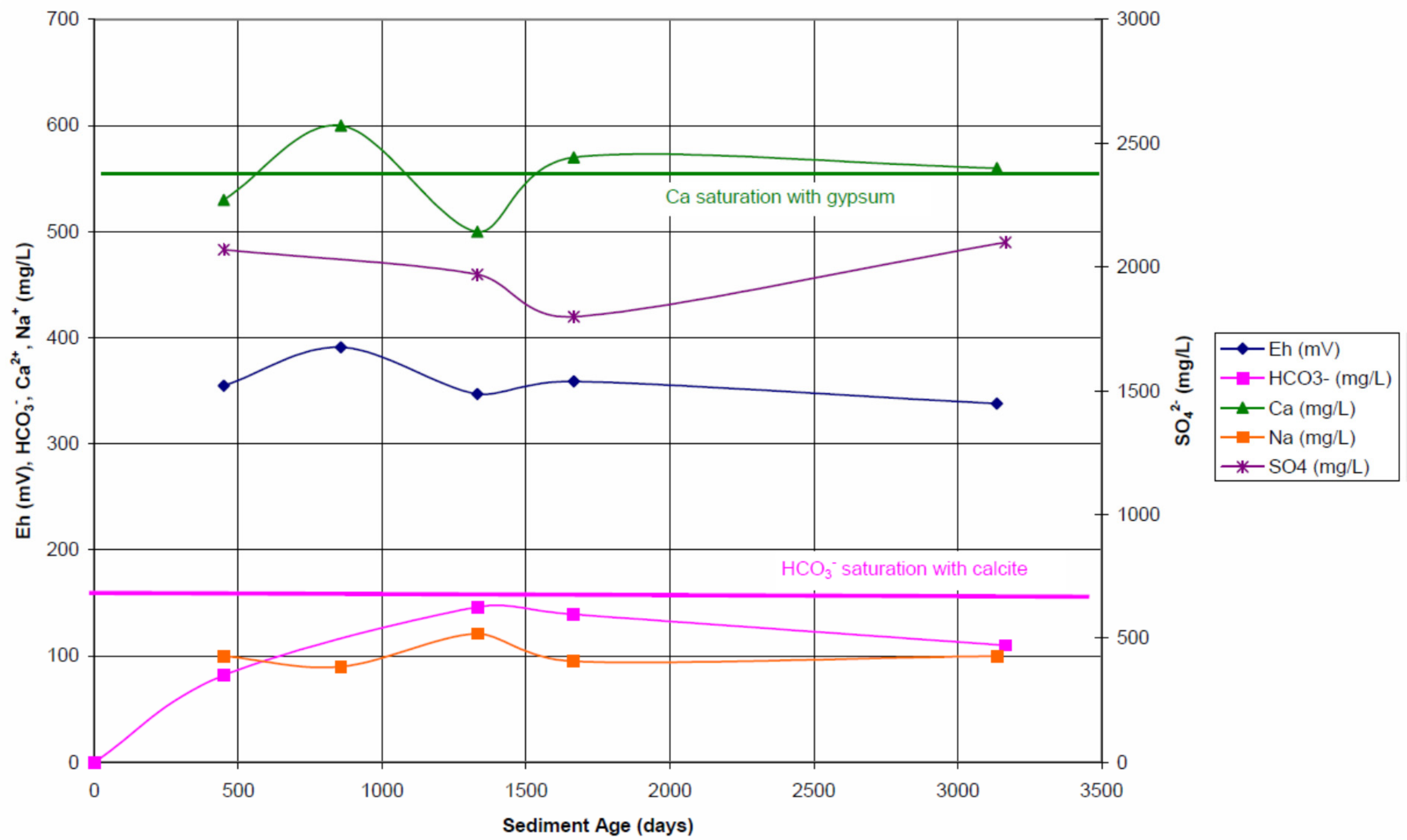
Sediment
As^{1-} = 0%
As^{3+} = 12%
As^{5+} = 88%

AREVA

Effect of Particle Size Distribution

Case Study #1

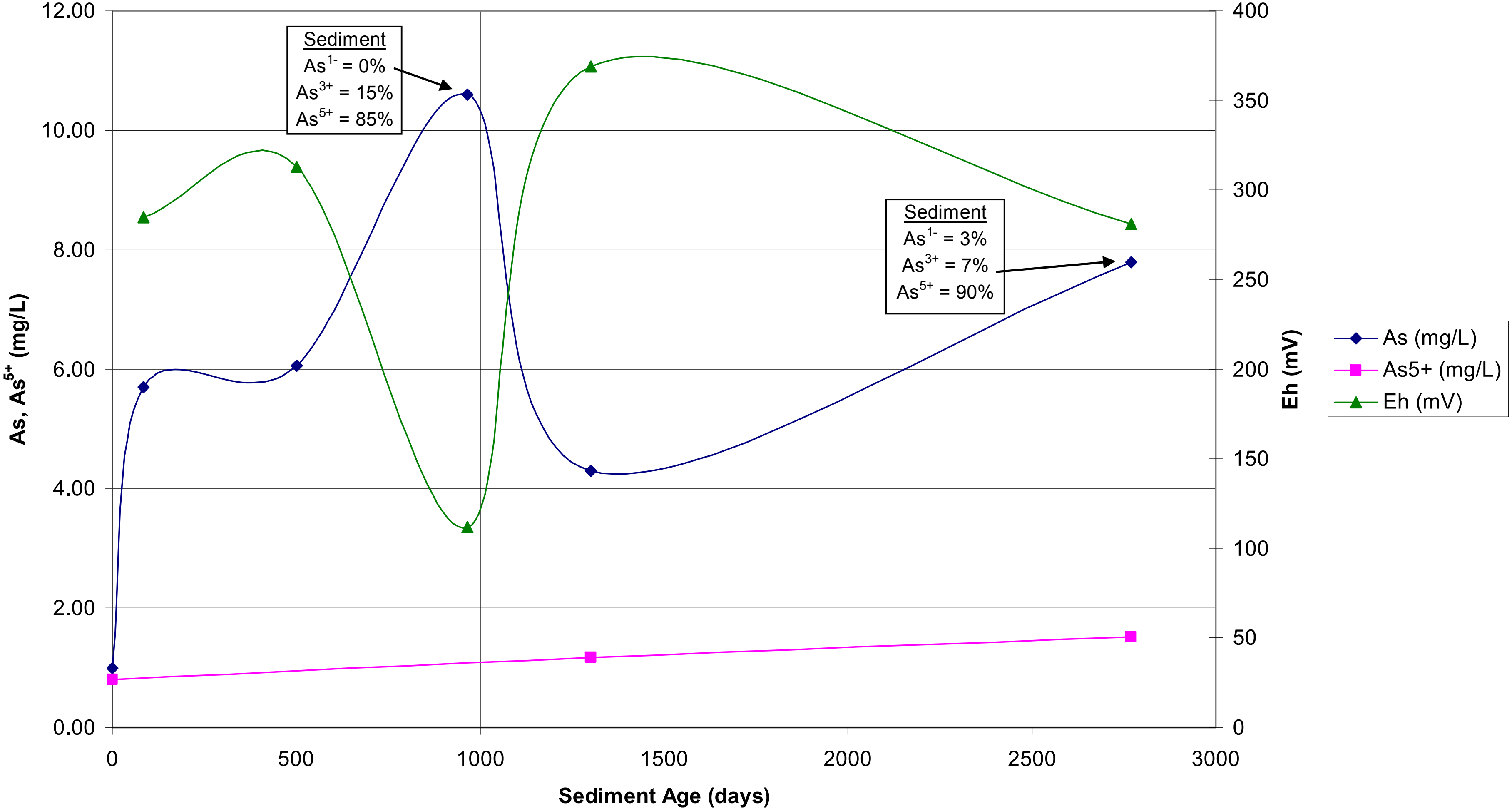
Sediment Aging of Whole Tailings – Eh and Major Ions



Effect of Particle Size Distribution

Case Study #2

TMF Sediment Aging of Coarse Tailings – As, As^{5+} and Eh



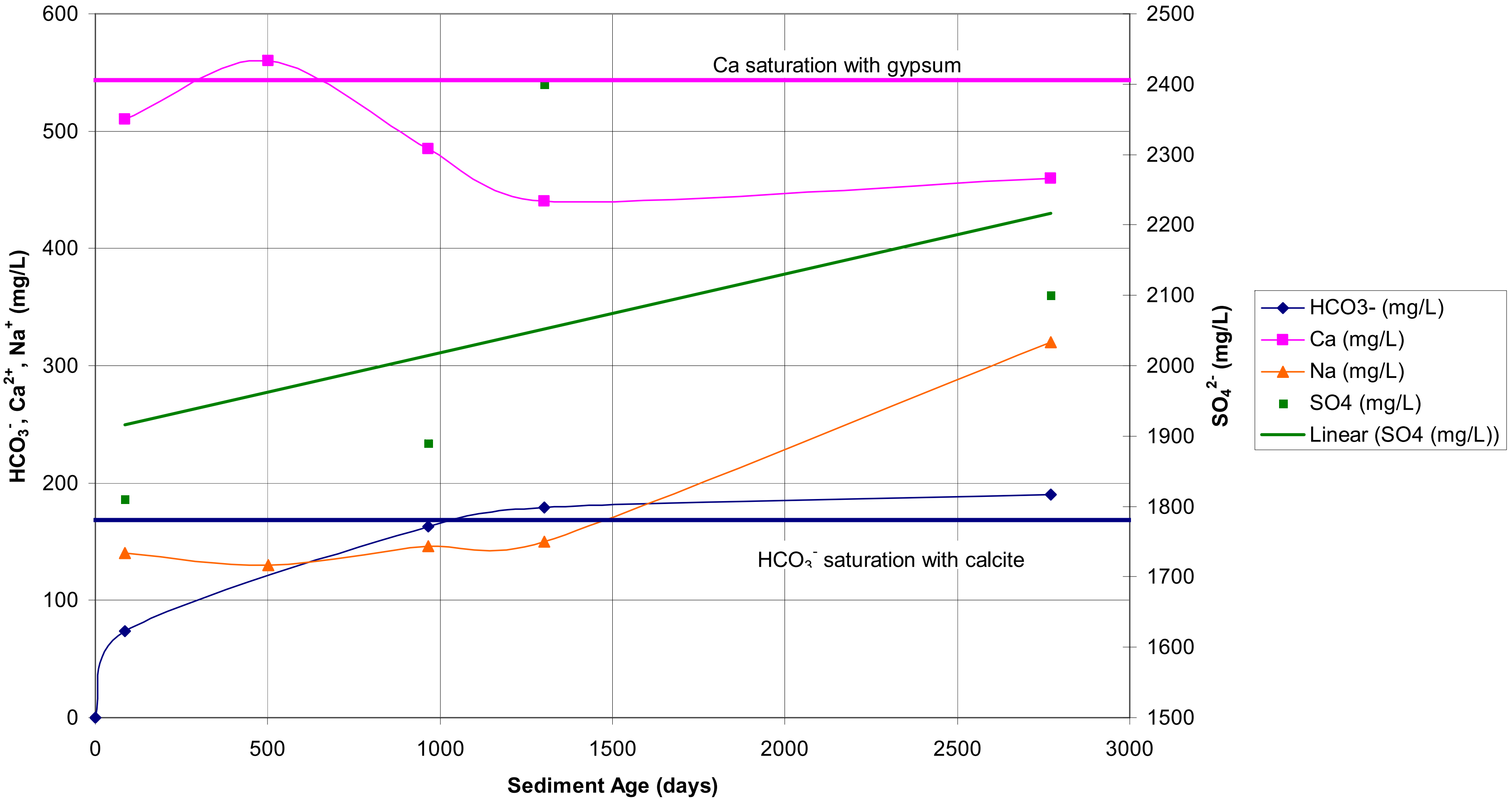
Sediment
As^{1-} = 0%
As^{3+} = 15%
As^{5+} = 85%

Sediment
As^{1-} = 3%
As^{3+} = 7%
As^{5+} = 90%

Effect of Particle Size Distribution

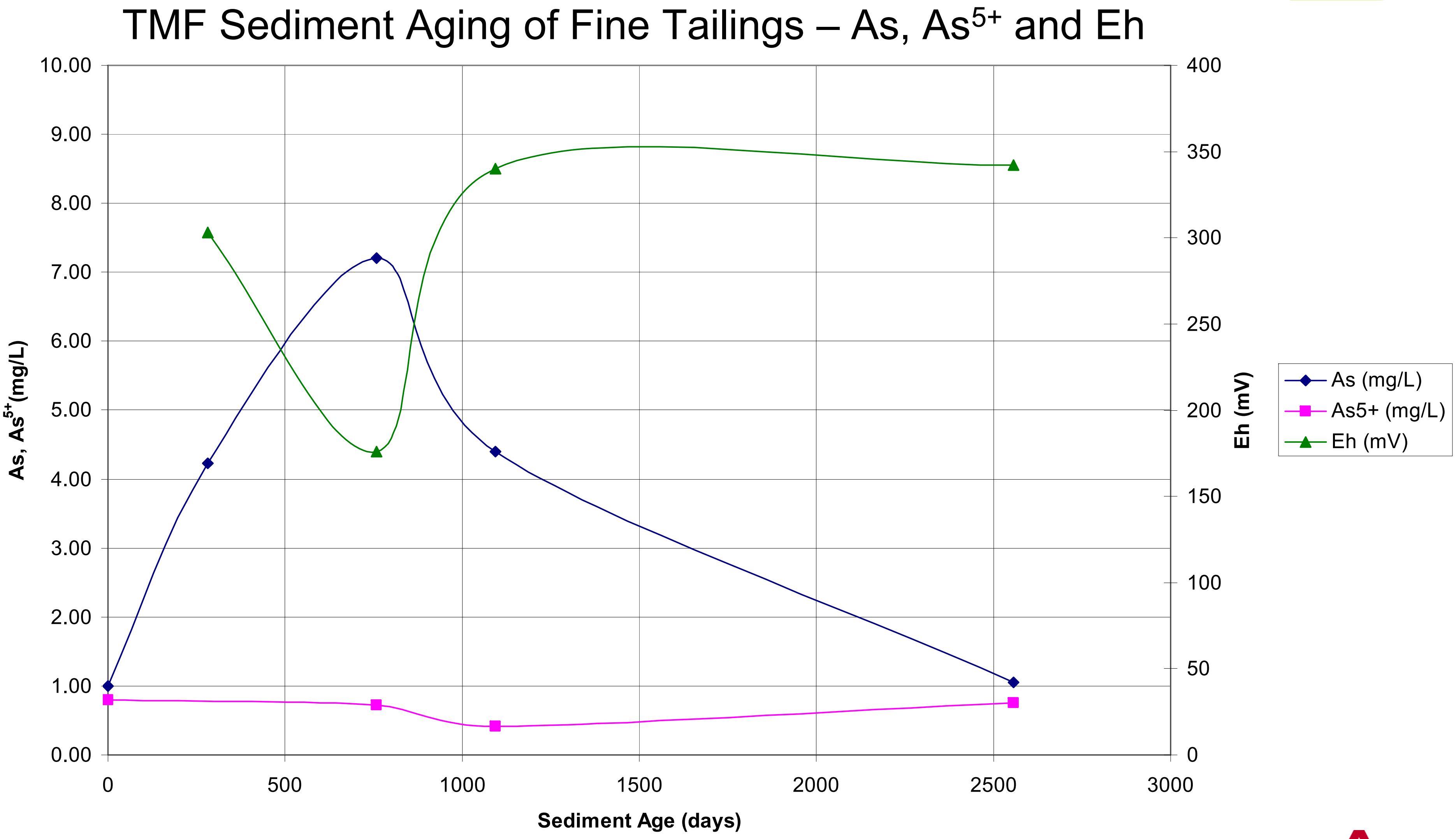
Case Study #2

TMF Sediment Aging of Coarse Tailings – HCO_3^-, Ca^{2+}, Na^+ and SO_4^{2-}



Effect of Particle Size Distribution

Case Study #3

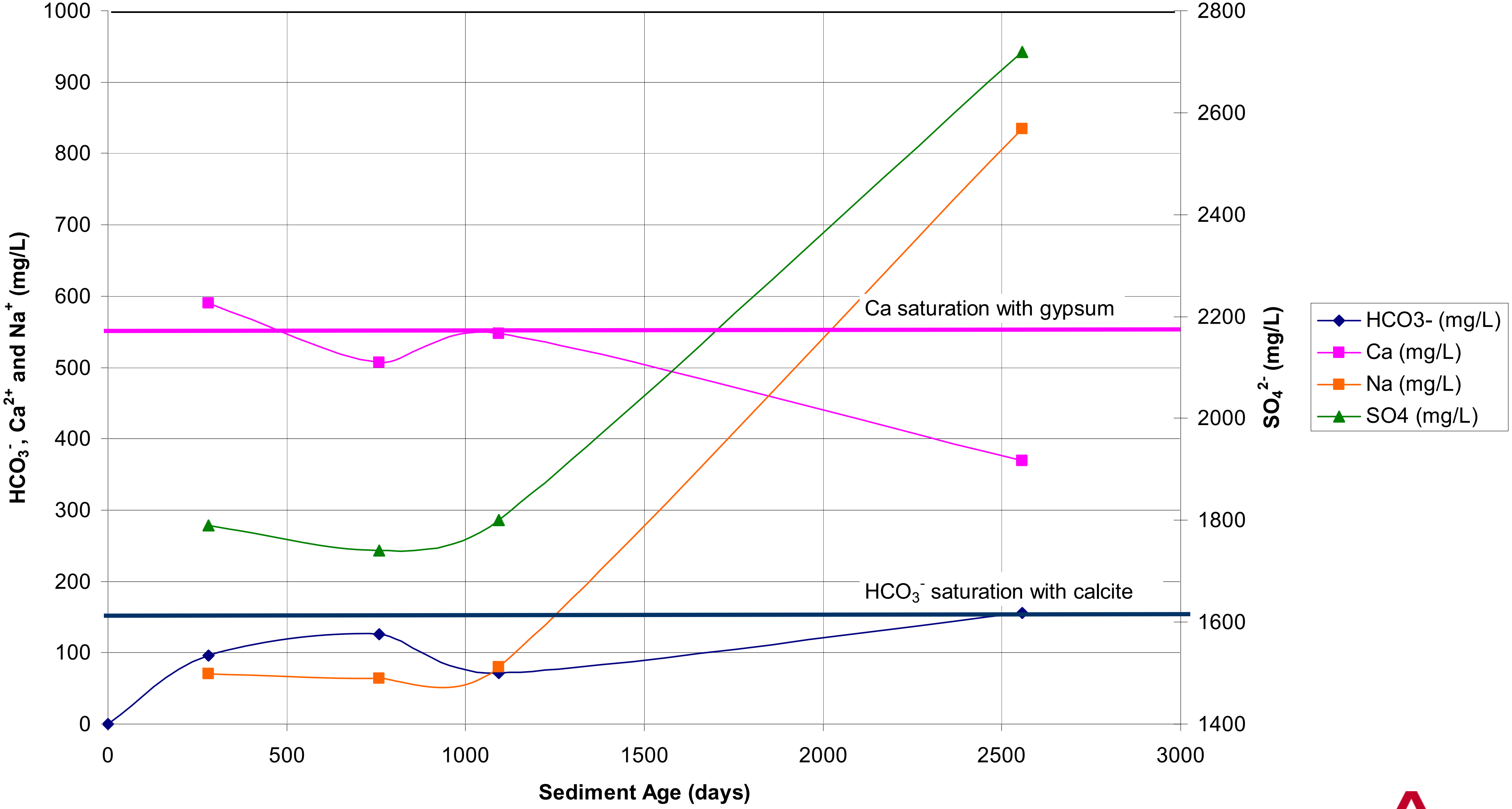


AREVA

Effect of Particle Size Distribution

Case Study #3

TMF Sediment Aging of Fine Tailings – HCO_3^-, Ca^{2+}, Na^+ and SO_4^{2-}



Conclusions

Confirmation of Engineered Tailings Geochemistry Concept

- **10+ years of TMF operation have verified that COCs are controlled to near constant values in tailings pore water**
- **the tailings COC pore water concentrations are independent of sediment COC concentrations**
- **geochemically, the sequestered COCs are characteristic of chemical/mineral phases and stable under TMF conditions**
- **investigative efforts continue concerning COC mineral identification (nano-scale structures) and their long term aging behaviour**
- **particle size segregation in placed tailings introduces spatial and temporal variations in geochemical observations**

AREVA