U.S. EPA Hardrock Mining Conference 2012 (Advancing Solutions for a New Legacy)

"ARD REMEDIATION WITH SLAG: AN APPLICATION TO BERKELEY PITLAKE WATER"

Courtney A. Young

Dept Head and Lewis S. Prater Professor
Metallurgical & Materials Engineering
Montana Tech
Butte MT 59701

Denver, CO | **Monitoring and Treatment Session 8** | **April 3-5, 2012**

Co-Authors and Researchers

Dick Berg, State Geologist, MBMG
Montana Tech, Butte MT

Larry Twidwell, Professor Emeritus, M&ME
Montana Tech, Butte MT

Krag Filius, Project Engineer
MSE Technology, Butte MT

Eric Streich, Process Engineer
Holcim Cement, Trident MT

Outline

- Berkeley Pitlake
- Previous Research
- Silicate Slags
- Objectives
- Procedures
- Results & Discussions
- Conclusions
- Acknowledgements

Outline

- **Berkeley Pitlake**
- **Previous Research**
- **Silicate Slags**
- **Objectives**
- **Procedures**
- **Results & Discussions**
- **Conclusions**
- **Acknowledgements**


Interstate-15
tailings pond
road
Continental Pit
terraces
tailings
Treatment Plant
Horseshoe Bend Water
Berkeley Pit
MR Concentrator
Viewing Stand
Butte
Walkerville
Interstate 15/90
N

Brief History of Berkeley Pit

1880 - Butte was an early copper-mining town:

- Referred to as "The Richest Hill on Earth"
- One of the world's largest sulfide ore deposits

1920 - ACC controlled most mines

1955 - ACC began phasing out underground mining

1977 - ARCO purchased all operations

1982 - Operations halted and pumps turned off

1983 - Water first appeared in the pit

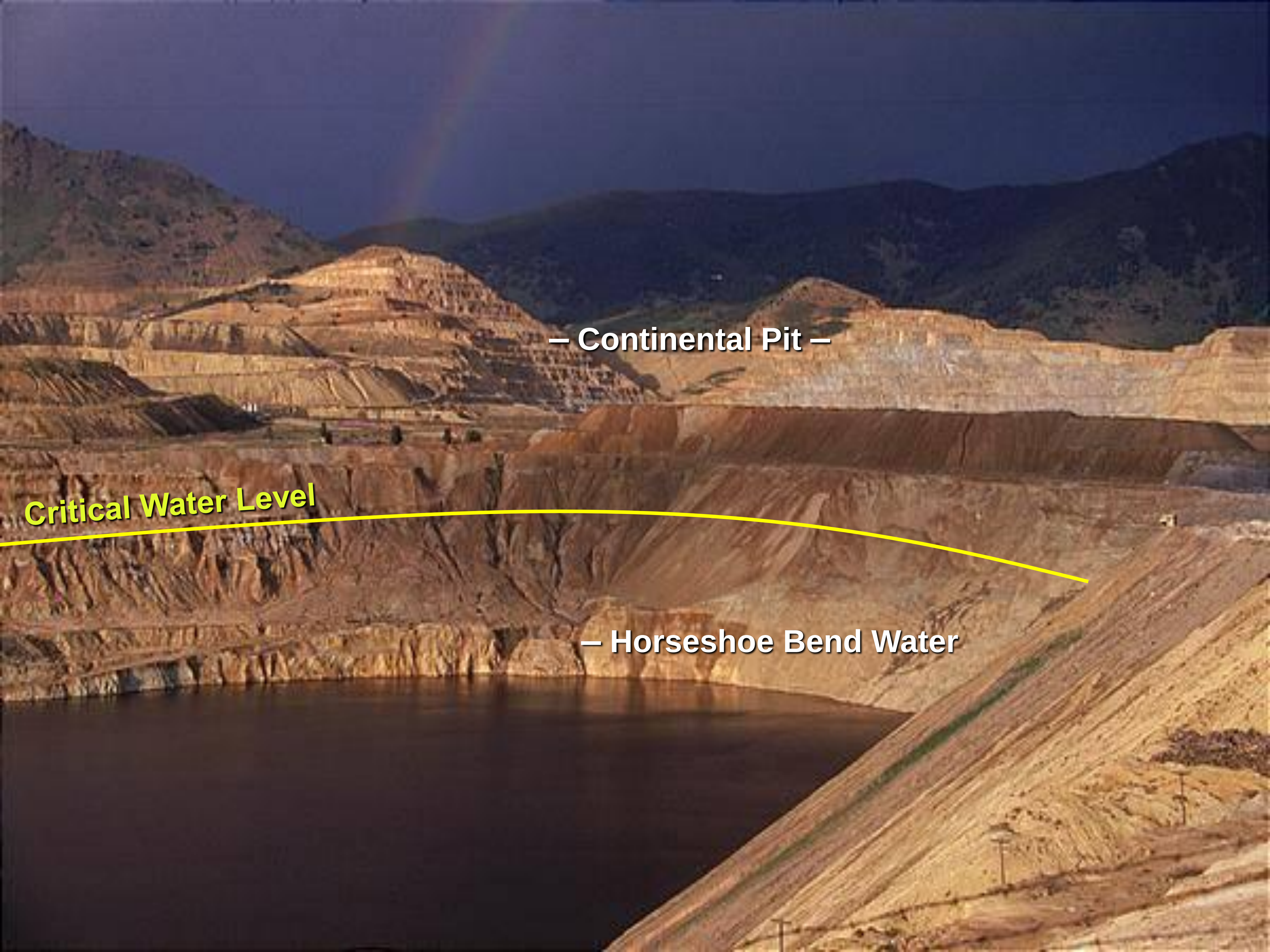
- Listed as a Superfund site
- Part of the largest mining Superfund site

Berkeley Pitlake Water:
- **is acidic near pH 2.5**
- **contains metals at high concentrations (99% Water):**

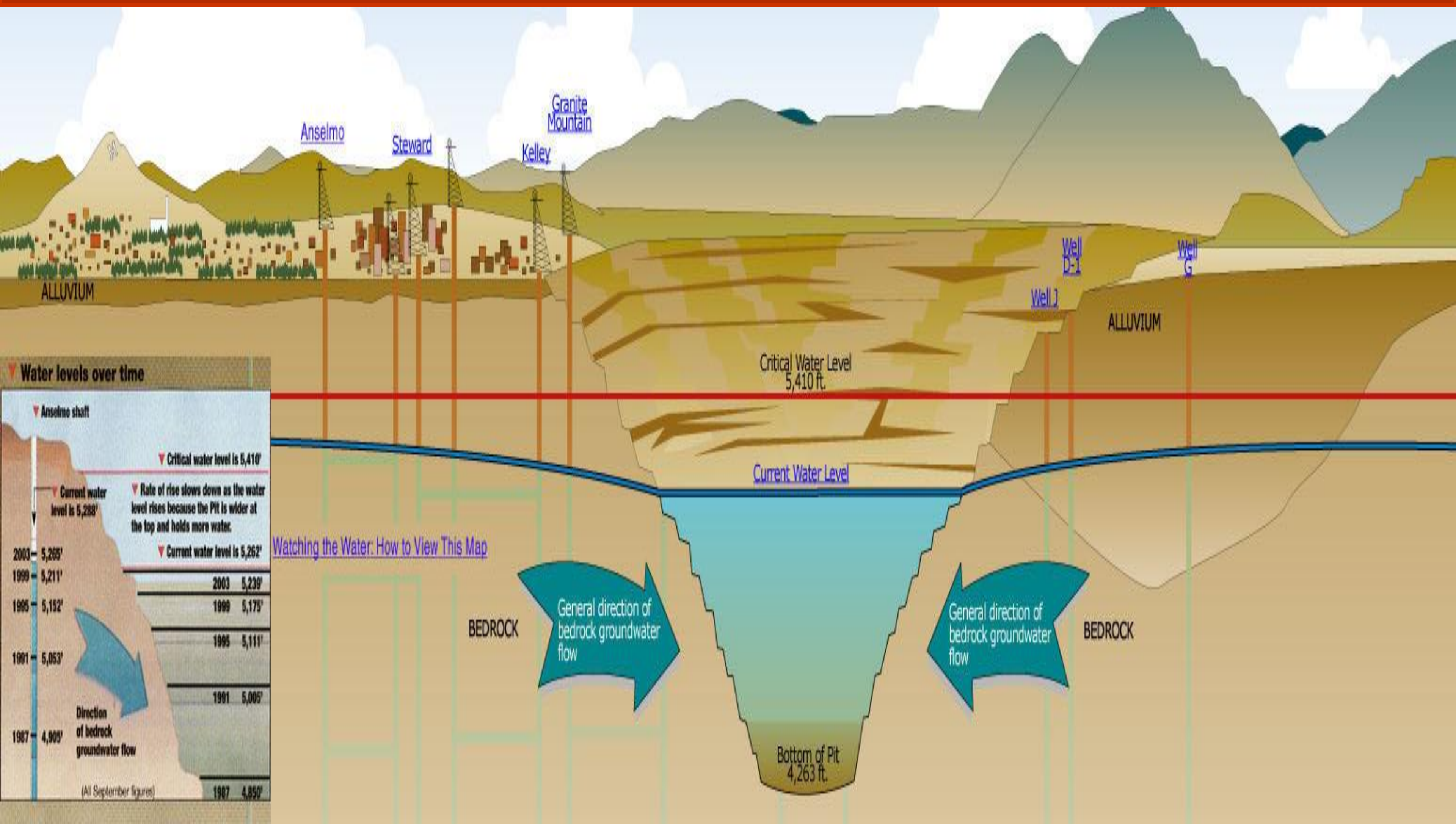
SO_4	(7500 ppm)
Fe	(1000 ppm)
Zn	(650 ppm)
Al	(300 ppm)
Mn	(250 ppm)
Cu	(200 ppm)
Cd	(2.5 ppm)
As	(0.5 ppm)

Concentrations change with position, depth and time

Berkeley Pitlake Water:
- **encompasses ~700 acres**
- **is ~1,000 feet deep**
- **contains ~40 billion gallons**
- **fills at 2.6 million gallons per day**
- **will reach “critical level” in 2023**


– Continental Pit –
Critical Water Level
– Horseshoe Bend Water

Monitoring the Water Level



Brief History of Berkeley Pit

1995 - HSBW also diverted to pond (3M GPD)
- MR starts operating Continental Pit to the east
- ARCO and MR named responsible parties

2000 - MR halts operations including diversion

2003 - HSBW Treatment Plant is commissioned
- two-stage lime precipitation process
- diversion of treated water begins
- sludges are disposed into the BPL

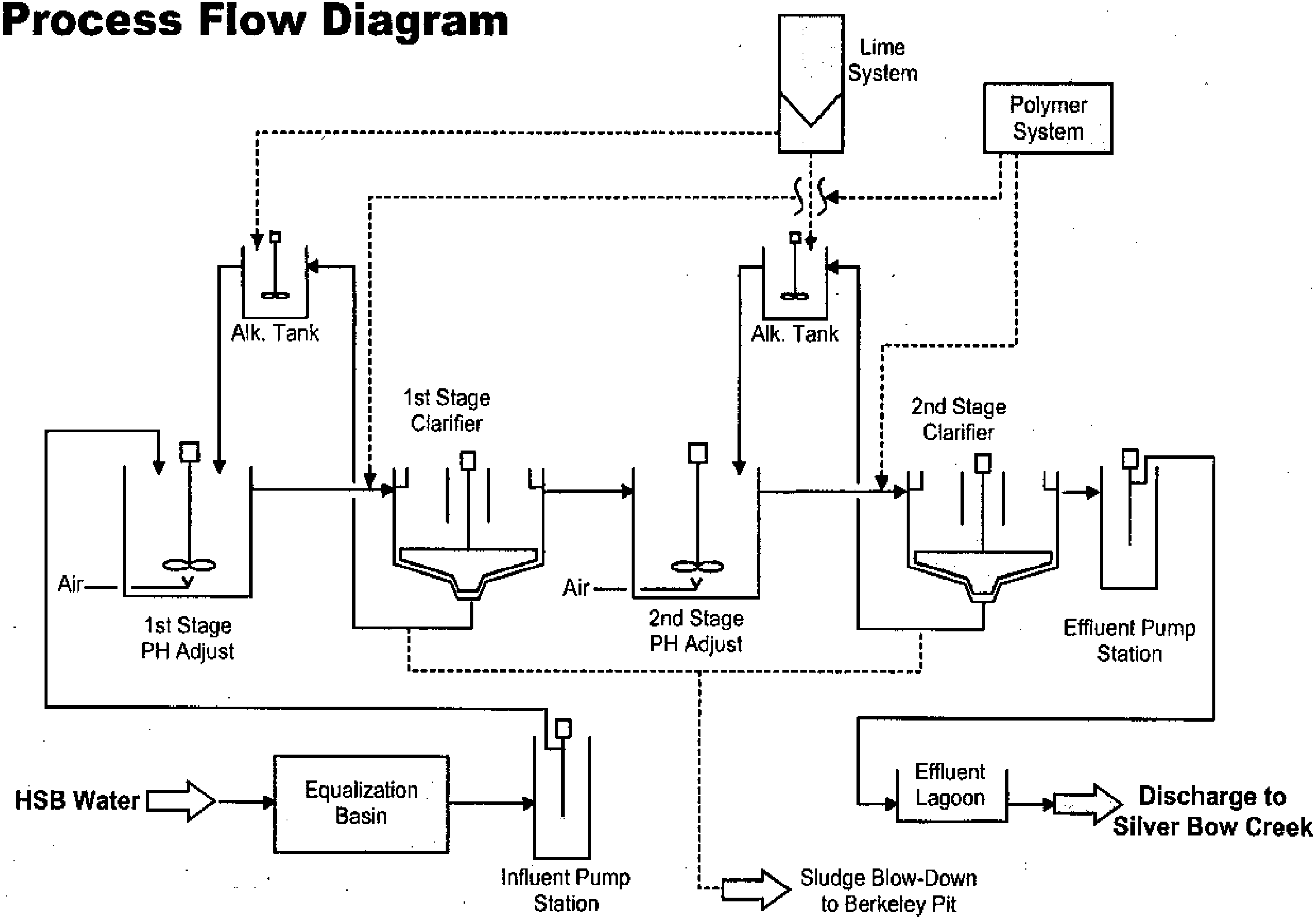
2004 - MR reopens and begins full operations

2005 - MR pumps BPL water to Cu-cementation

Horseshoe Bend Water Treatment Plant


Horseshoe Bend Water Treatment Plant

ARCO / Montana Resources
Horseshoe Bend Water Treatment Facility
Process Flow Diagram



Outline

- ✓ Berkeley Pitlake
- **Previous Research**
- Silicate Slags
- Objectives
- Procedures
- Results & Discussions
- Conclusions
- Acknowledgements

Previous Research

- Participate in a “series” of 5 studies to summarize available information

- Generate new information to formulate conceptual environmental models for the Berkeley Pitlake from all of its features

- Provide data for the development of advanced treatment technologies

Series I – Selective Recovery

	Fe	As	Mn	Cu	Cd	Zn	Al
Initial BPL Water	1019.8	5.9	214.2	151.2	2.3	566.3	243.5
Stage 1A - H_2O_2/UV	8.43	< 0.11	198.5	146.3	1.9	529.7	222.7
Stage 1B - $KMnO_4$	0.23	< 0.11	4.5	138.8	1.84	495.6	213.2
Stage 2 - Na_2S	0.27	< 0.11	4.9	0.09	1.7	482.6	203.2
Stage 3 - Na_2S	0.22	< 0.11	4.2	< 0.05	< 0.02	49.4	186.2
Stage 4 - NaOH	< 0.04	< 0.11	3.72	< 0.05	< 0.02	18.2	0.24
Drinking Standard	0.3	0.05	0.05	1.3	0.005	5	0.2

Stage 1A: $H_2O_2 = 2OH^\bullet$; $Fe^{2+} + OH^\bullet = Fe^{3+} + OH^-$; $Fe^{3+} + 3OH^- = Fe(OH)_3$

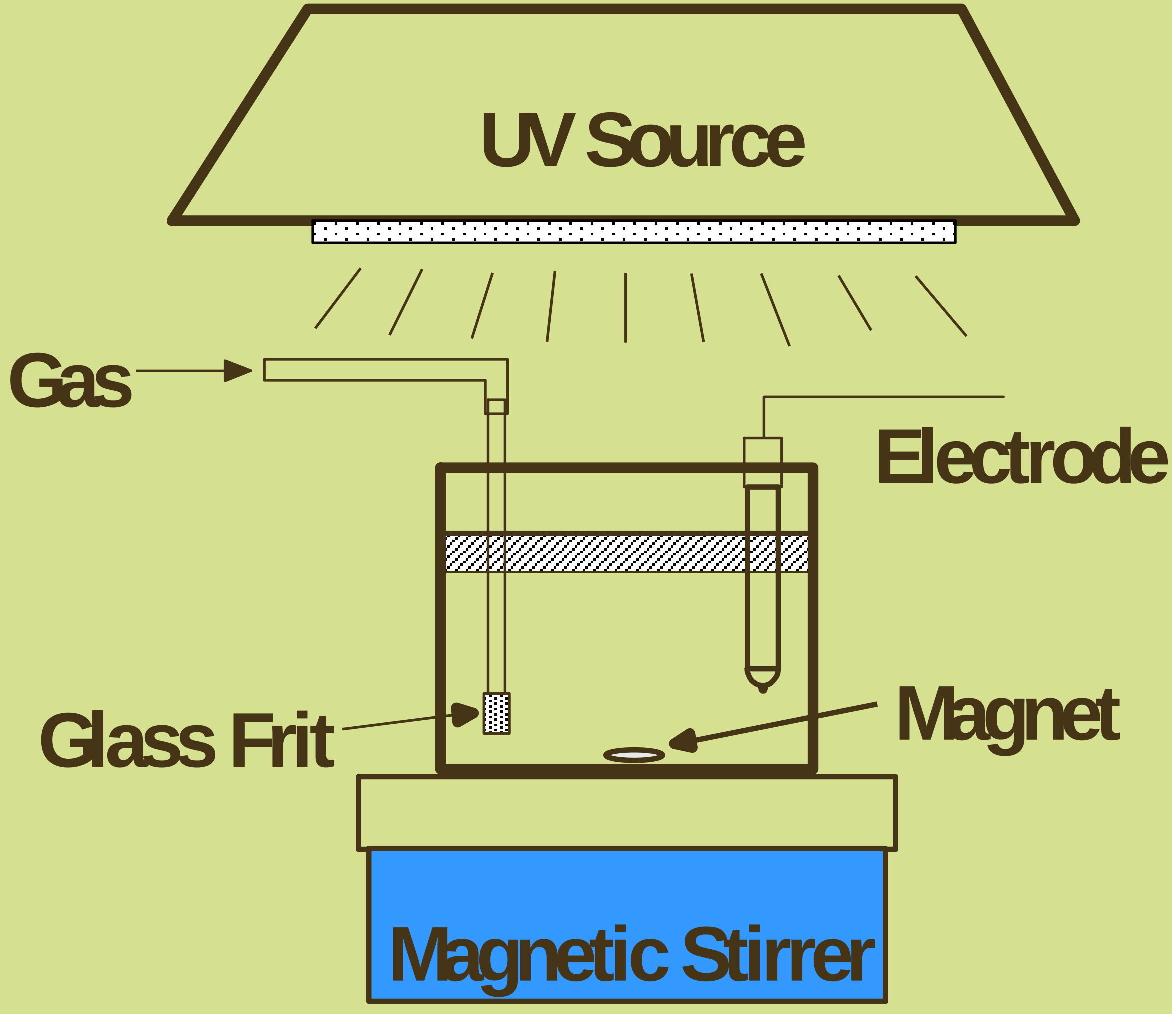
Stage 1B: $3Mn^{2+} + 2MnO_4^- + 2H_2O = 5MnO_2 + 4H^+$

Stage 2: $Cu^{2+} + S^{2-} = CuS$

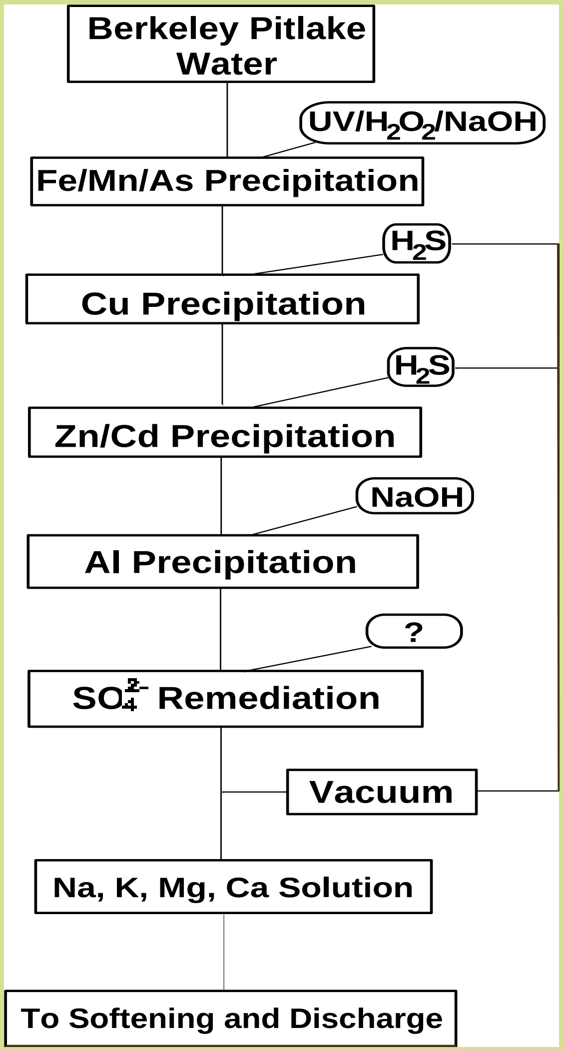
Stage 3: $Cd^{2+} + S^{2-} = CdS$; $Zn^{2+} + S^{2-} = ZnS$

Stage 4: $Al^{3+} + 3OH^- = Al(OH)_3$

Series I – Selective Recovery

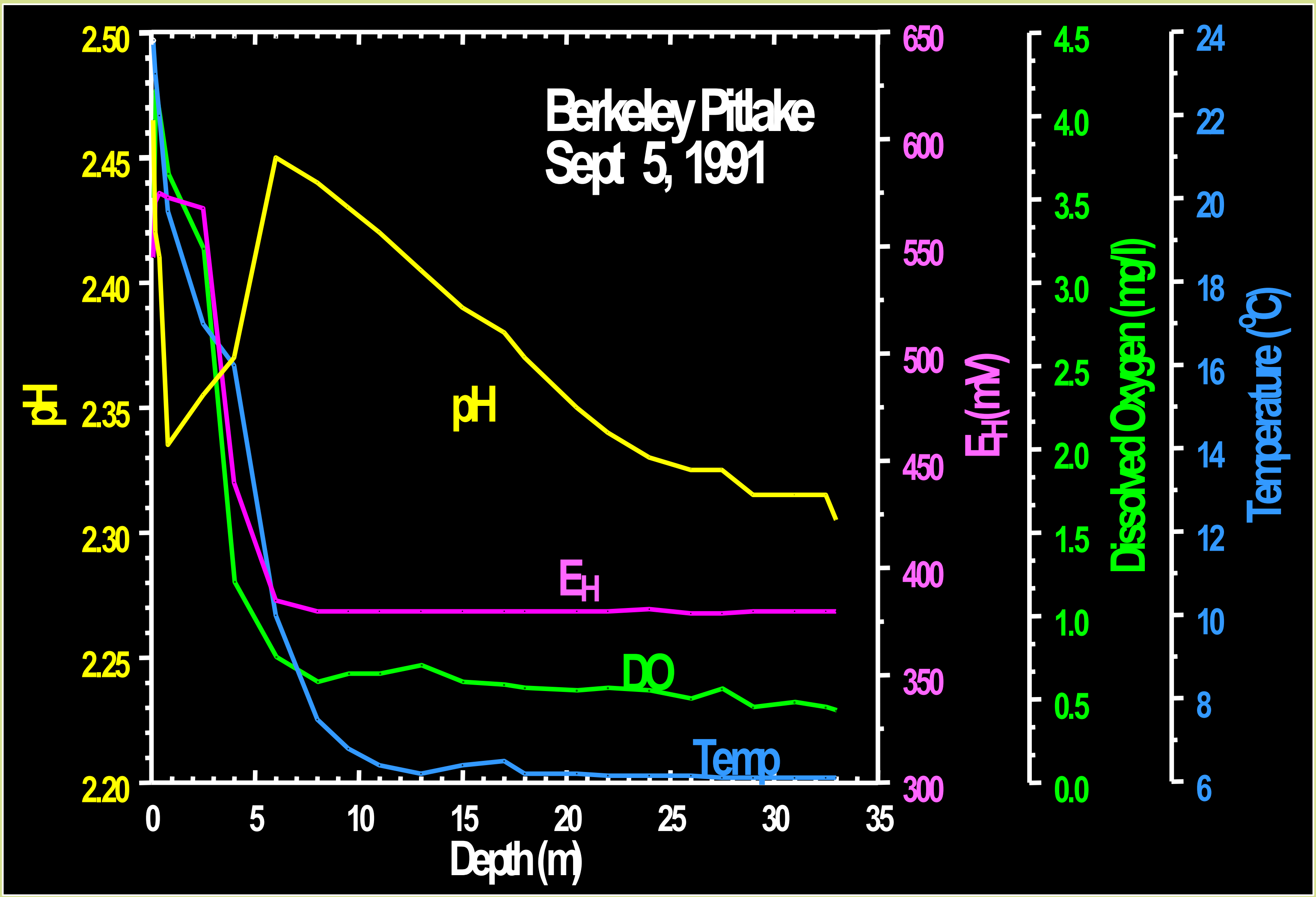


Series I – Selective Recovery

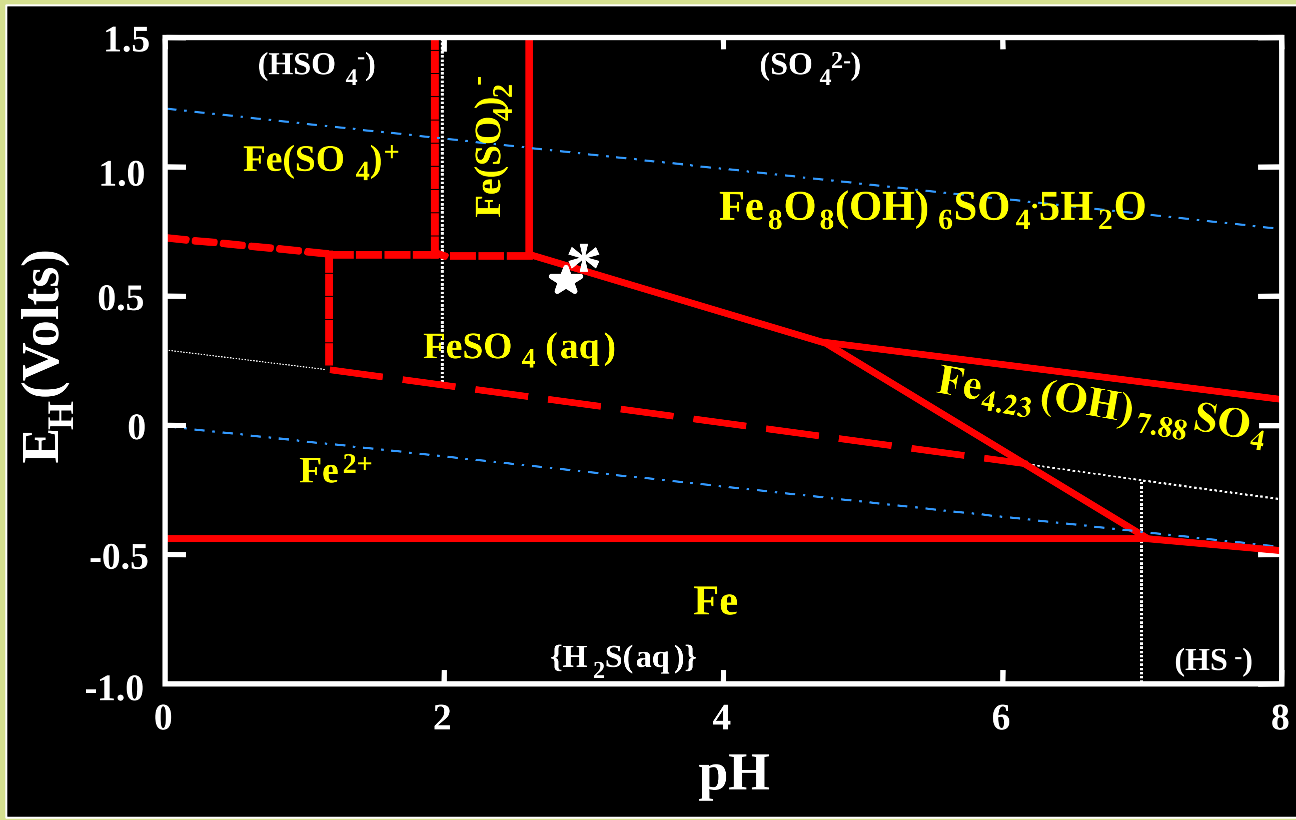


- Selective metal recovery is possible
- A 7-stage process has been envisioned and shown to work (in batch mode)
- Fe, As, Cu and Cd met DWS
- Al almost met DWS
- Mn and Zn did not meet DWS
- $KMnO_4$ addition needs to be precise
- Zn may have precipitated amorphously
- SO_4 removal was not done but options are
  - Freeze Crystallization
  - Reverse Osmosis
  - Gypsum Precipitation
  - SRB Bioreduction
  - Chemoreduction
  - Photoreduction
  - Reductive Precipitation
- Softening to remove Na, K, Mg and Ca

Series II – Surface Waters



Series II – Surface Waters



Series II – Surface Waters

- Profiles indicated chemoclines/thermoclines existed and were successfully reproduced in lab
- They have been explained by, but can not be totally attributed to
  - HSBW being less dense than BPLW so, when it enters the pitlake, it floats on top rather than mixes in, and
  - Biological activity which should increase DO as well as pH
- Experiments showed that the interaction of sunlight (UV radiation) and air with BPL water plays a significant role

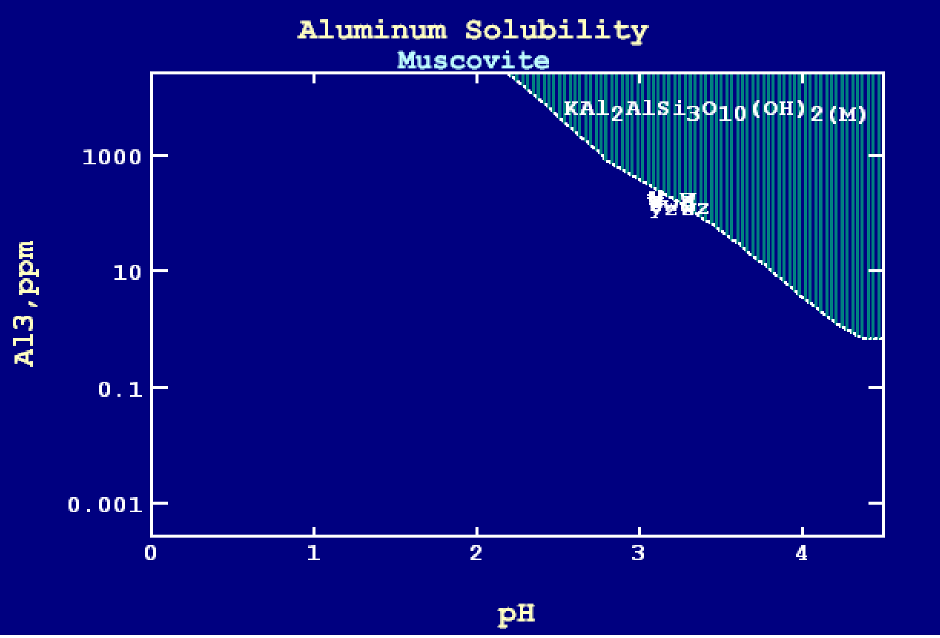
Series III – At Depth

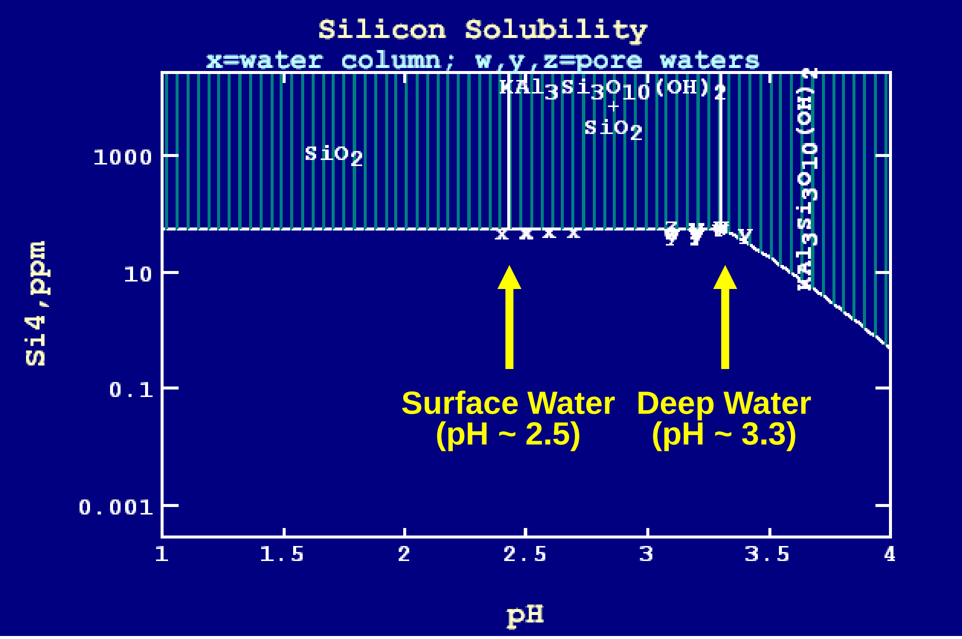
(Deep Water, Pore Water and Sediment)

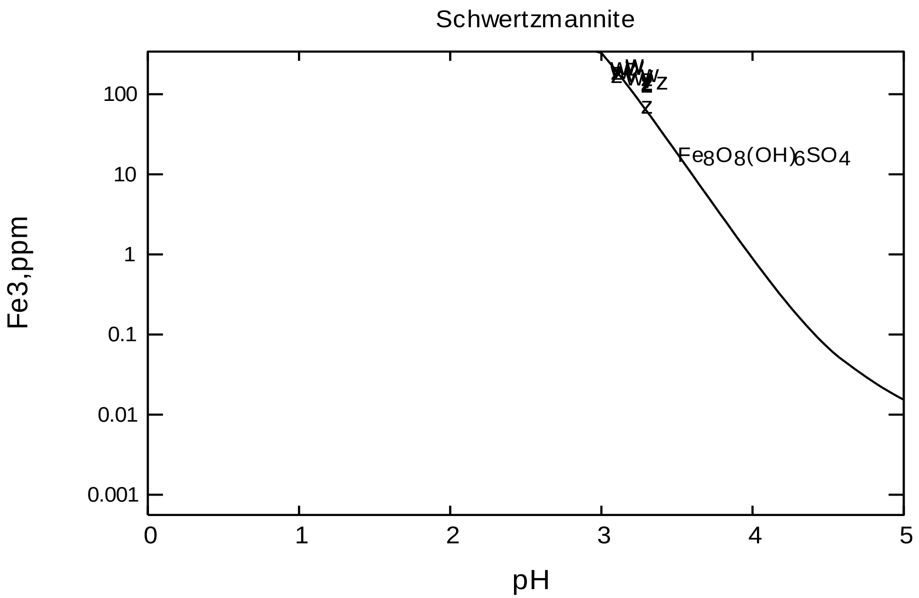
Siphon/Filter Off
Deep/Pore Water

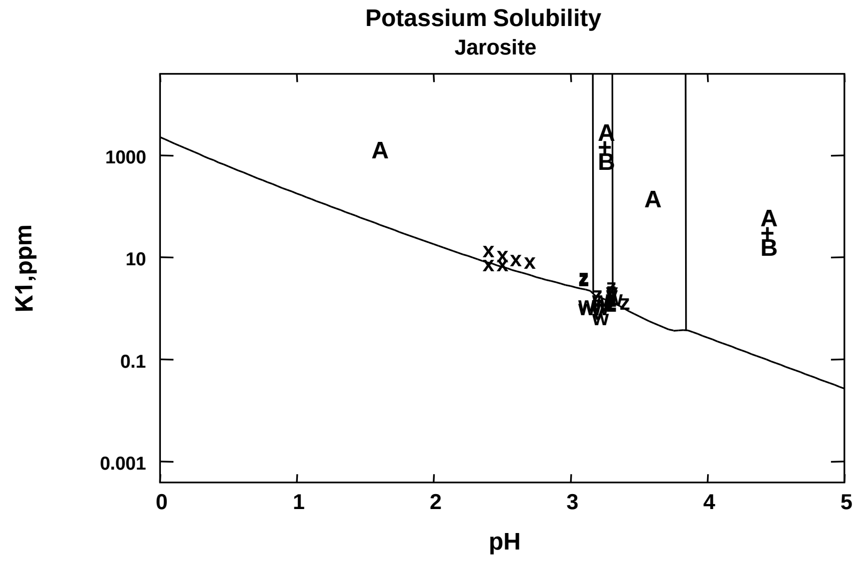
Analyze the Water
& Solid Contents

Concentrations are controlled by the solubility of identified minerals and precipitates!









Series III – At Depth

(Deep Water, Pore Water and Sediment)

- Muscovite [$KAl_3Si_3O_{10}(OH)_2$] controls Al^{3+} concentration
- Quartz (SiO_2) controls Si^{4+} concentration
- Schwertmannite [$Fe_8O_8(OH)_6SO_4$] precipitate controls the Fe^{3+} concentration
- Jarosite [$KFe_3(SO_4)_2(OH)_6$] precipitate controls K^+ concentration
- Cu^{2+}, Fe^{2+}, Zn^{2+} and Cd^{2+} concentrations could not be associated with a mineral or precipitate are therefore considered to be unsaturated
- However, Cu^{2+}, Fe^{2+}, Zn^{2+} and Cd^{2+} concentrations were found to increase with depth giving the appearance that supergene deposition is occurring

Series IV – Sidewalls

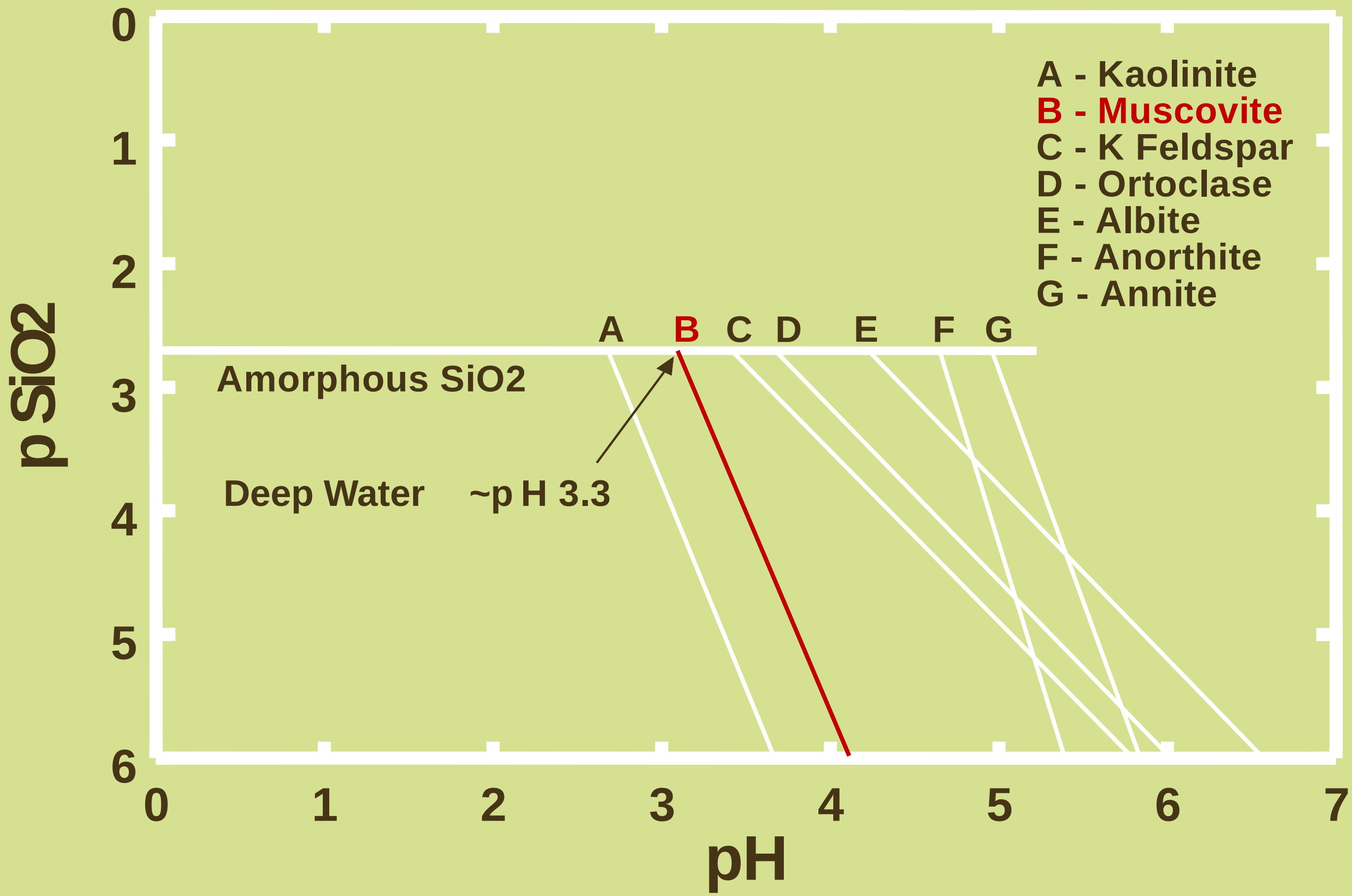
Mineralogy is essentially the same except fine native rock (granite) and gypsum precipitate are more abundant:

Native:
- Granite (38%)
- Quartz (33%)
- Muscovite (4%)

Precipitate:
- K-jarosite (22%)
- Gypsum (3%)

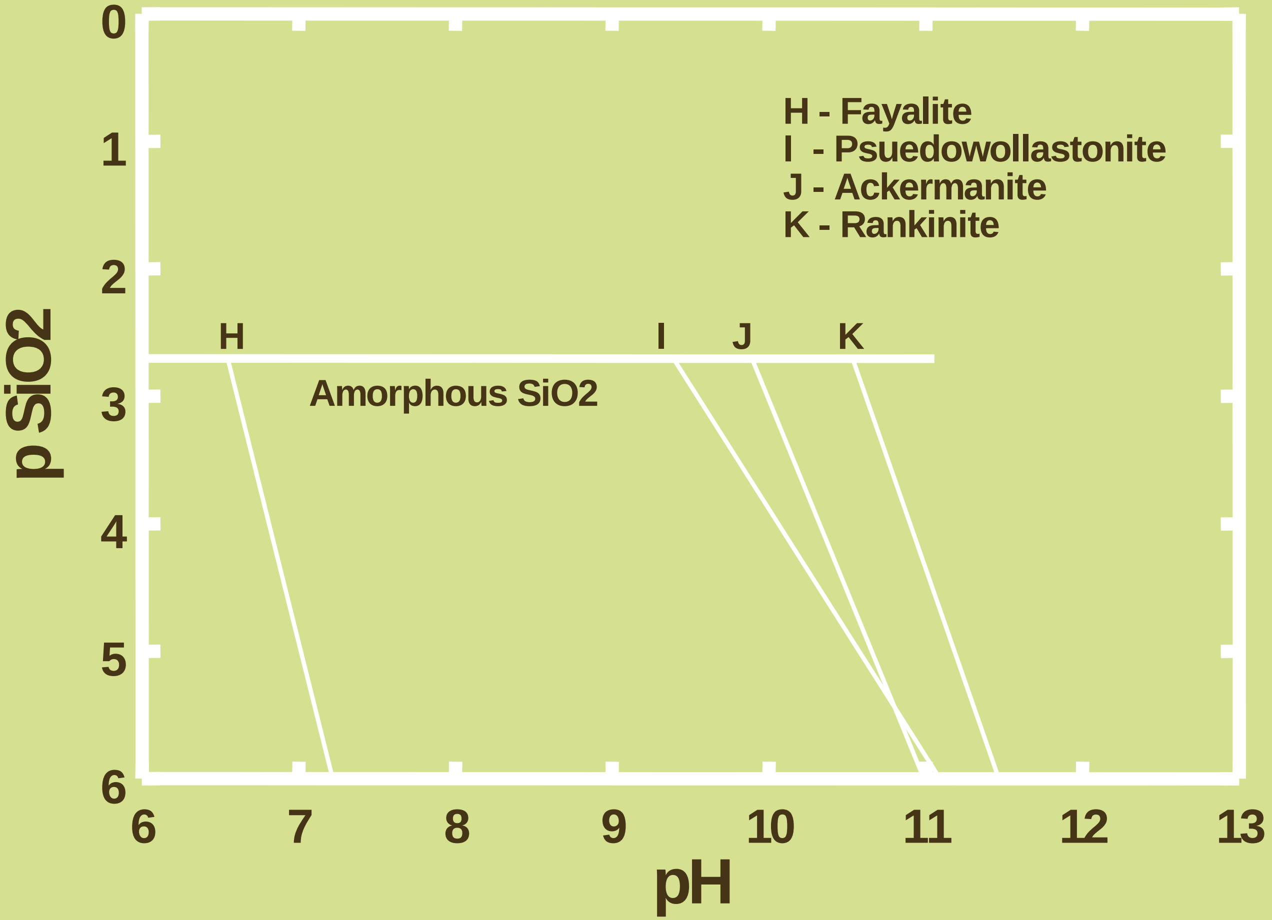
Series IV – Sidewalls

Chemical controls should be about the same as at depth



Series V – Silicate Slags

Silicate (and oxide) slags should do the same thing!



Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- **Silicate Slags**
- Objectives
- Procedures
- Results & Discussions
- Conclusions
- Acknowledgements

Silicate Slags

Source of Silicate (and lime)

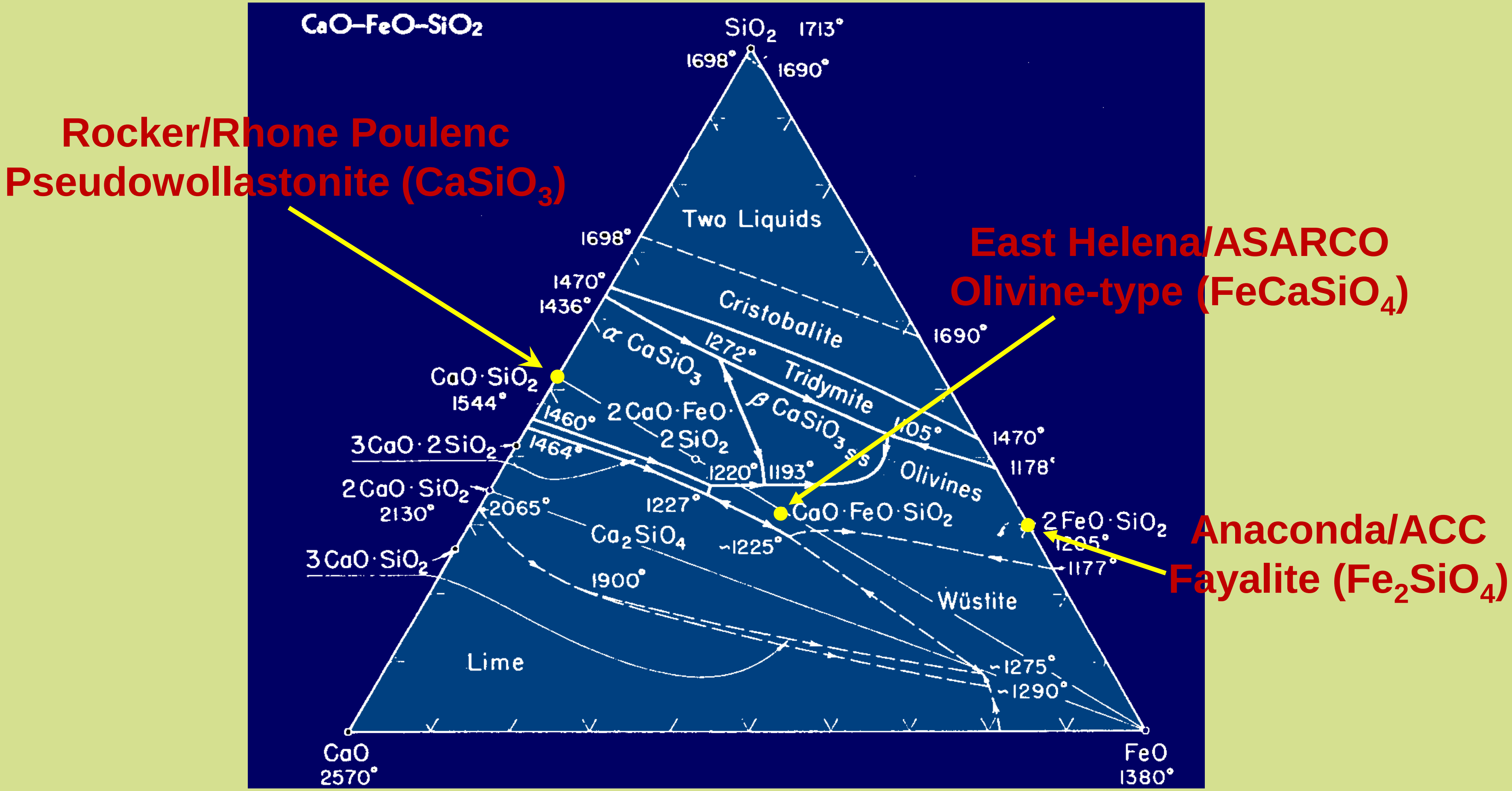
Act as pH-Buffers (replace lime)

Available in Montana (inactive)

- Anaconda (ARCO) - Fayalite, Fe_2SiO_4
- East Helena (ASARCO) - Olivine-type, $CaFeSiO_4$
- Rocker (Rhone) - Pseudowallastonite, $CaSiO_3$

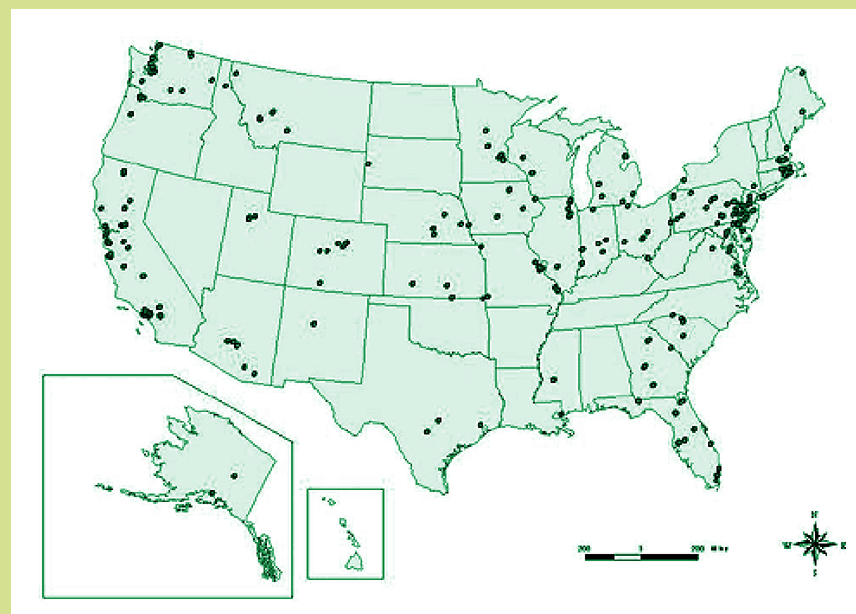
Slag	Ca (%)	Fe (%)	Si (%)
Rhone	30.3	0.4	19.0
ASARCO	14.0	27.6	12.7
Anaconda	2.6	30.9	15.8

Silicate Slags



Silicate Slags

- Other Global Sources
  - Columbus (Stillwater)
  - Salt Lake City (Kennecott)
  - Trail, BC (Teck Cominco)
- Dual Ecosystem Enhancement
  - Remove Slag Piles
  - Remediate Berkeley Pitlake
  - *In-Situ* or *Ex-Situ*
- Provide Entertainment
  - Golf Courses
  - Parks & Walkways
  - Sports Complexes
- Attract Businesses



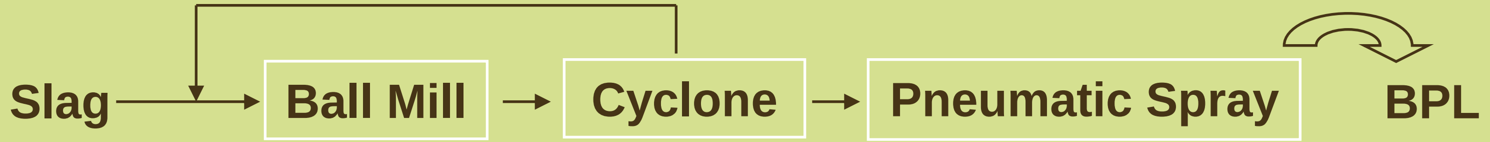
Outline

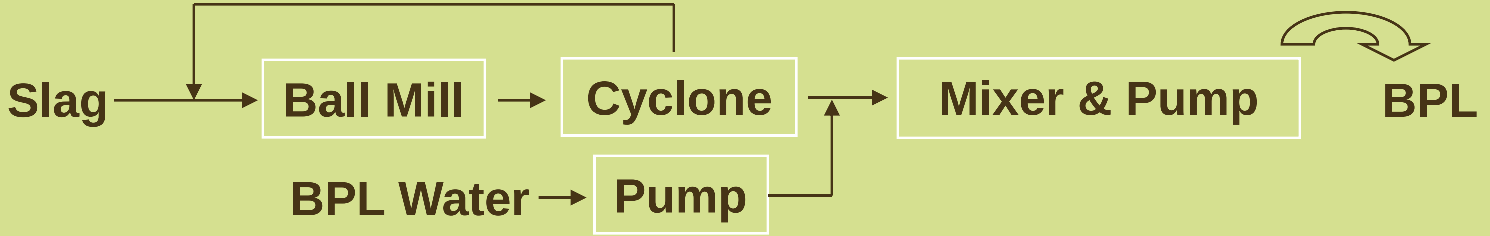
- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- Objectives
- Procedures
- Results & Discussions
- Conclusions
- Acknowledgements

Objectives

Conceptual Flowsheet Designs

Dry Grinding





Wet Grinding

Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- ✓ Objectives
- **Procedures**
- Results & Discussions
- Conclusions
- Acknowledgements

Procedures

- Characterize Montana Slags
  - Bond Work Index
  - SEM/EDX/MLA Analysis
  - Remediation Potential
- Model Effects
  - Parameters
    - Slag Type (Fe/Si Ratio)
    - Particle Size (100-400 Mesh)
    - Slag Amount (200-800 g/L)
  - Experimental Design (StatEase)

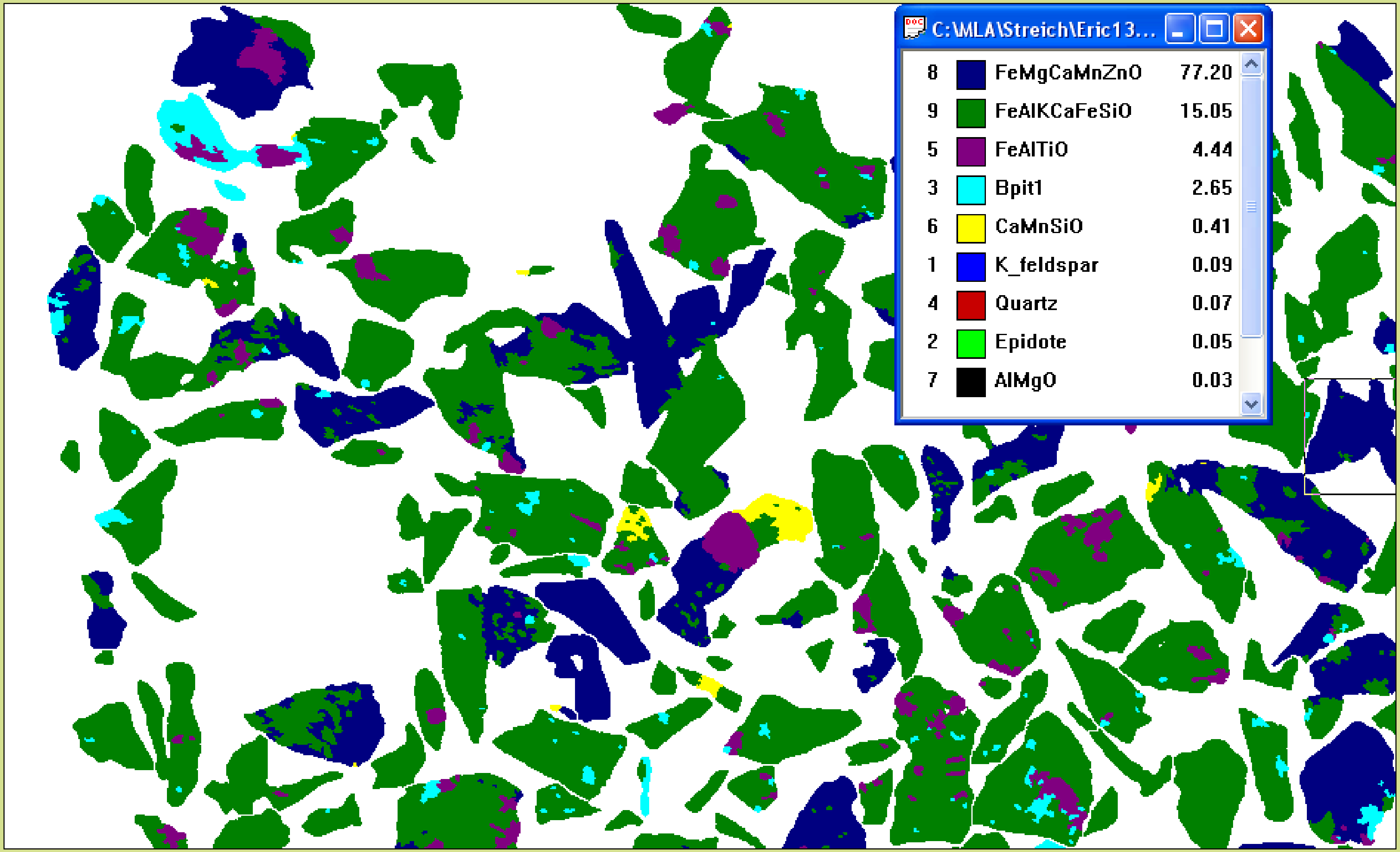
Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- ✓ Objectives
- ✓ Procedures
- Results & Discussions
- Conclusions
- Acknowledgements

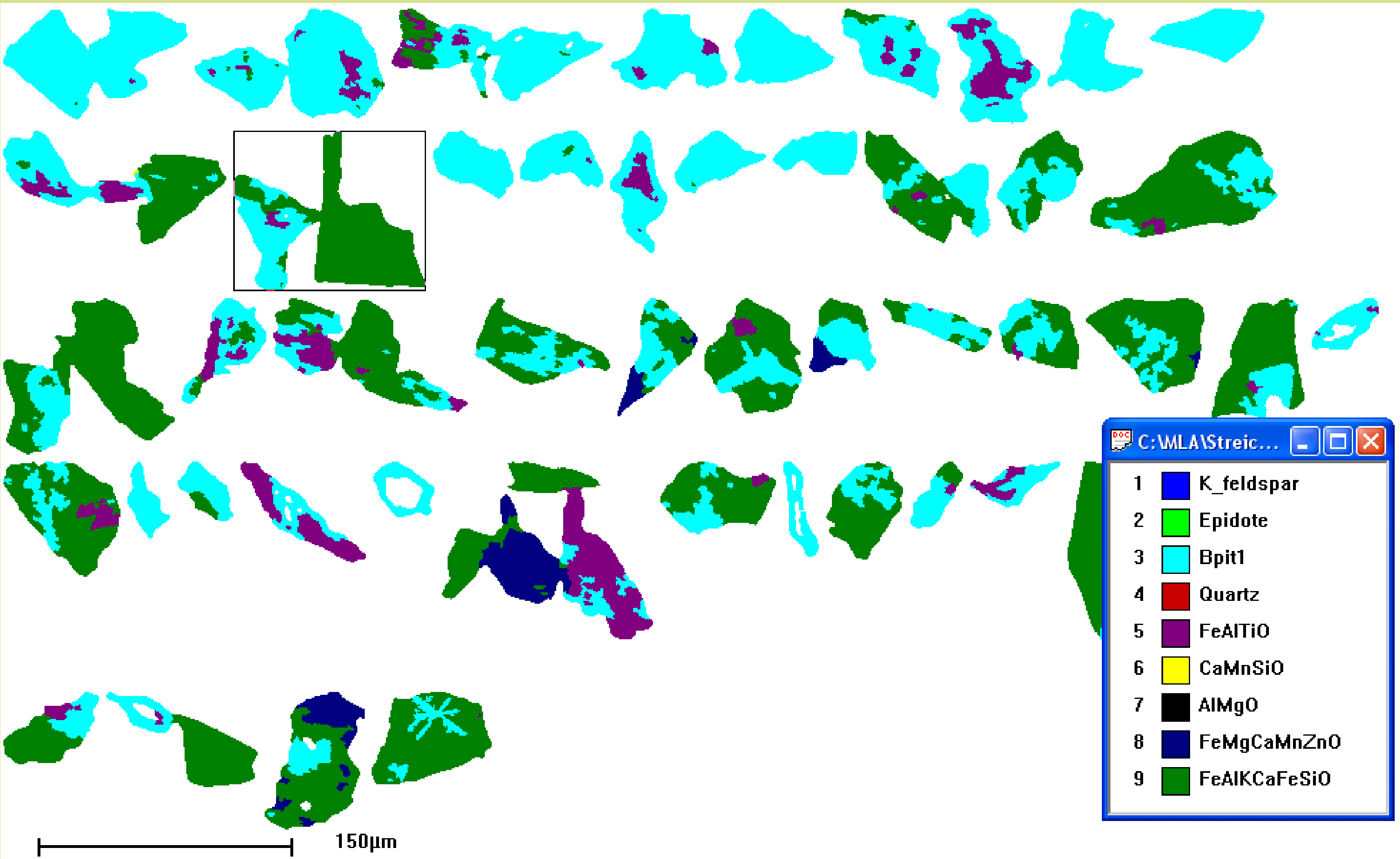
Bond Work Index

Date	Slag	Target Size Mesh (mm)	F80 (mm)	P80 (mm)	Avg Gbp	Bond Work Index
1/29/05	ACC	48 (0.295)	2.825	0.205	0.95	20.52
2/17/05	ACC	100 (0.147)	2.603	0.117	0.94	20.44
2/20/05	ACC	200 (0.074)	2.603	0.058	0.53	24.86
1/29/05	ASARCO	48 (0.295)	2.652	0.230	1.76	16.26
2/12/05	ASARCO	100 (0.147)	2.555	0.113	1.24	15.93
1/30/05	ASARCO	200 (0.074)	2.603	0.053	0.50	24.68
2/26/05	RP	48 (0.295)	1.414	0.251	2.79	14.18
3/4/05	RP	100 (0.147)	1.414	0.121	1.53	15.48
3/4/05	RP	200 (0.074)	1.414	0.063	0.76	20.66

SEM/EDX/MLA Analysis
(150 um Asarco Slag Before)

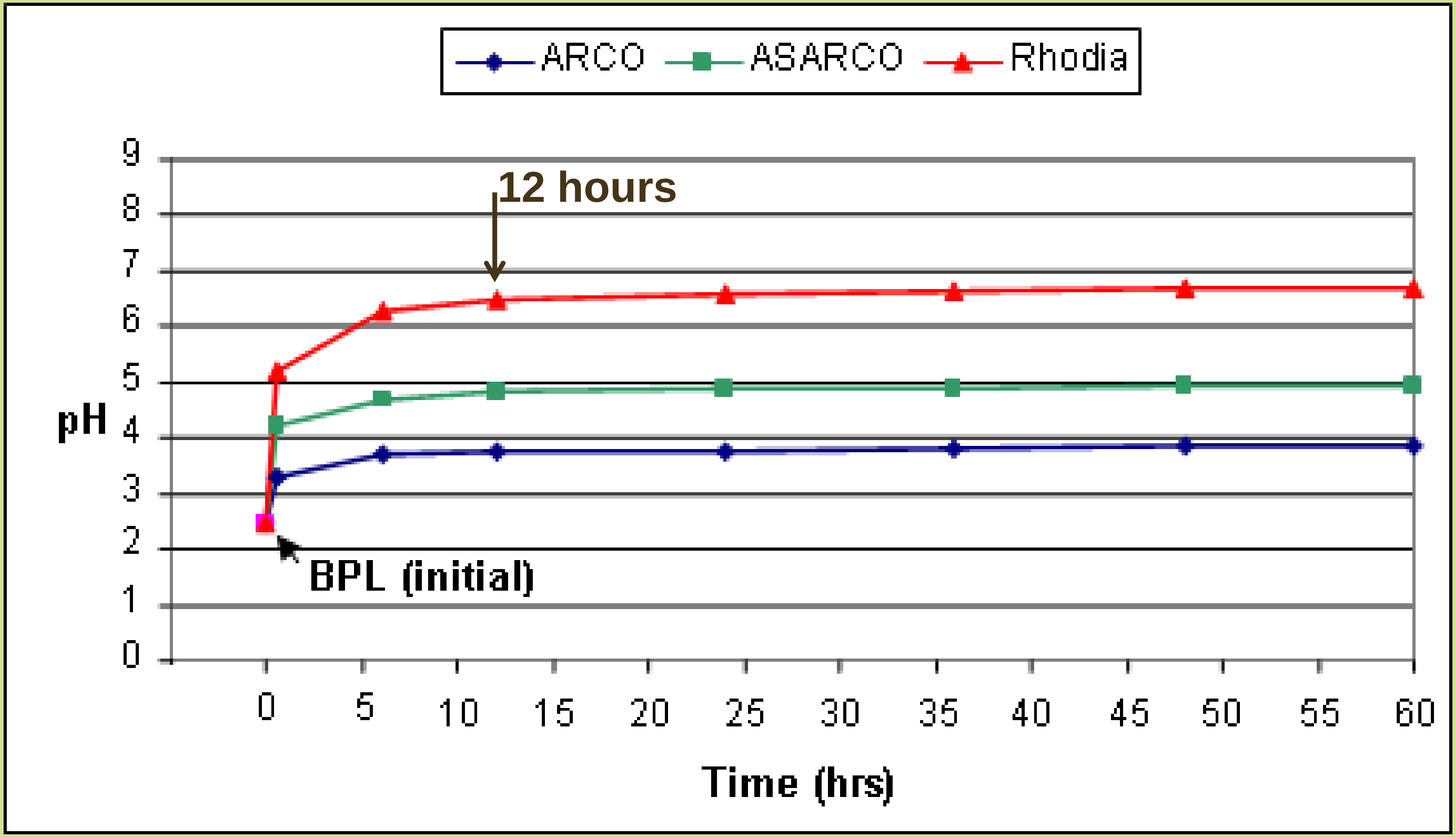


SEM/EDX/MLA Analysis
(150 um Asarco Slag After)



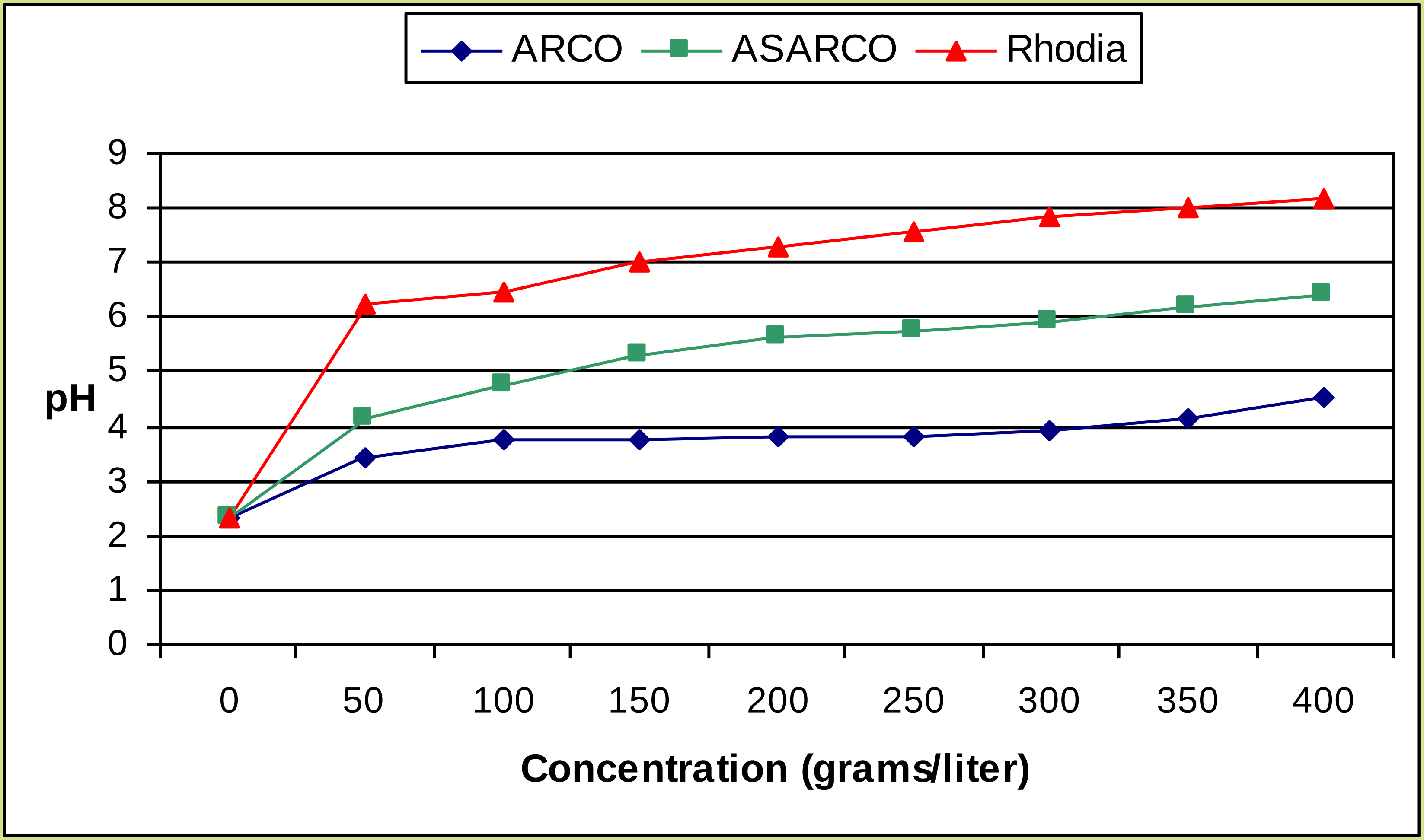
Remediation Potential
(Bottle Roll Tests)

Size = 53 um; Amount = 100 g/L



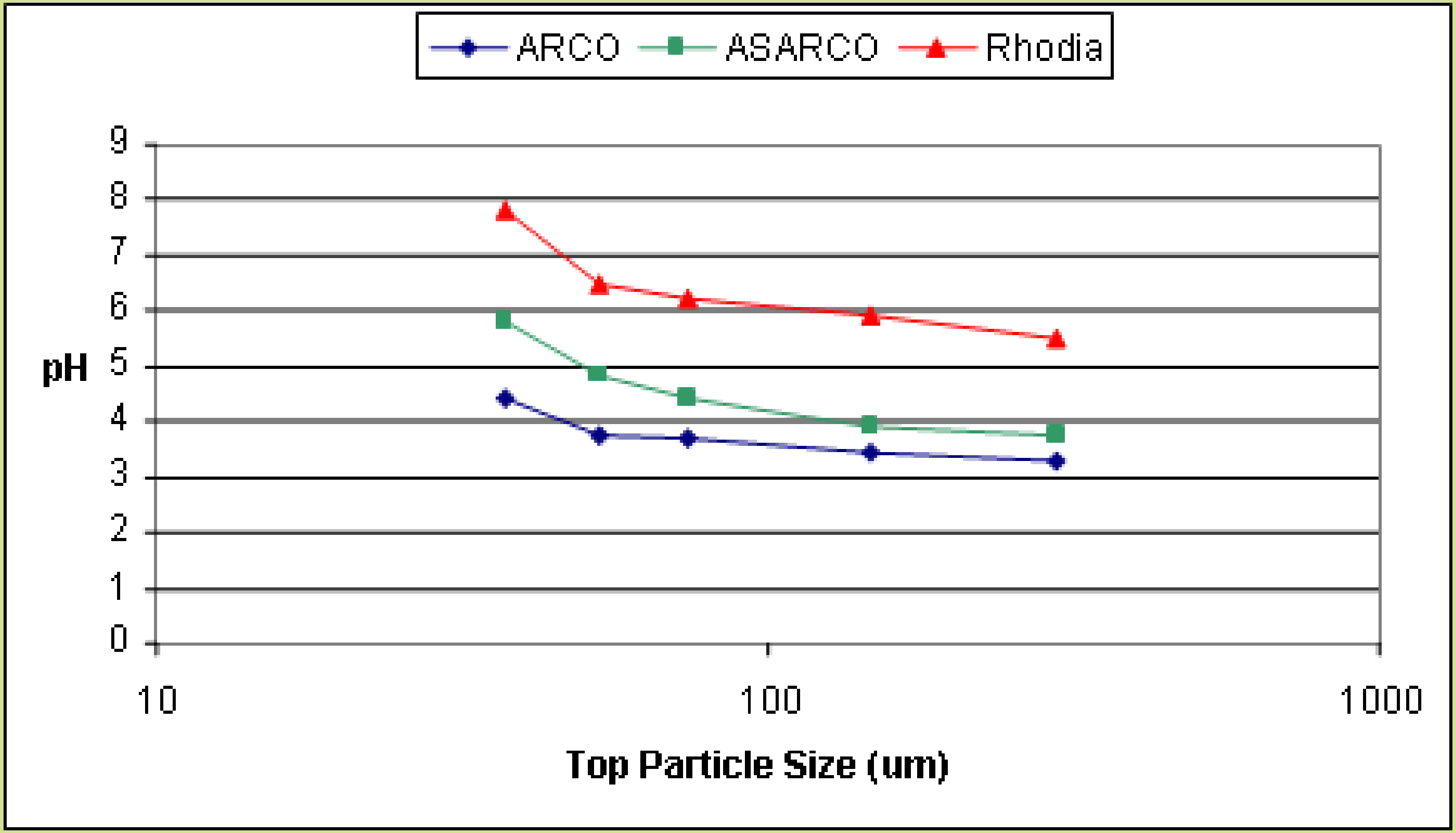
Remediation Potential
(Bottle Roll Tests)

Size = 53 um; Time = 12 hrs



Remediation Potential
(Bottle Roll Tests)

Amount = 100 g/L; Time = 12 hrs



StatEase Design of Experiments
(Box-Behnken Matrix)

Run	Slag Type (Fe/Si Ratio)	Particle Size (μm)	Slag Amount (g/L)
1	0 = Rhodia	-37 = 400 mesh	500
2	2 = ARCO	-37	500
3	0	-147 = 100 mesh	500
4	2	-147	500
5	0	-74 = 200 mesh	200
6	2	-74	200
7	0	-74	800
8	2	-74	800
9	1 = ASARCO	-37	200
10	1	-147	200
11	1	-37	800
12	1	-147	800
13	1	-74	500
14	1	-74	500
15	1	-74	500

Test Run	pH	Al	As	Cd	Cu	Fe	Mn	SO_4^{2-}	Zn
	BPL Concentrations (mg/L)								
	2.5	289	0.15	2.1	168	793	276	2723	621
	Final Responses (mg/L)								
1	9.08	0.043	0.0025	0.002	0.19	0.29	4.42	829	0.24
2	5	6.32	0.09	2.1	2.26	95	276	1980	621
3	7.77	0.20	0.001	0.034	0.063	0.069	57.8	1075	2.02
4	5.19	11.6	0.09	1.69	34.2	772	276	2210	621
5	7.68	0.20	0.0008	0.055	0.136	0.096	83.7	619	3.84
6	4.55	37.8	0.15	2.1	168	793	268	2450	621
7	8.42	0.041	0.001	0.002	0.179	0.014	5.13	879	0.11
8	5.52	0.37	0.039	1.13	0.566	271	276	1720	531
9	5.62	1.39	0.0049	1.03	0.39	6.99	266	1680	601
10	4.74	26.1	0.021	1.57	18.05	595	265	2045	621
11	6.89	0.20	0.0014	0.059	0.095	0.069	181	1270	24.1
12	6.16	0.444	0.0023	0.38	0.141	2.37	248	1395	212
13	6.02	0.62	0.0023	0.44	0.174	4.77	250	1410	278
14	6.08	0.53	0.0023	0.42	0.139	3.76	248	1410	254
15	6.08	0.51	0.0022	0.45	0.277	3.67	252	1450	257
	Drinking Water Standards (mg/L)								
	6.5 - 8.5	0.05	0.01	0.005	1.3	0.3	0.05	250	5

StatEase Model Equations

A = Fe/Si Ratio (0-2); B = Size (um); C = Amount (g/L)

$pH = 8.31 – 3.49A – 0.0012B + 0.0018C + 0.006AB + 0.7A^2$

$Log [H] = -8.31 + 3.49A + 0.0012B – 0.0018C – 0.006AB – 0.7A^2$

$Log [Al] = 2.05 + 1.44A + 0.0063B – 0.0011C – 0.0011AC$

$[As]^{0.5} = 0.39 + 0.48A + 0.0015C – 0.006AC + 3.35A^2$

$[Cd]^{0.5} = 16.77 + 20.36A – 0.027*C$

$Log [Cu] = 2.29 + 0.17A + 0.0074B – 0.0019C + 0.0083AB – 0.0023AC – 0.00002BC + 0.59A^2 + 0.0000038C^2$

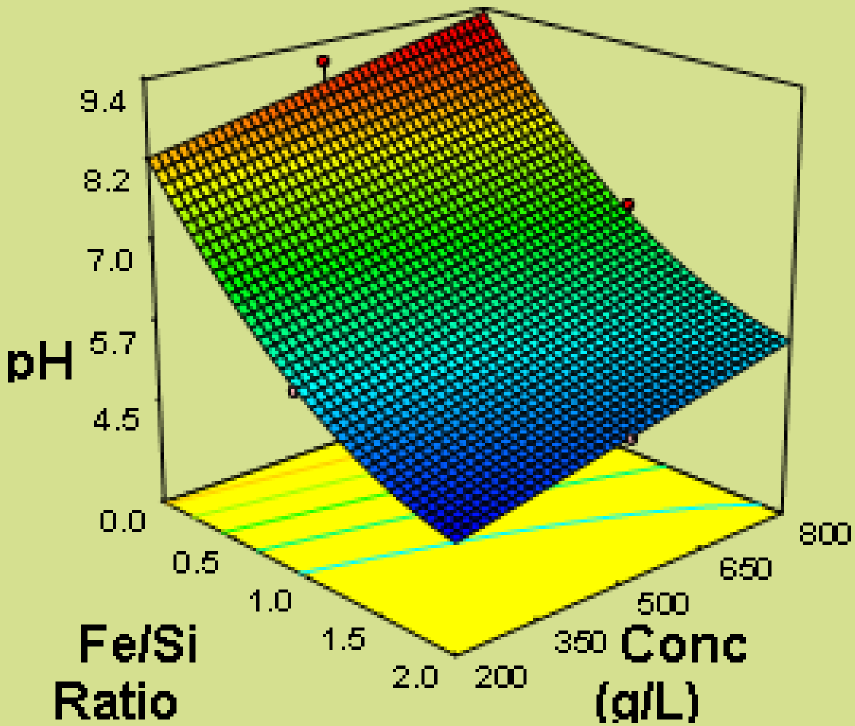
$Log [Fe] = 2.1 + 1.95A + 0.0099B – 0.0025C$

$[Mn] = 738886 + 26555A + 252B – 127C + 63.5AC – 86310A^2$

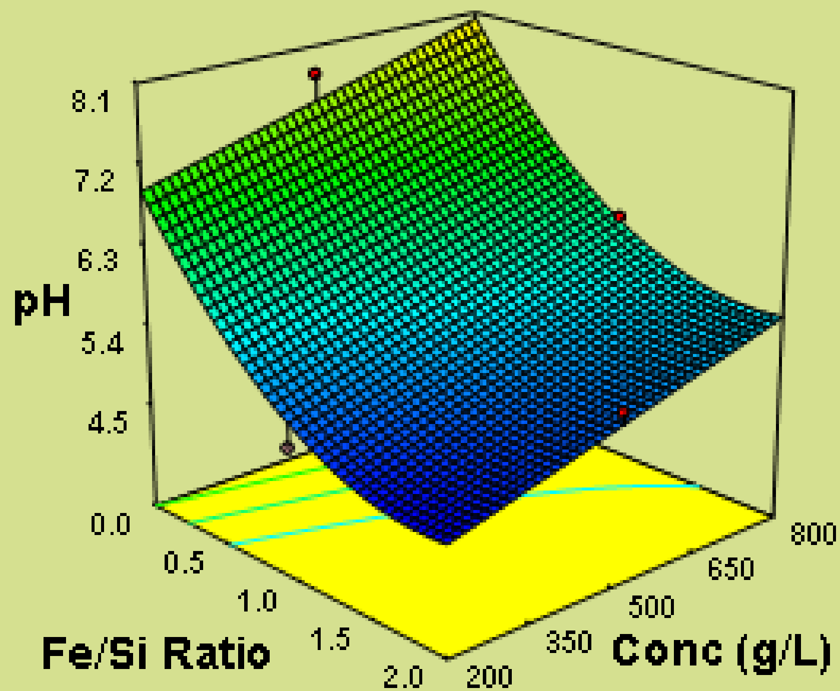
$[Zn]^{0.5} = 315.4 + 420A – 0.49C$

StatEase Model Plots

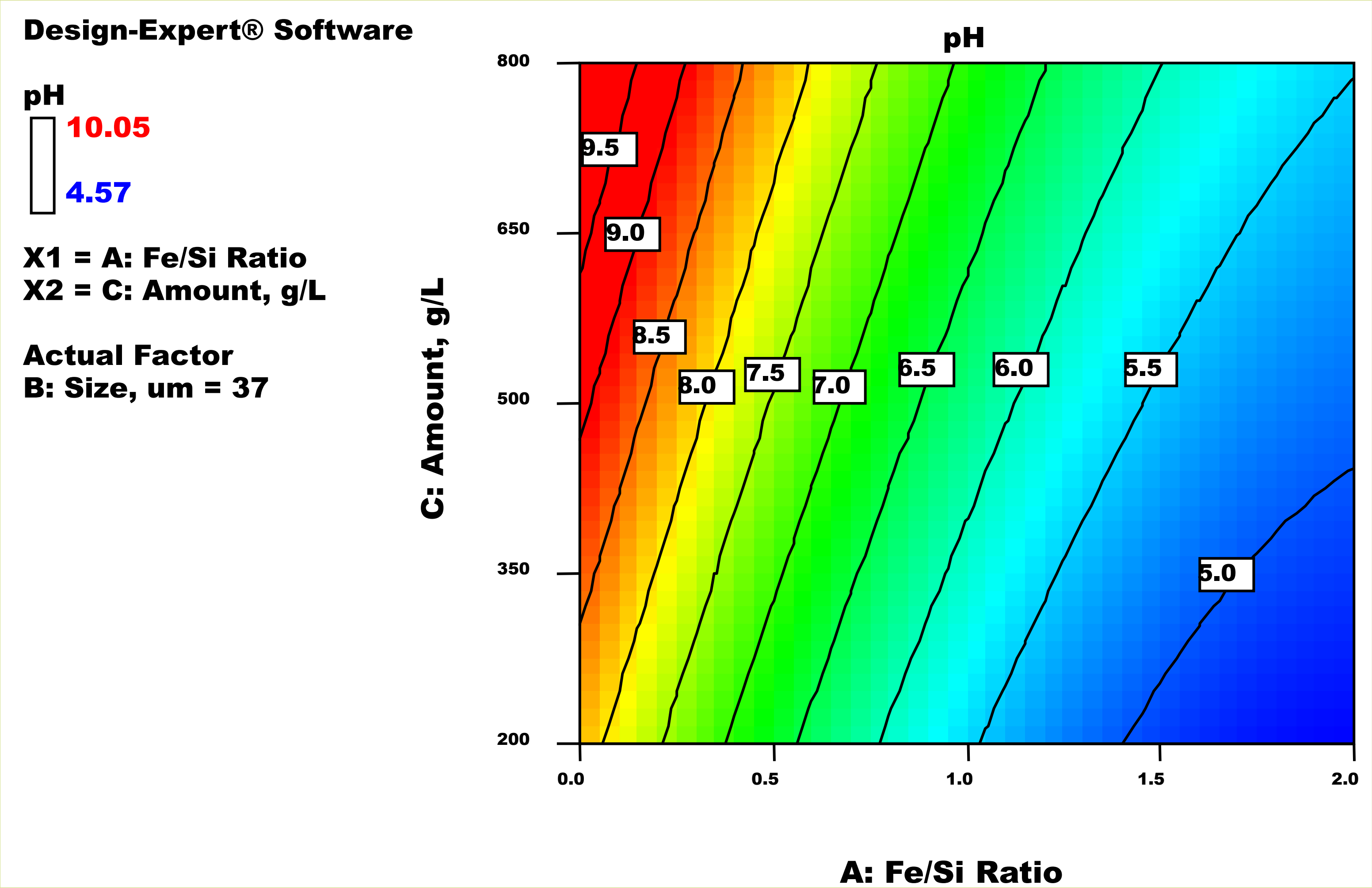
Size = 37 µm



Size = 147 µm

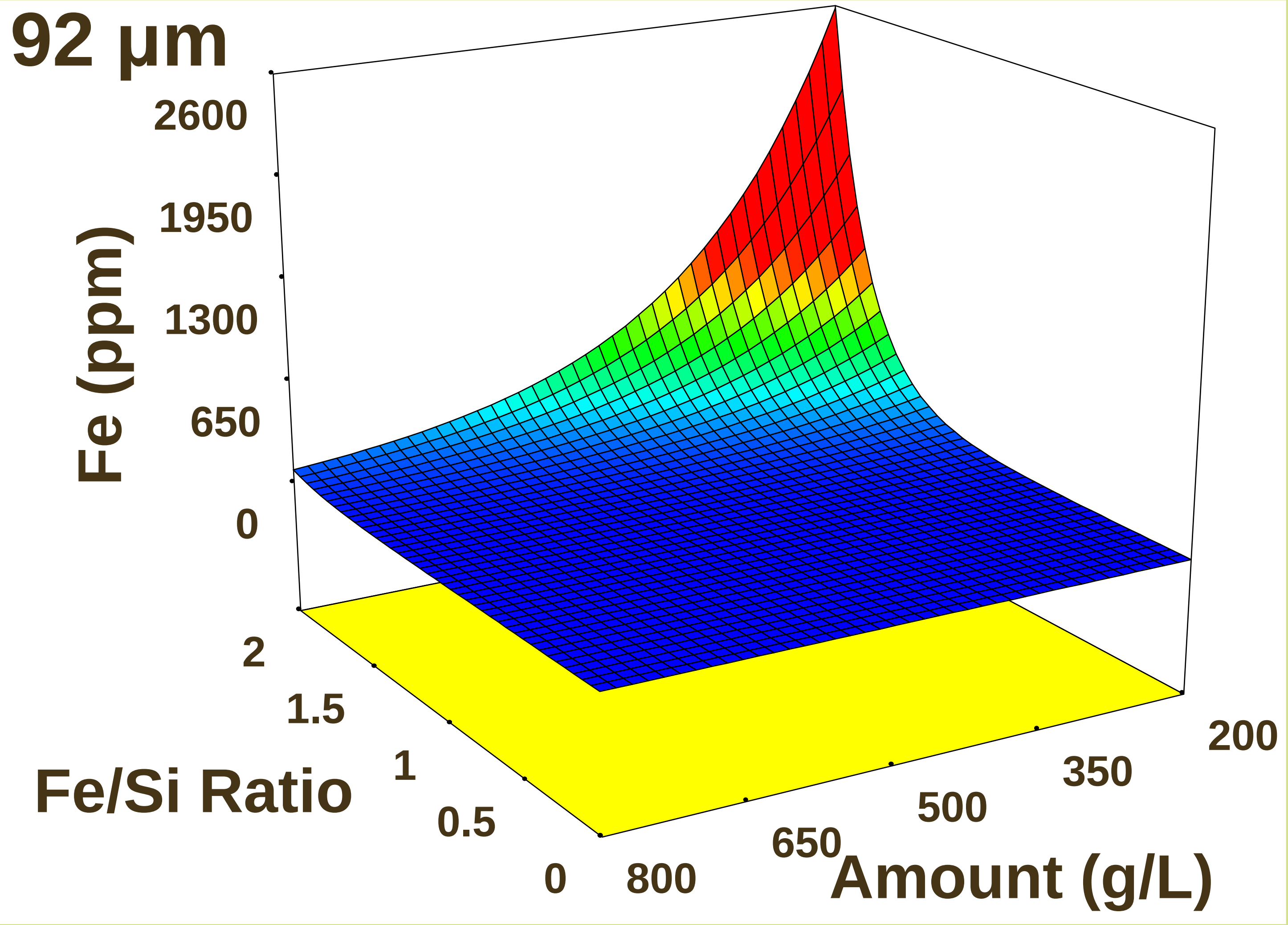


StatEase Model Plots

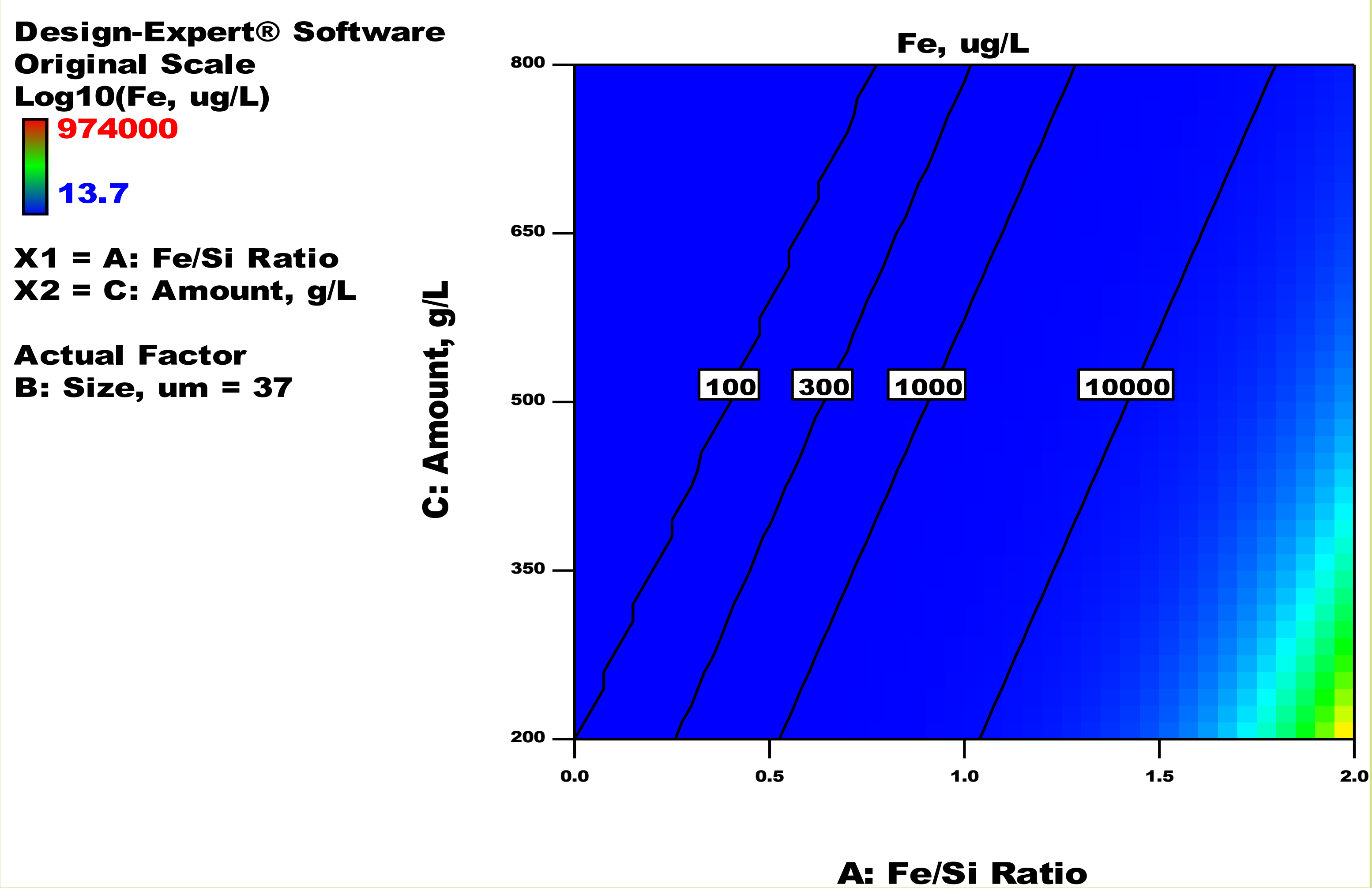


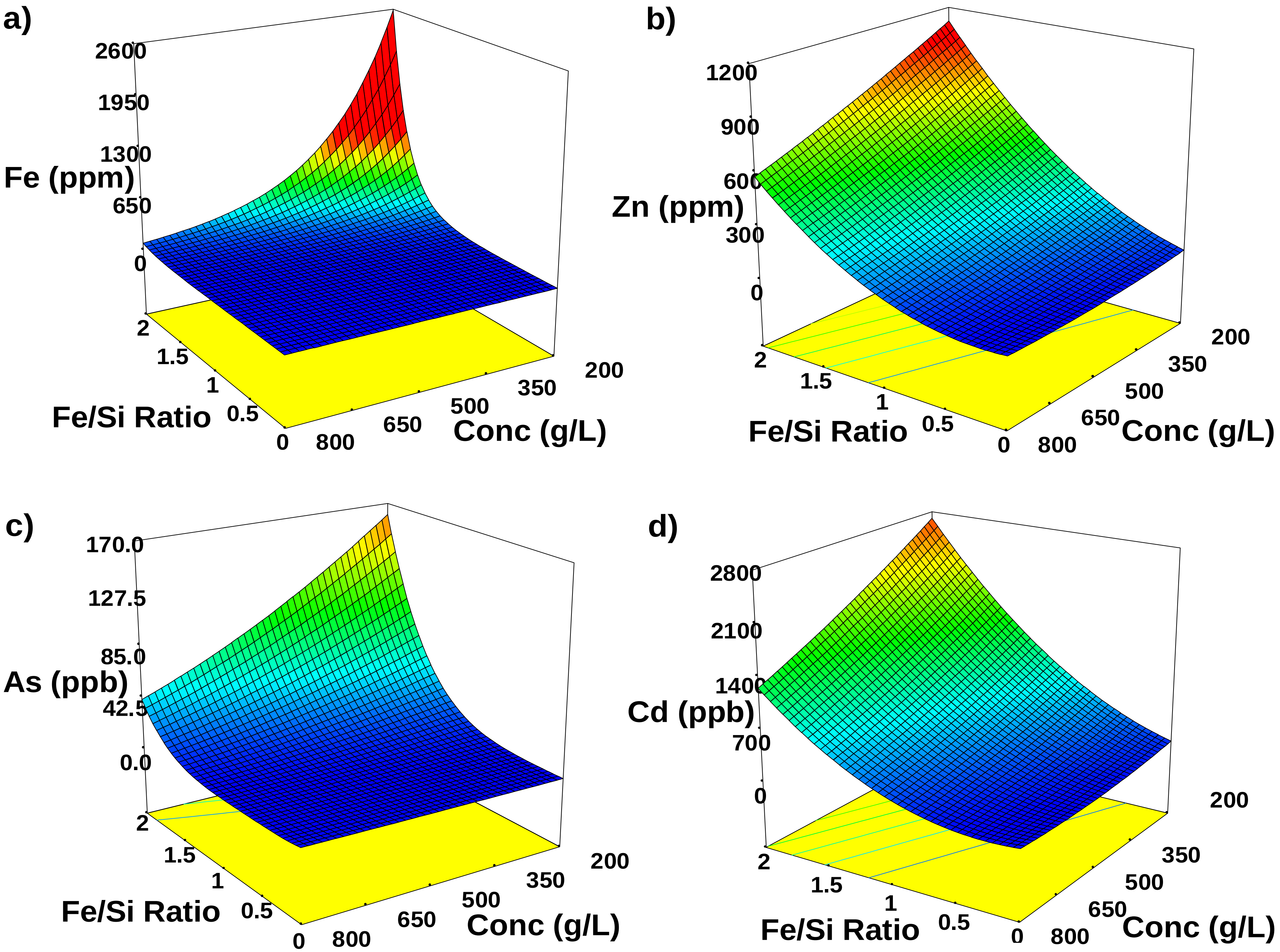
StatEase Model Plots

Size = 92 µm



StatEase Model Plots




a)
Fe (ppm)
2600
1950
1300
650
0
Fe/Si Ratio
2
1.5
1
0.5
0
Conc (g/L)
800
650
500
350
200
b)
Zn (ppm)
1200
900
600
300
0
Fe/Si Ratio
2
1.5
1
0.5
0
Conc (g/L)
800
650
500
350
200
c)
As (ppb)
170.0
127.5
85.0
42.5
0.0
Fe/Si Ratio
2
1.5
1
0.5
0
Conc (g/L)
800
650
500
350
200
d)
Cd (ppb)
2800
2100
1400
700
0
Fe/Si Ratio
2
1.5
1
0.5
0
Conc (g/L)
800
650
500
350
200

Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- ✓ Objectives
- ✓ Procedures
- ✓ Results & Discussions
- Conclusions
- Acknowledgements

Conclusions

- ✓ **Slags can be an effective for remediating ARD**
- ✓ **Their use could or will:**
  replace lime (pseudowollastonite slag)
  diminish lime consumption (fayalite/olivine)
  lead to remediation of two ecosystems
- ✓ **Depending on the slag type and particle size:**
  effluent pH from 5-9 can result
  effluent concentrations can meet DWS
- ✓ **Al and Cu concentration profiles are similar to Fe**
- ✓ **Likewise, Al and Cu redissolution at high pH is minimal similar to Fe**

Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- ✓ Objectives
- ✓ Procedures
- ✓ Results & Discussions
- ✓ Conclusions
- Acknowledgements

Acknowledgements

This research was previously funded by the MWTP via an Interagency Agreement (IAG) between the U.S. EPA and the U.S. DoE, IAG No. DW89935117-01-0.

Thanks are also extended to the Department of Metallurgical & Materials Engineering at Montana Tech for bearing the costs for some analyses and the MBMG for helping collect samples: James Madison and Ted Duaime.

Sincere appreciation is given to the workforce who have worked on these projects over the years. MS students included Ray Ziolkowski, Tom McMillan, Yu Chuan Tai, Eric Streich and Krag Filius. BS students include Sonny Adams, Jennifer Gambill and Brian Ross.

We are always on the lookout for funding Series VI to ∞!

Outline

- ✓ Berkeley Pitlake
- ✓ Previous Research
- ✓ Silicate Slags
- ✓ Objectives
- ✓ Procedures
- ✓ Results & Discussions
- ✓ Conclusions
- ✓ Acknowledgements

Thanks For Your Attention!

MONTANA TECH
De Re Metallica
THE UNIVERSITY OF MONTANA

U.S. EPA Hardrock Mining Conference
(Advancing Solutions for a New Legacy)
Denver CO April 3-5, 2012

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY