Accelerated Ferrous Oxidation with a Multiple Orifice Spray Reactor

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in cooperation with

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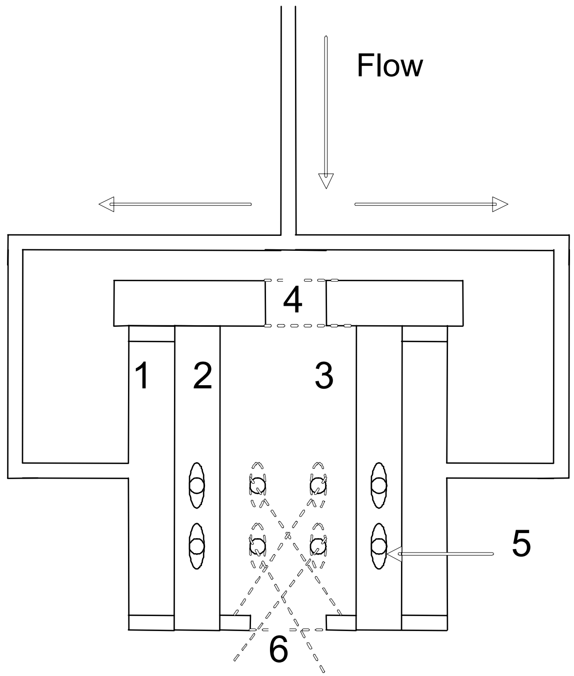
Background

- Focus on an innovative active treatment of ferrous iron containing AMD
- Application: to mine-mouth systems, land-limited locations, potential mine-pool "blow-out" locations

Nature of Technology

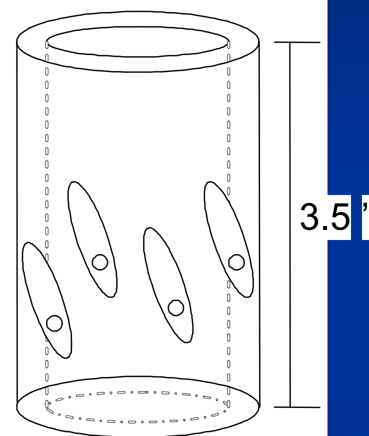
- **Multiple Orifice spray reactor: a system containing multiple "venturi-type" orifices that allow high-rate oxidation and aeration.**

Schematic of Laboratory Scaled Multiple Orifice Reactor

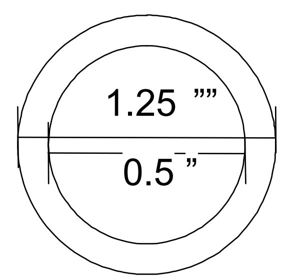


MOSR Cross Section

1 – Annulus
2 – Inner cylinder
3 – Reaction Zone (center of 2)
4 – Alkaline Agent Feed, suction port
5 – Angled orifice
6 – Discharge port



MOSR Inner cylinder



Top View of Inner Cylinder

Laboratory MOSR

Prototype Turbojett® - MOSR

External Design

Internal Design

Laboratory Development

- Purpose:
  - Understand the enhanced kinetics of ferrous iron oxidation by the MOSR;
  - Application of the MOSR to St. Michaels Acid Mine Drainage
  - Evaluate potentials for iron reclamation when using MSOR oxidation

Ferrous Iron Oxidation

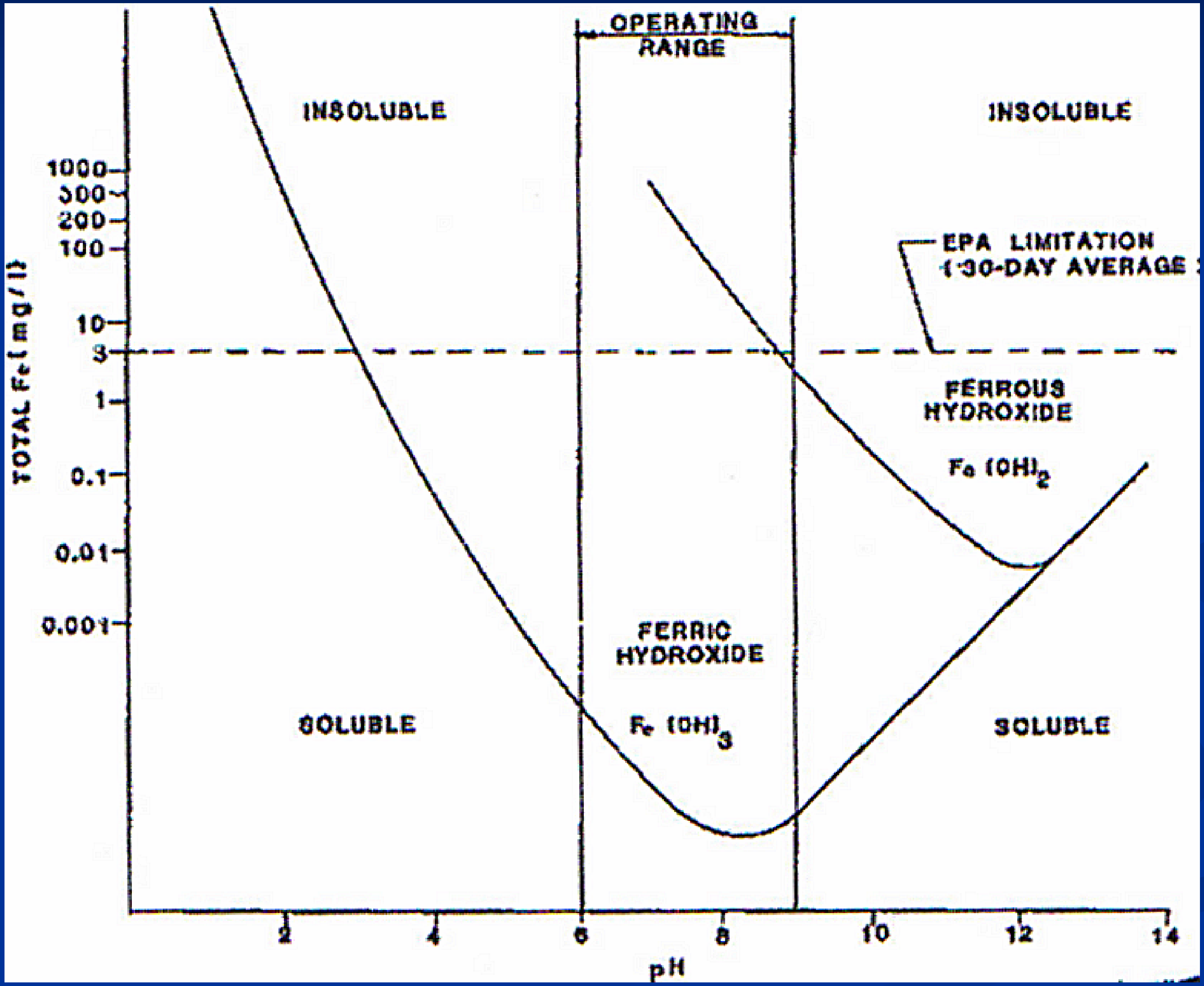
Ferrous iron oxidation forms ferric iron

- $Fe^{+2} + \frac{1}{4}\ O_2 + H^+ \rightarrow Fe^{+3} + \frac{1}{2}\ H_2O$

At a pH of about 4, ferric ion forms ferric hydroxide with minimum solubility ~ pH = 8

- $Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Iron Equilibrium



Thermodynamics vs. Kinetics

- Equilibrium tells you what will happen
- Kinetics tells you how the rate of reactions (how fast it gets there)

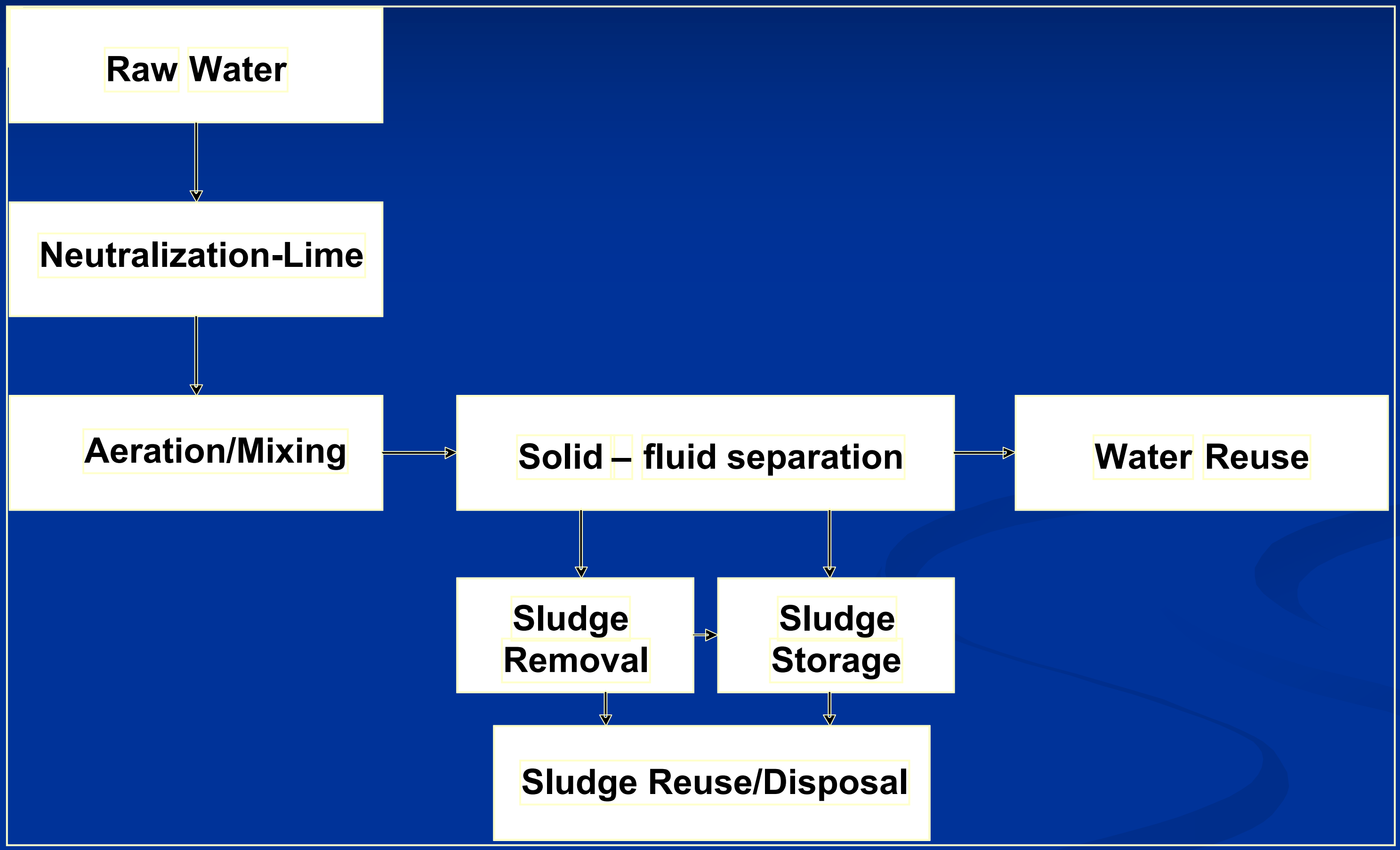
Generally Accepted Ferrous Iron Oxidation Kinetics

- $-d[Fe(II)]/dt = k[OH^-]^2 P_{O2}[Fe(II)]$

  \- as the pH increases by one unit, the rate of ferrous iron conversion increases 100 fold;

  \- the rate of ferrous iron oxidation is proportional to the "partial pressure" of oxygen, or O_2 concentration in water ["DO"]

Conventional AMD Technology



Conventional Technology-Limitations

- Common to use of lime for AMD management;
  - Inexpensive alkaline agent
  - Operators often allow pH values to be >>8 to accelerate ferrous oxidation kinetics
  - Need to neutralize high pH waters prior to discharge
  - Need to dispose of large volumes of lime containing ferric hydroxide sludge

Cost Elements: **lime, acid, electricity,**

sludge dewatering & disposal

Use of a MOSR

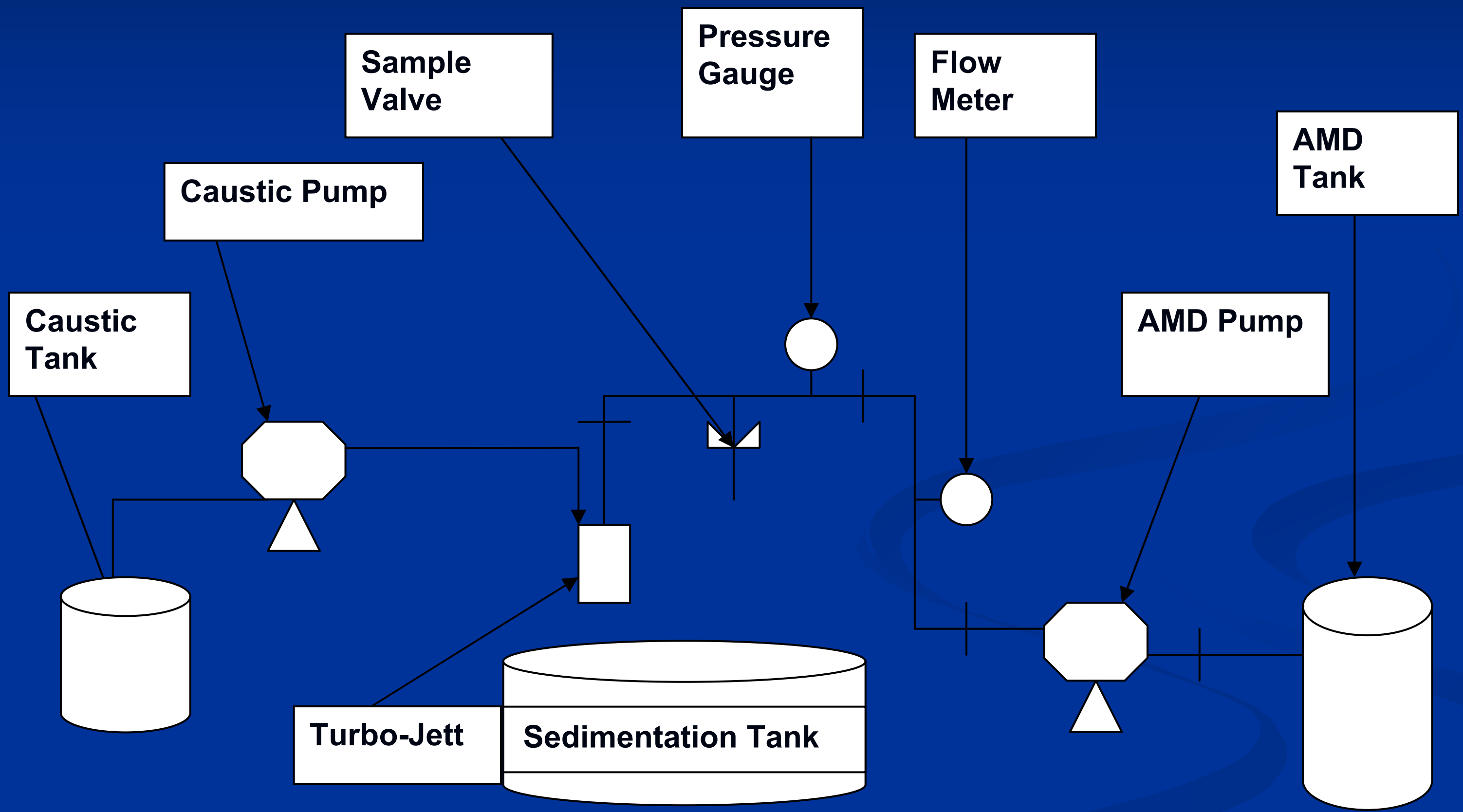
- Accelerate the apparent rate of ferrous ion oxidation;
- Controlled use of alkaline agent so that residual pH is controlled to design discharge levels without further acid-neutralization;
- Enhanced oxidation of ferrous iron suggesting alternative mechanisms taking place.

Pitt Acid Mine Drainage Research
St. Michaels, PA

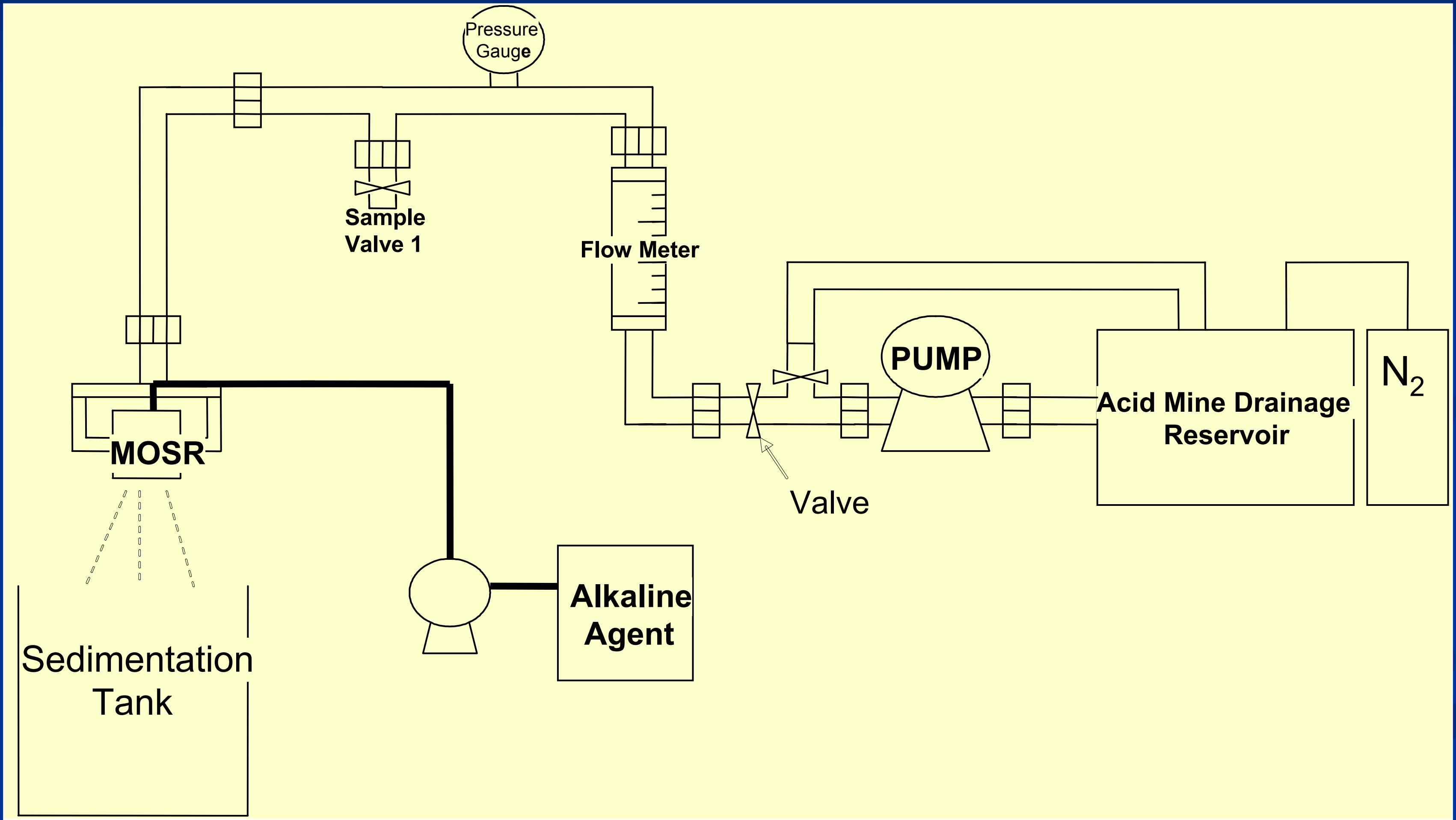
St. Michaels AMD Discharge

Students Sampling

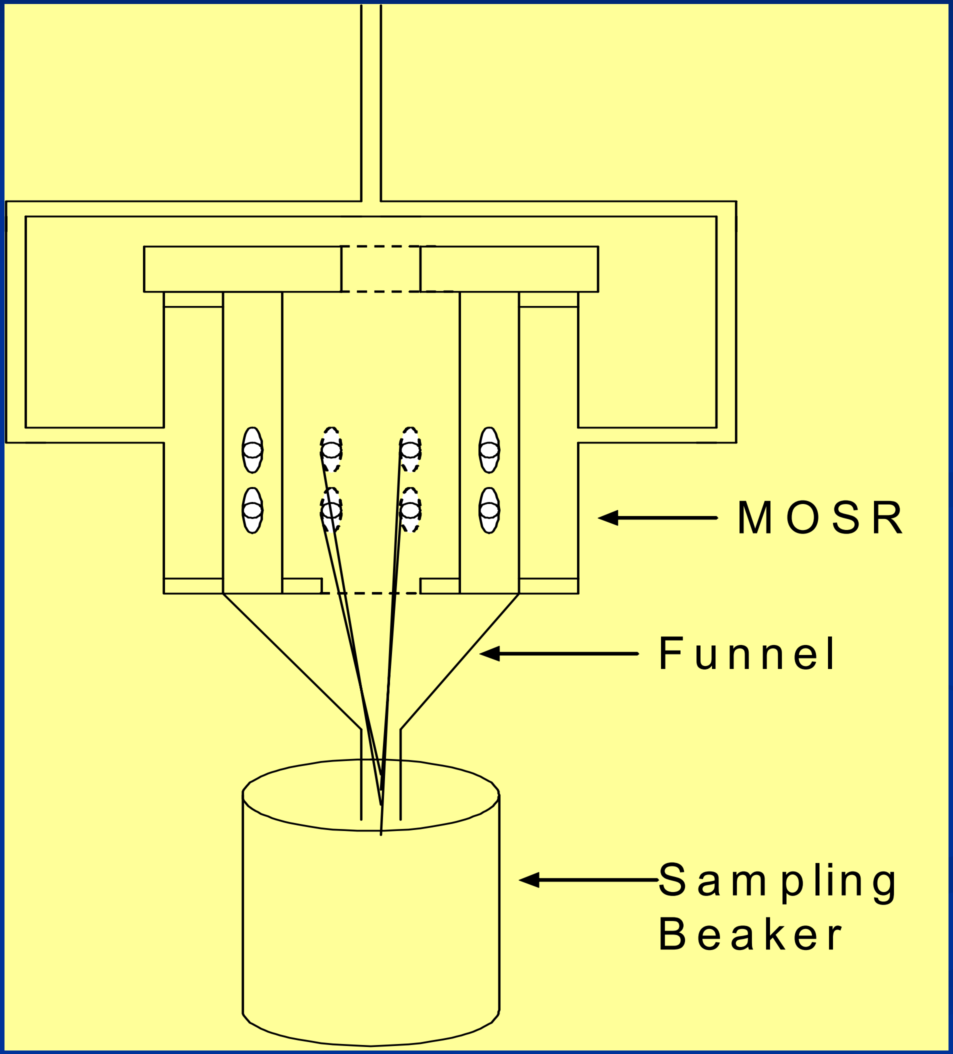
Experimental Set-up



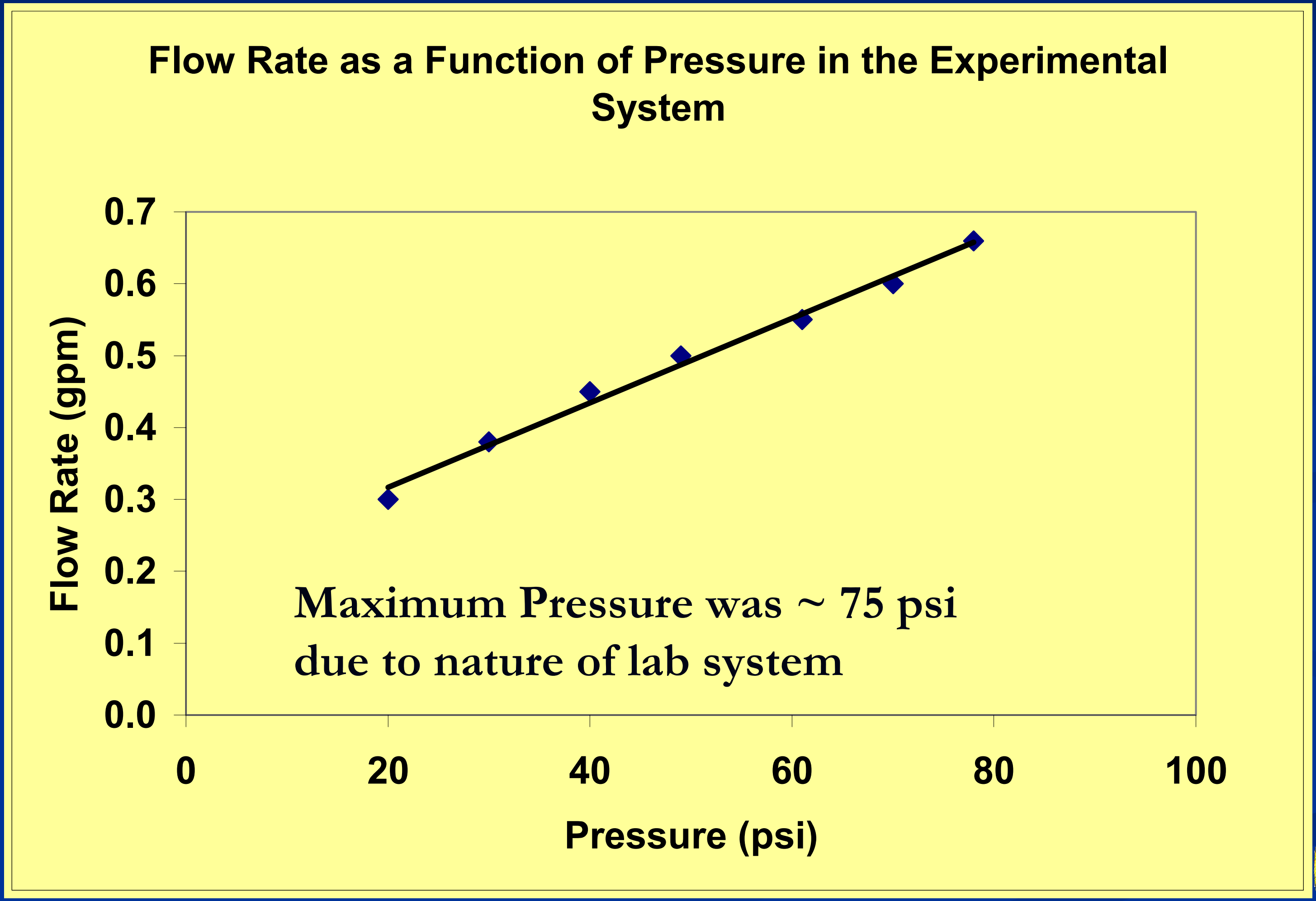
Experimental Set-up



Bench Sampling Scheme to minimize air entrainment

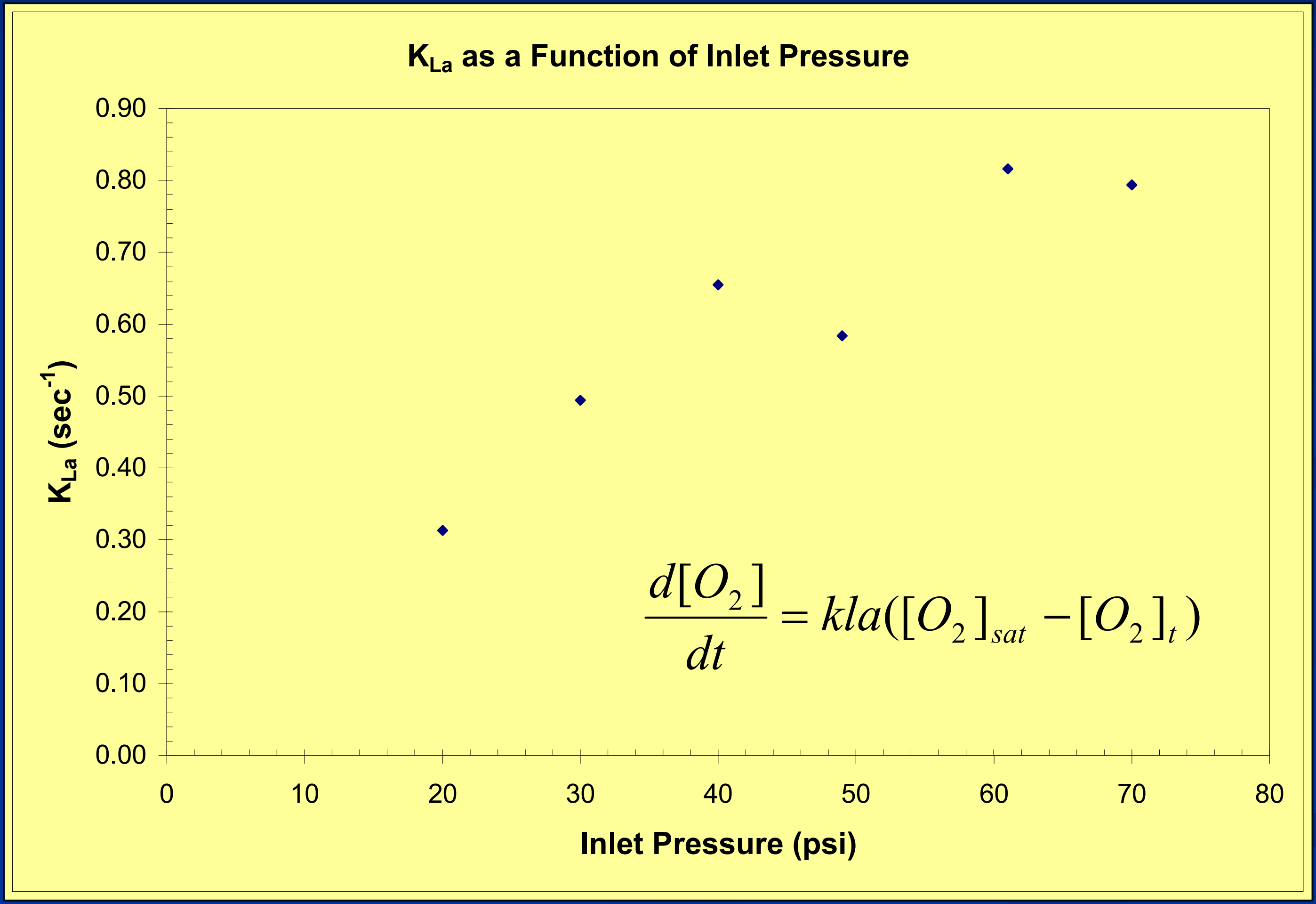


Results-Bench System

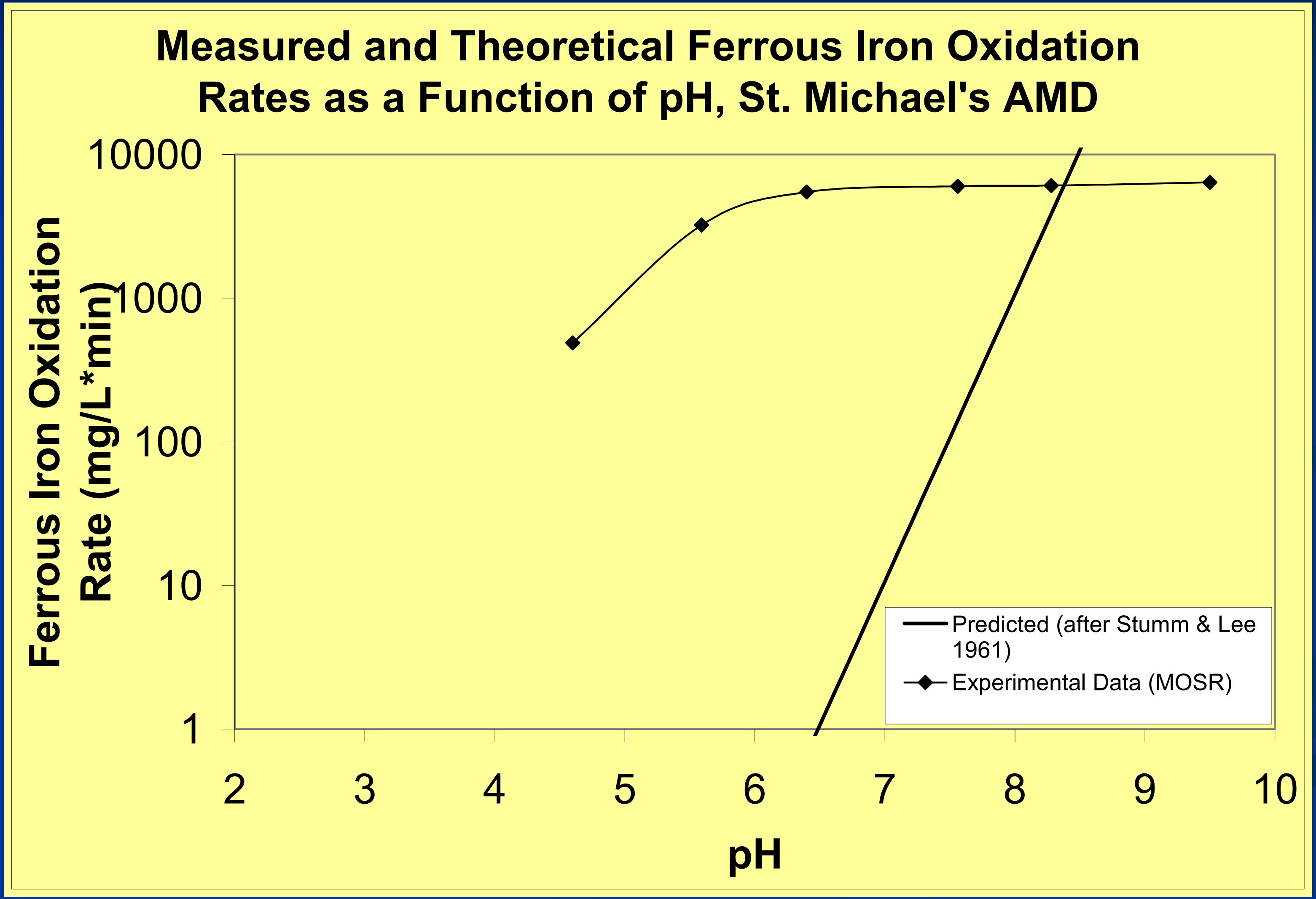


$$\frac{d[O_2]}{dt} = ko_2([O_2]_{sat} - [O_2]_t)$$

Gas Transfer Coefficient (k_{la}) varies with inlet pressure



Results – Bench System

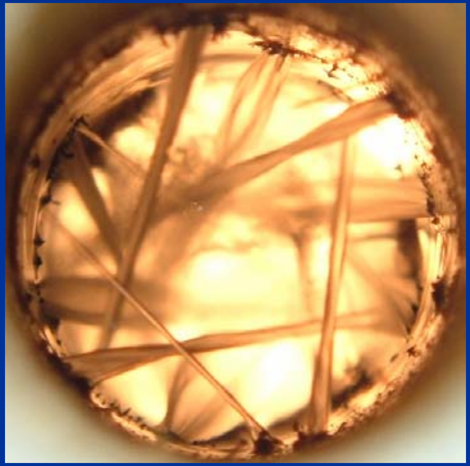


Observations Bench Unit

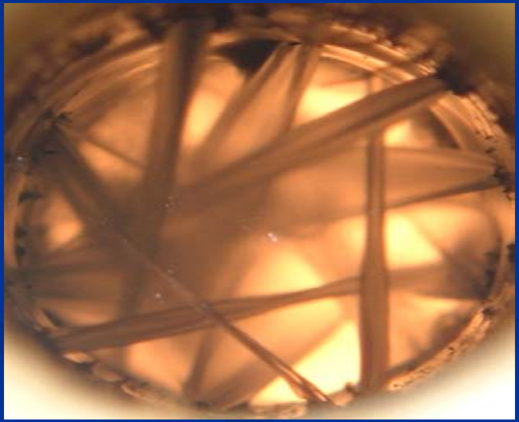
- At discharge values of pH < 8, the measured ferrous ion oxidation & conversion rates are greater when using the MOSR than predicted from the literature.
- At discharge pH values of 6.5 -7, the apparent rate of conversion is ~ 4 orders of magnitude greater than predicted from the literature.

Enhanced Rates of Iron Conversion Flow Patterns looking inside reactor

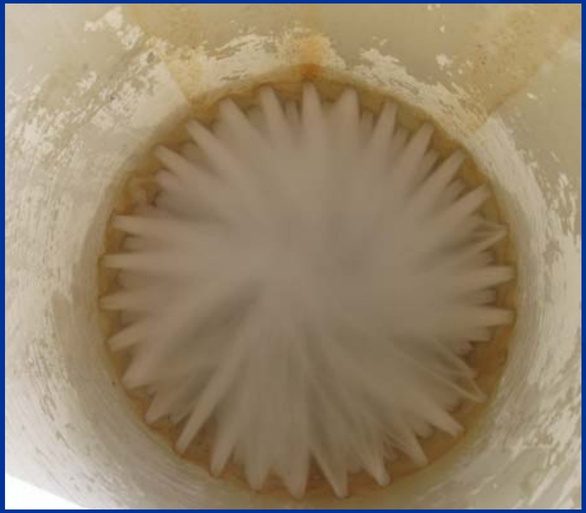
10 psi – Bench Unit



60 psi Bench Unit



Field Scale Turbojett



Exiting Spray Patterns (bench unit)

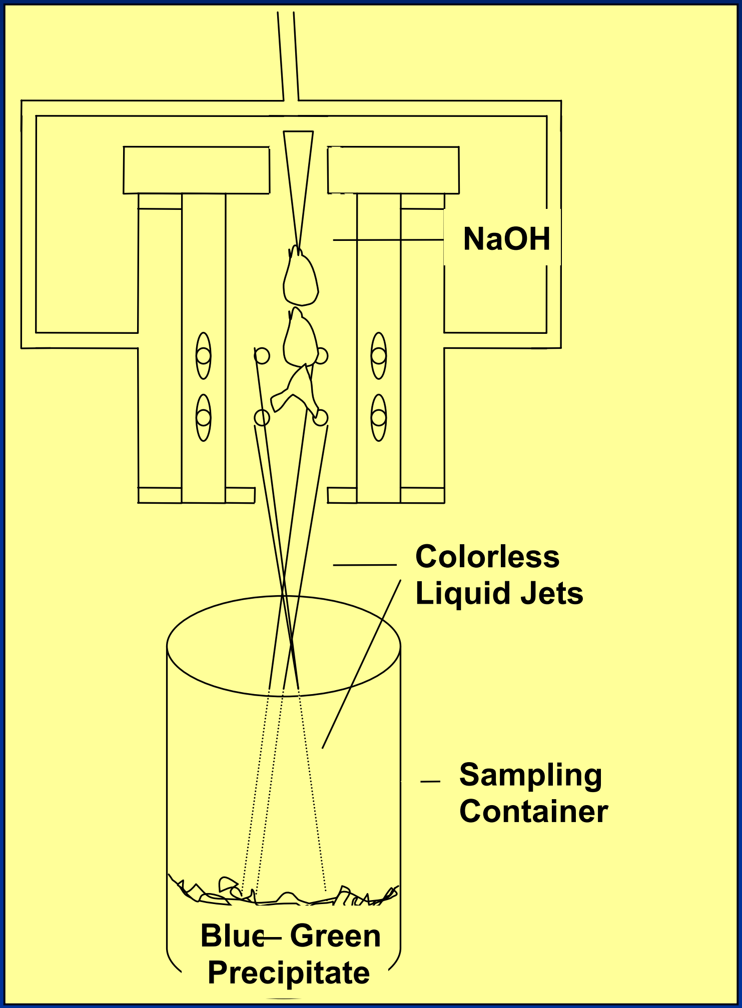
10 psi

60 psi

Possible Mechanisms

1. Localized high pH within the MOSR causing elevated reaction kinetics.
2. Cavitations taking place causing formation of free radicals that rapidly oxidize ferrous ion to the ferric form;
3. Cavitation resulting in gas phase reactions.

Experimental Observations



1. Blue-Green Precipitate initially forms within sampling container.
2. Precipitate settles rapidly.
3. Precipitate turns rust-colored red within the next few minutes within the sampling container.

Field Observations Turbojett® with PPC Corp.

Operating Turbojett®

Ferric Hydroxide
Precipitating within Basin

Field Observations Turbojett® with PPC Corp. (2)

Precipitation within Basin

At the end of the day

Conclusions

- The rate of ferrous iron oxidation in the MOSR is much greater than in control samples which reflect conventional active treatment technologies.

- The oxygen transfer rates of the MOSR were evaluated. The results show that k_{la} increases as a function of pressure. It was also shown that virtually all of the mass transfer takes place inside of the inner cylinder of the MOSR.

Conclusions (continued)

- The MOSR greatly increases ferrous iron oxidation rates above theoretical limits by relatively high mass transfer rates of oxygen due to multiple orifices. At an effluent pH of 6.5 the MOSR oxidizes ferrous iron to ferric iron at a rate about 4 orders of magnitude higher than theoretically predicted.

Conclusions (3)

- Cavitation may be playing a controlling role.
  - Cavitation can produce free oxidative radicals
  - Cavitation can produce a vapor phase within the MOSR core: gas phase mass transfer rates are considerable higher than liquid phase rate;
- In addition, oxidation ferrous iron may continue to take place during the “time of flight” of the discharge spray.

Conclusions (4)

- The MOSR is an effective remediation technology for the treatment of acid mine drainage. Due to the MOSR's unique geometrical configuration there is an increased oxidation potential and consequent ferrous iron oxidation. Increased rates are due to: a larger surface area resulting from liquid flow through an orifice; oxidation due to the effects of hydrodynamic cavitation; and a probably inherent vapor phase reaction.

Suggestions for Further Work

- Fundamental work to improve the technology and transfer it to the private sector:
  - Solids settling, dewatering & drying
  - Kinetic modeling and applications to design
  - Differential metal speciation and recovery

Suggestions for Further Work

- Field prototype work to obtain design information for commercial installations and economic O&M cost data.
  - Optimization of chemical and energy costs;
  - Field metal recovery;

Suggestions for Further Work

- Coordination of field and bench research, development and demonstration.
  - Multiple "independent variables" to be studied at the bench scale;
  - Most favorable variables demonstrated in the field.


Thanks for
your attention
Questions ?