# SULFUR-MODIFIED IRON (SMI) PROCESS FOR ARSENIC REMOVAL[1]

by

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Abstract: Many waters associated with mining and mineral processing contain high concentrations of arsenic, and effluent typically must meet increasingly stringent human health standards. A new proprietary technology for arsenic removal has been developed by Peter F. Santina to cost-effectively meet these discharge limits. Hydrometrics, Inc. has performed, under contract to Peter F. Santina, further lab tests to prove and test limits of the efficacy of the process. In the sulfur-modified iron (SMI) process, arsenic is removed by an iron/sulfur matrix. Arsenic concentrations below 0.005 mg/L have been obtained using SMI in jar tests and column tests, and the iron/sulfur residue has passed the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) test. A 10-gpm federally-funded pilot test is underway to further develop this promising technology. The purpose of pilot testing is to identify specific design parameters and operational procedures which can be used for full-scale production application of the SMI process. Projected operating costs for SMI are lower than alternative arsenic removal technologies such as iron salt addition, reverse osmosis and activated alumina. Cost savings would increase proportionally with higher flow rates and higher arsenic concentrations. The SMI process is potentially very promising for simple, cost-effective treatment of mining and other industrial effluents, drinking water and other arsenic-containing waters.

Additional Key Words: zero-valent iron, arsenate, arsenite, drinking water

## Introduction

Many waters associated with mining and mineral processing contain high concentrations of arsenic, and effluent typically must meet stringent discharge standards which are lower than the federal drinking water standard of 0.05 mg/L. In addition, EPA is required by the 1996 revised Safe Drinking Water Act to enact a new drinking water standard for arsenic by January 1, 2001. A National Academy of Sciences report commissioned by the EPA recently recommended lowering the standard of 0.05 mg/L. Arsenic human health standards are based upon EPA risk factors of $10^{-4}$ to $10^{-5}$ in most states. As a result, arsenic human health standards in most states are one to two orders of magnitude lower than the drinking water standard, which poses a significant problem for mines and other water-discharging industries.

From all the evidence gathered to-date, the proprietary SMI process (Santina 1996, 1999) is a very promising technology to cost-effectively meet these stringent arsenic limits. The process potentially has the following advantages compared to alternative processes such as iron hydroxide precipitation (iron salt addition):

1. Can produce treated water containing less than 0.005 mg/L;
2. Expected to have lower operating and capital costs; and
3. Can produce waste products which are nonhazardous and lower in volume.

Successful SMI column tests were the basis for a matching federal grant of $74,000 from the Montana Water Center to further explore the technology. The grant is funding a 10-gpm pilot test which is presently being conducted using drinking water which contains naturally high concentrations of arsenic (greater than 0.05 mg/L) in the Reno, Nevada area. The purpose of the pilot test is to identify specific design parameters and operational procedures leading to successful full-scale application of the SMI process. Pilot test data will be presented at the conference as it is available. After successful demonstration of the SMI process at the pilot scale, its use will be seriously

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[1] Paper presented at the 1999 National Meeting of the American Society for Surface Mining and Reclamation, Scottsdale, Arizona, August 13-19, 1999.

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Proceedings America Society of Mining and Reclamation, 1999 pp 551-556
DOI: 10.21000/JASMR99010551

https://doi.org/10.21000/JASMR99010551

considered at several production-scale drinking water facilities in Nevada and California.

## Technology Description

In the sulfur-modified iron (SMI) process, an iron/sulfur slurry is contacted with arsenic-contaminated water. Arsenic is believed to precipitate directly onto the sponge iron or coprecipitate with iron hydroxide.

After initial testing, the SMI process appeared to be applicable for treatment of mining, mineral processing, industrial or drinking waters to obtain very low arsenic concentrations. Hydrometrics, under contract to Pete Santina, evaluated and further tested the SMI process beginning in 1997, in order to compare treatment effectiveness and costs to those of existing technologies for arsenic removal. Jar tests and continuous-flow column tests were performed on mine effluent and simulated mine effluent containing different concentrations and oxidation states of arsenic.

## Jar Tests

Bench-scale experiments were performed in Hydrometrics' laboratory to determine adsorption isotherms at pH values of 7 and 8. Adsorption isotherms generated from bench-scale tests can be used to predict the amount of arsenic removed for a given amount of iron and sulfur. The removal rate predicted from an isotherm is the theoretical maximum amount adsorbed at equilibrium conditions.

### Materials and Methods

The purpose of the first experiment was to determine an adsorption isotherm at pH 8 by measuring arsenic concentrations at various iron addition rates after a 24-hour reaction time. Water containing approximately 1.0 mg/L of arsenic was obtained from an operating gold mine.

Table 1. Adsorption Isotherm Results - pH 8

| Jar | Fe:As Ratio | Dissolved Arsenic Concentration (mg/L) |
|---|---|---|
| raw water | 0 | 0.632 |
| 1 | 633 | < 0.005 |
| 2 | 316 | < 0.005 |
| 3 | 158 | 0.005 |
| 4 | 79 | 0.028 |
| 5 | 40 | 0.060 |

### Results

This test showed arsenic can be reduced down to or below the detection limit used in the experiments (0.005 mg/L) at an iron-to-arsenic (Fe:As) ratio of approximately 160 (Table 1). The arsenic concentration of this water would have been reduced from 0.632 mg/L to approximately 0.05 mg/L at an Fe:As ratio of approximately 50, or 20 mg of adsorbed arsenic per gram of iron. This is obtained by interpolating the data in Table 1 or by plotting the data (Figure 1).

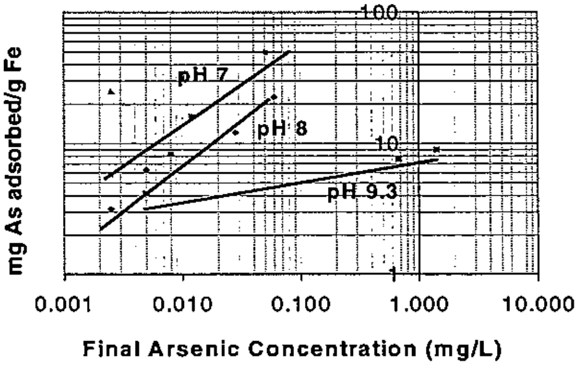

Figure 1. Adsorption Isotherm

The experiment was repeated at pH 7 by acidifying the mine water with 12 N HCl. Lower Fe:As weight ratios were used in this experiment because based upon previous results (data not shown), improved arsenic removal was expected at lower pH.

This experiment showed that arsenic could be removed even more effectively at pH 7 (Table 2). Isotherm data at both pH 7 and pH 8 are shown in Figure 1 along with their respective best-fit lines. Also shown are data at pH 9.3 from a previous experiment.

Table 2. Adsorption Isotherm Results - pH 7

| Jar | Fe:As Ratio | Dissolved Arsenic Concentration (mg/L) |
|---|---|---|
| raw water | 0 | 0.112 |
| 1 | 225 | < 0.005 |
| 2 | 170 | < 0.005 |
| 3 | 112 | 0.008 |
| 4 | 56 | 0.012 |
| 5 | 28 | 0.010 |
| 6 | 11 | 0.051 |

As expected, the data show more effective arsenic removal at lower pH values. The data also show that more iron is required (i.e., the value on the y-axis, "mg As adsorbed/g Fe," is lower) to obtain progressively lower final arsenic concentrations at a given pH.

## Column Tests

As the first step in scaling up the SMI process, packed-bed (column) experiments were conducted to see whether removal capacities from the isotherm experiments could be repeated in a continuous-flow treatment system.

### Materials and Methods

The first seven experiments used small columns containing approximately 75 $cm^3$ of media, while the last experiment used a column approximately 50 times as large. All columns used a mixture of sand (for increased permeability), sponge iron and elemental sulfur as media, after initial testing in a column filled with only sponge iron and sulfur showed that significant flow at normal operating pressures would be difficult. The variables examined in these experiments were:

- Residence time
- Sand type
- Sand:iron ratio
- Iron particle size
- Column size
- Arsenic concentration
- Arsenic oxidation state ($As^{3+}$ vs. $As^{5+}$)
- Influent pH.

A summary of the key variables and results for seven experiments is shown in Table 3.

### Results

Significant arsenic removal occurred over the course of several days to several weeks in column experiments at packed-bed residence times of 5 to 15 minutes. Significant removal of both arsenate and arsenite was obtained. Flow distribution problems were evident in the small columns (0.56-inch diameter) used in most of the experiments, as several columns became partially plugged and higher arsenic removal was observed with reduced flow rates. Typical influent and effluent arsenic concentrations measured in one of the columns are shown in Figure 2. The improved arsenic removal which occurred was probably not due to increased residence time but instead due to water being forced into contact with media which was not yet saturated with arsenic.

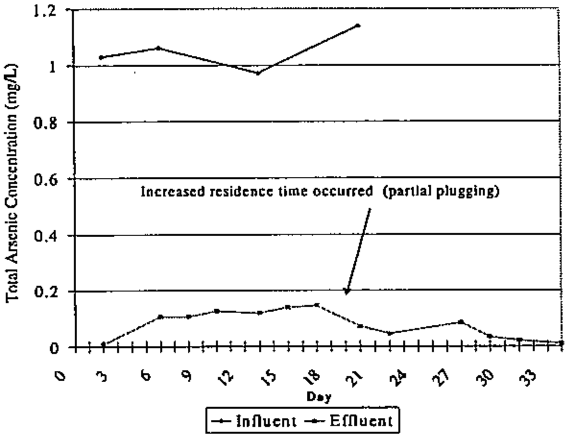

Figure 2. Column #6 Concentrations

The highest measured adsorption capacity (11 mg As removed/g Fe) occurred in a larger column (3.5-inch diameter). However, this capacity was still significantly below theoretical capacities predicted from adsorption isotherms and flow distribution was still a problem in the larger column, as noted by variable effluent concentrations (data not shown).

Sand alone did not remove arsenic in the column experiments. Spent media from one column passed the Toxicity Characteristic Leaching Procedure (TCLP) for arsenic, which means the media (a combination of sand, sponge iron and sulfur) would be classified as nonhazardous waste.

An oxidation-reduction reaction, such as the oxidation of elemental iron to ferric iron and reduction of elemental sulfur to sulfide, probably occurred in the columns:

$$2\,Fe + 3\,S + 6\,H_2O \text{ ----> } 2\,Fe(OH)_3 + 3\,H_2S \qquad (1)$$

This reaction is thermodynamically favorable and would explain the following results observed in the columns:

- Presence of sulfide
- Lowering of oxidation-reduction potential (ORP)
- Reduction in pH (due to generation of $H^+$ ions)

Table 3. Summary of SMI Column Experiments[1]

| | Column # | | | | | | |
|---|---|---|---|---|---|---|---|
| Parameter | 1 | 2 | 3 | 4 | 5 | 6 | 8 |
| Date Started | 2/10/98 | 2/24/98 | 2/24/98 | 3/5/98 | 3/5/98 | 3/17/98 | 3/30/98 |
| Flow (ml/min) | 1.5 | 3.9 | 3.9 | 3.9 | 3.9 | 1.3 | 55 |
| Residence Time (min) | 15 | 5 | 5 | 5 | 5 | 15 | 15 |
| Media | Silica sand: Grade B | Silica sand only | Silica sand: Grade B | Silica sand only | Silica sand: Grade B | Fine sand: MH-100 | Fine sand MH-100 |
| Fe Weight % | 24 | 0 | 7 | 0 | 7 | 14 | 20 |
| Influent [As], mg/L | 0.9 - 0.27 (As$^{3+}$) | 0.2 (As$^{3+}$) | 0.98 (As$^{3+}$) | 1.0 (As$^{5+}$) | 1.0 (As$^{5+}$) | 1.0 (As$^{5+}$) | 5.0 (As$^{5+}$ |
| Influent pH | 7.8 ---> 6.5 | 6.5 - 7.0 | 6.5 - 7.0 | 7.0 - 7.3 | 7.0 - 7.3 | 7.6 - 7.8 | 7 |
| Total Iron (mg/L) | < 0.03 (days 2,3) | --- | --- | --- | --- | 0.5 - 1.0 (day 27) | 0.07 (day 2 |
| Diss. Iron (mg/L) | < 0.03 (days 2,3) | --- | --- | --- | --- | 0 | 0 |
| Runtime (days) | 22 | 8 | 8 | 11 | 11 | 34 | 22 |
| Loading (mg As/g Fe) | 1.8 | 0 | 8.3 | 0 | 7.3 | 5.6 | 11.4 |
| Max. loading expected at that pH | 20 | 0 | 50 | 0 | 50 | 30 | 50 |

(1) Column #7 results are not reported.

- Low concentrations of soluble iron and the appearance of yellow precipitate (ferric hydroxide)
- Arsenic removal.

Arsenic removal probably occurred after ferric hydroxide was formed, similar to the process using ferric chloride or ferric sulfate addition. Amorphous iron oxides have a high point-of-zero charge ($pH_{ZPC}$) of about 8.6 (Stumm and Morgan, 1981). This means they become more positively charged as pH decreases, and efficiently scavenge arsenic oxyanions such as arsenate and arsenite. The combined arsenic-iron oxide particles are then precipitated as ferric hydroxide at a neutral-to-alkaline pH. Coprecipitation of arsenate with ferric iron is "recognized as the most effective and practical existing method of arsenic removal" (Vance 1995). The SMI process achieved the same or better arsenic removal in bench tests compared to iron salt addition, and SMI does not produce the low-density, high-volume sludge created by iron salt addition.

## SMI Treatment Systems

### Applications

The SMI process potentially is an effective, low-cost process for treating drinking water, mining water and other industrial wastewaters containing arsenic to meet increasingly stringent human health standards for arsenic. During development of the SMI process, arsenic concentrations between 0.1 and 5 mg/L were lowered to effluent concentrations ranging from below 0.005 mg/L (the selected laboratory analytical detection limit) to below 0.05 mg/L (the EPA drinking water standard). It is envisioned that in a full-scale process, premixed iron slurry would be removed (followed by replacement with fresh slurry) or regenerated.

### Possible Configurations

Potential treatment systems which could use the SMI process are:

1. A packed-bed reactor
2. A fluidized-bed reactor
3. A passive *in situ* reactor.

Bench-scale packed-bed reactors (columns) removed significant loads of arsenic to achieve low effluent concentrations. However, adsorption capacities were less than the theoretical maximum predicted from adsorption isotherm experiments. Uniform flow distribution in the columns appears to be a critical factor in achieving optimum results. Column variables such as height, diameter, media type and media particle size play an important role in determining the flow distribution.

If a packed-bed system can be optimized in the pilot test, a system such as that shown in Figure 4 is envisioned. If the adsorption capacity can be increased significantly by reducing the pH (e.g., from 20 mg As/g Fe at pH 8 to 50 mg As/g Fe at pH 7), pH reduction would be an economical step to include in the SMI process.

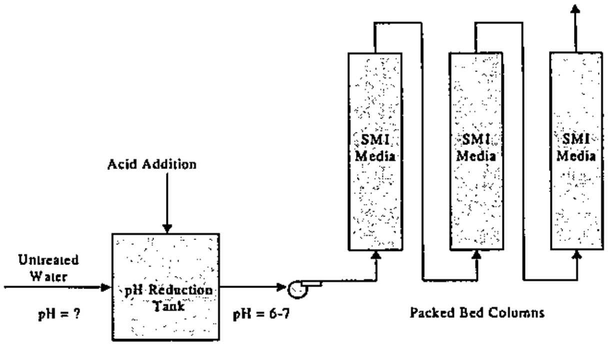

Figure 4. SMI Process (Packed Bed)

A fluidized-bed system would probably avoid the flow distribution systems that can occur in a packed-bed system, yet would still provide intimate contact between the SMI and arsenic-laden water. A fluidized-bed system would be more energy-intensive than a packed-bed system. However, in addition to possibly enhancing arsenic removal, it could simplify the material handling process for installing fresh SMI and removing spent material. The material handling issues for column change-outs have not yet been addressed for a packed-bed system, since the experiments to-date have been small in scale and relatively short in duration. A fluidized-bed system using SMI may also be run during the Reno pilot test.

A passive *in situ* system for arsenic removal, similar to the patented "iron wall" process for removal of chlorinated organics from groundwater, would be ideal for many applications. However, the flow-distribution issues for a packed-bed system should be addressed before a passive system using SMI is seriously considered.

Operating Costs

Using the adsorption isotherm data at pH 7 and pH 8, projected operating costs for SMI were compared to operating costs for an iron hydroxide precipitation process using ferric sulfate addition. The assumptions in the comparison shown in Table 4 are:

- The initial arsenic concentration of 1.2 mg/L must be treated to achieve an effluent concentration of 0.05 mg/L or less.
- The treatment flow rate is 100 gallons per minute (gpm).
- Adsorption capacities are those predicted by Hydrometrics' isotherm data.
- The required iron-to-arsenic (Fe:As) ratio for ferric sulfate addition to meet the effluent concentration target is 10, as seen in experiments at Hydrometrics' lab.
- SMI waste will pass TCLP (Hydrometrics' data) and has a nonhazardous waste disposal cost of $30 per ton.
- Ferric sulfate sludge will not pass TCLP (Hydrometrics' data) and has a hazardous waste disposal cost of $250 per ton.
- Delivered raw material prices (per pound of iron) are $0.50 for sponge iron and $1.22 for ferric sulfate.

Table 4. Operating Cost Comparison

| | Sulfur-Modified Iron | | Ferric Sulfate |
|---|---|---|---|
| | pH 7 | pH 8 | pH 7 |
| Adsorption Capacity (mg As/g Fe) | 50 | 20 | 100 |
| **Required Weight Ratio (Fe:As)** | **20** | **50** | **10** |
| Delivered Raw Material (RM) Cost/lb Fe | $0.50 | $0.50 | $1.22 |
| RM Cost/1000 gal | $0.10 | $0.25 | $0.12 |
| Other RM Cost/1000 gal (polymer) | $0.00 | $0.00 | $0.03 |
| **Total RM Cost/1000 gal** | **$0.10** | **$0.25** | **$0.15** |
| Total RM Cost/Yr | $5,263 | $13,157 | $7,998 |
| Tons Waste/Yr | 5 | 13 | 36 |
| Disposal Cost/Ton | $30 | $30 | $250 |
| Disposal Cost/Yr | $158 | $395 | $9,000 |
| **Annual Operating Cost @ 100 gpm** | **$5,421** | **$13,522** | **$16,998** |

SMI offers a significant cost advantage compared to ferric sulfate addition when SMI is operated at pH 8 or less, and even greater cost savings compared to alternative technologies for arsenic removal such as reverse osmosis or activated alumina ("high-adsorption capacity" alumina removes approximately 6 mg As/g Al [Vicevic 1997]). These savings would be greater at higher flow rates and higher arsenic concentrations.

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