PHYSICAL SOLUTIONS FOR ACID MINE DRAINAGE AT REMOTE SITES DEMONSTRATION PROJECT, PHASE I[1]

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Abstract. The overall objective of MWTP, Activity III, Project 42, *Physical Solutions for Acid Mine Drainage at Remote Sites* is to design, construct, and test the operation and functionality of a treatment facility to remove arsenic and heavy metals from the selected demonstration site, the Susie/Valley Forge Mine discharge in Rimini, Montana. The concept for this novel approach would be to utilize the physical characteristics of the mine in such a way as to enhance the overall efficiency of the proposed treatment process. The goal for the Process is to treat the Susie Mine water to meet the Montana Circular WQB-7 Standards or to less than 10 µg/L. The bench-scale results and work to date will be presented and discussed in this presentation.

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Project Description

Background

The information in this paper is taken from the Interim Report for Mine Waste Technology Program (MWTP), Activity III, Project 42, *Physical Solutions for Acid Mine Drainage at Remote Mine Sites Demonstration Project*. The interim report provides information on the work completed and the findings by MSE Technology Applications, Inc. (MSE) and contract project personnel during the execution of the bench-scale testing as outlined in the Phase I scope of work in the project work plan (MSE, 2003a) and the project quality assurance test plan (MSE, 2004).

Representatives from the Montana Department of Environmental Quality (MDEQ) Environmental Management Bureau and Mine Waste Cleanup Bureau, EPA Region 8, CDM Federal Programs Corporation (CDM), and MSE met in Helena, Montana on March 26, 2003. The purpose of the meeting was to discuss options for source control and reduction of metals loading from acid mine drainage (AMD) to the Tenmile Creek in the Rimini Mining District, which is approximately 15 miles West of Helena, Montana. The *Upper Tenmile Creek Mining Area Site Remedial Design Acid Mine Drainage Study*, (CDM, 2003) prepared by CDM for EPA in consultation with the MDEQ, was discussed. This report highlighted 17 mine discharges as contributing to metal loadings in Tenmile Creek. The project and how it could support sustainable remediation efforts for the Tenmile Creek drainage were also discussed. Representatives from both the MDEQ and EPA Region 8 requested that MSE, as part of this project, perform treatability studies on 3 of the 17 mine waters to determine viable treatment options. The three metal laden mine waters, which contribute over 65 percent (%) of the metals loading, were the Susie/Valley Forge, Lee Mountain, and Red Water. It was also decided that the same treatability studies would be performed on a combination water comprised of the three mine waters. The reasoning behind evaluating the combination water was that the MDEQ had been approached previously by the Corp of Engineers with the concept of collecting these metal laden mine waters prior to their entering the Tenmile Creek and treating them in a single treatment system. The treatability work performed in this project would support that concept.

In addition to the Rimini Mining District waters, two metal laden waters at the American Smelting and Refinery Company (ASARCO) East Helena, Montana Smelter Superfund Site were also selected for testing. These waters were the Plant Stormwater and a groundwater monitoring well water in the town of East Helena identified as Groundwater Monitoring Well EH-100. Treatability tests were also performed on a combination of the Plant Stormwater and Groundwater Monitoring Well EH-100.

MSE developed a test plan (MSE, 2004) to perform a number of treatability tests on each of the seven project waters. Both arsenic (As) and zinc (Zn) were selected as the critical constituents of concern for project quality assurance/quality control parameters for the test plan. Zinc is a metal while As is a metalloid element. Within ambient systems As can occur as arsenate [As(V)] or arsenite [As(III)]. Over the natural pH range of most soils and waters, the principal species of As(V) is $H_2ASO_4^{-2}$ and of As(III) is H_3AsO_3. Other elemental analyses were performed, but not designated critical.

In May 2004, MSE presented the treatability test results to the EPA National Risk Management Research Laboratory (NRMRL) Project Officer, representatives from the MDEQ, EPA Region 8, and CDM. During this meeting, the Susie/Valley Forge Mine was selected as the demonstration site. The criteria used to select the Susie/Valley Forge Mine were: 1) significance to the Tenmile Creek drainage Record of Decision to determine alternative treatment for AMD; 2) accessibility to the mine site; 3) opportunity for sustainable treatment of the water; and 4) compatibility with future plans (i.e., EPA Region 8 and MDEQ) to treat the water and/or identify source control options in the mine workings. Additional treatability tests were performed on the Susie/Valley Forge Mine water to confirm results from earlier testing and to develop process design information. A process consisting of pH adjustment using sodium hydroxide (NaOH) or hydrated lime [$Ca(OH)_2$], combined with adsorption of metals onto ferric hydroxide precipitate followed by a polishing step using granular ferric hydroxide (GFH), was determined most appropriate to treat the Susie/Valley Forge Mine water.

The treatability test results for the seven project waters are presented in the interim report (MSE, 2006). Only the test results for the Susie/Valley Forge Mine water will be discussed in this paper.

General Overview

Acid mine drainage is a serious environmental problem facing many abandoned, inactive, and active mine sites throughout the United States. The production of AMD occurs through the weathering of pyrite (FeS_2). The pyrite is dissolved over time by the groundwater, which is indicated by reaction 1 below. Mine water often has high acidity and, therefore, a lower pH due to acid being produced in the weathering of pyrite.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad (1)$$

[pyrite + oxygen + water → ferrous iron (Fe) + sulfate + acidity]

The second reaction is pH dependent and will proceed slowly under acidic conditions (pH 2 to 3) with no bacteria present and several orders of magnitude faster at pH values near 5 (Saint Vincent College Environmental Education Center, date unknown). The reaction, which occurs when the mine water comes in contact with oxygen, involves the conversion of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). The conversion of one mole of ferrous Fe to one mole of ferric Fe consumes one mole of acidity. Certain bacteria can increase the rate of oxidation from ferrous to ferric Fe. This reaction is referred to as the "rate determining step" in the overall acid generating sequence.

$$Fe^{2+} + ½\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+} + H_2O \qquad (2)$$

(ferrous Fe + oxygen + acidity → ferric Fe + water)

The third reaction that may occur is the hydrolysis of Fe^{+3}. Hydrolysis is a reaction that splits the water molecule. Three moles of acidity are generated as a byproduct. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate (solid) is pH dependent. Solids form if the pH is above 3.5.

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

(ferric Fe + water → ferric hydroxide + acidity)

Through the entire reaction, acidity is being produced and consumed. Without a buffer (i.e., limestone) present, the mine water discharge will be acidic.

The weathering process of other base metal sulfides is similar to the process described for pyrite, although it may not produce acid. The most common metals associated with AMD are cadmium (Cd), copper (Cu), Fe, manganese (Mn), Zn, and the metalloid As.

Conventional technologies for removing heavy metals from AMD use coagulation/filtration, adsorption media, and/or biological treatment processes. Topography, climate, cost, infrastructure, treatment volumes, and metals loading can present difficulties for any technology. Remote mine sites are especially impacted because they generally: 1) do not have electricity; 2) have extreme weather conditions; 3) have limited area available for a treatment plant; and/or 4) do not have year-round access. A need exists for a simple, low-maintenance technology to reduce heavy metals from AMD at remote sites. Experts in the field of applying passive treatment technologies for AMD are aware of the problems associated with high particulate loadings, total suspended solids (TSS), and high concentrations of total dissolved solids, (i.e., reactor plugging, media coating, etc). MSE was tasked to develop, design, and implement a low maintenance, continuous process to treat AMD at the Susie/Valley Forge Mine.

Adsorption of the heavy metals onto ferrihydrite, then coprecipitation followed by solid/liquid separation could be the most effective treatment process for AMD with high Fe to other metals ratio. A novel approach would be to use the physical characteristics of the mine in such a manner as to enhance the overall efficiency of the proposed treatment process. Some ways the physical characteristics of a mine could be used include, but are not limited to: 1) using the mine as a physical structure to house the treatment technology; 2) using the differential pressures created by elevation changes of the AMD stream in a mine system to generate electricity or to replace a process pump; 3) using the temperature of a mine water (if applicable) as a heat source to prevent treatment freezing issues associated with winter conditions; and 4) using the AMD chemistry to more efficiently remove metals of concern. In addition, alternative power sources such as solar power, fuel cells, and batteries could be used to provide cheap reliable power to monitor and control the treatment system.

Geochemistry Review

For general information needed to understand the results and terms discussed in the following sections, it is important to briefly review some dominant chemical reactions (i.e., ferrihydrite formation, precipitation/dissolution, adsorption, etc.) that occur in project waters. The geochemical processes controlling As mobility are reviewed below (USGS, 2001).

Two types of processes largely control As and heavy metal mobility in aquifers: 1) adsorption and desorption reactions; and 2) solid-phase precipitation and dissolution. Attachment of As and heavy metals to an Fe oxide surface is an example of an adsorption reaction. The reverse of this reaction is an example of desorption. Solid-phase precipitation is the formation of a solid phase from components present in aqueous solution. Precipitation of the mineral ferrihydrite from the ferric ion (Fe+3) in water is an example of solid-phase precipitation. The ferric ion is not stable in an aqueous environment above pH 7 and will precipitate as 1) ferrihydrite – $Fe(OH)_3$ and/or ferrioxy sulfates; 2) schwertmannite – $(Fe_8O_8(OH)_6SO_4$; and 3) greenrust – $(Fe_4Fe_2(OH)_{12}SO_4$ (Robins, 1984; Jambor, 1998). Fig. 1 is an Eh/pH stability diagram showing Fe speciation in the Susie/Valley Forge Mine water. Solid-phase precipitation and dissolution reactions are controlled by solution chemistry: pH, oxidation-reduction potential (ORP) or redox, and chemical composition. Whether ferrihydrite forms or not depends on the sulfate concentration. For the example shown in Fig. 1, where sulfate is appreciable, ferrioxysulfates will likely form.

Figure 1. Iron speciation diagram for Susie/Valley Forge Mine water.

The chemical reaction for the formation of ferrihydrite ($Fe_5HO_8.4H_2O$) is shown below:

$$5Fe^{+3} + 12H_2O \rightarrow Fe_5HO_8.4H_2O_{(s)} + 15H^+ \qquad (4)$$

Arsenic adsorption and desorption reactions are influenced by changes in pH, redox reactions, presence of competing anions, and solid-phase structural changes at the atomic level. Arsenic is a redox-sensitive element. Arsenate and arsenite are the two forms of As commonly found in groundwater (Masscheleyn et al., 1991). As (V) generally predominates under oxidizing conditions. As (III) predominates when reducing conditions are present. Under the pH conditions of most waters, As (V) is present as the negatively charged oxyanions $H_2AsO_4^-$, $HAsO_4^{2-}$, or AsO_4^{-3} and As (III) is predominately present as the uncharged species $H_3AsO_3^o$.

Adsorption during coprecipitation of arsenate and ferric hydroxide is illustrated in reaction 5:

$$AsO_4^{-3} + Fe\ (OH)_{3(S)} \rightarrow Fe(OH)_{3(S)} + AsO_4^{-3}{}_{(ad)} \qquad (5)$$

The dissolved As is removed from the oxidized water by a lime neutralization in reaction 6 in the presence of the Fe^{+3} that results in the formation of As-bearing ferrihydrite (hydrous ferric oxide). Acid neutralization with NaOH can also be utilized.

$$Ca(OH)_2 + 2H^+ \rightarrow Ca^{+2} + 2H_2O \qquad (6)$$

The ferrihydrite may be formed by the natural presence of Fe in solution or it may be added as a reagent (i.e., ferric chloride, ferric sulfate, or ferrous sulfate) in sufficient quantities to effectively remove the dissolved As. Studies have shown that if Fe^{+3} is present in solution, the maximum adsorption capacity for As onto the ferrihydrite is 0.7 mole As(V) per mole Fe. However, if Fe^{+3} is added, then the maximum adsorption capacity is 0.2 mole AsV per mole Fe (Nishimura and Umetsu, 2000; Nishimura et al., 2000). Previous tests have indicated that this adsorption capacity is not affected to any noticeable extent with the sequence of reagent (Fe^{+3}, lime) additions. A solid-liquid separation may then be performed and accomplished by a process involving conventional settling/flocculation followed by pressure filtration.

Adsorption of heavy metals also occurs during the ferrihydrite precipitation process.

A number of studies have indicated that various complexes are formed in the adsorption of arsenate on ferrihydrite (Manceau, 1995; Sun and Doner ,1996; Fendorf et al., 1997). Extended x-ray absorption fine structure (EXAFS) studies on As bearing ferrihydrite formed at pH >7, have shown that arsenate is adsorbed onto ferrihydrite as a strongly bonded inner-sphere complex with either monodentate or bidentate attachment (Waychunas et al., 1993; Waychunas et al., 1995). It has also been reported that monodentate attachment predominates near the optimal pH 4 to 5 for adsorption.

The adsorption of arsenite onto ferrihydrite has also been investigated, but the optimal adsorption in this case occurs at pH 8 to 9 (Nishimura and Umetsu, 2000) and, although it seems an efficient process, there is no evidence that the adsorbed species is in fact arsenite. It may be that during the process, oxidation of arsenite will occur with some ease, being balanced by the reduction of ferric Fe to ferrous Fe in the ferrihydrite structure. It is well known that ferrous Fe substitution in ferrihydrite does occur (Nishimura et al., 2000).

Statement of Project Objectives

The main objectives of this project are to develop, design, and implement a treatment process at the selected site, to reduce metal loadings associated with AMD that require minimal operational and maintenance supervision.

The specific objectives for Phase 1 of this project were to:

- conduct treatability studies on each of the project waters defined earlier;
- evaluate the ability of each technology to significantly reduce the heavy metals concentration in the project waters;
- compare the technical capabilities of each technology to remove heavy metals from each project water;
- compare the economic feasibility of the treatment systems;
- determine the most appropriate technology to treat each project water based on ability to remove heavy metals, operating costs, and amount of waste product generated;
- select the demonstration site; and
- design the treatment system for the selected demonstration site.

The MDEQ provided direction in determining discharge requirements for a mine discharge treatment system in the Rimini Mining District. The MDEQ point of contact stated that the Montana Numeric Water Quality Standards, Circular WQB-7, will be the standard used to determine discharge requirements considered for any treatment system discharging to Tenmile Creek (MDEQ, 2004). For the primary contaminants of concern, Circular WQB-7 standards are listed below in Table 1. The 2004 standards are calculated using the Chronic Aquatic Life Standard based on 100 milligrams per liter (mg/L) hardness and total recoverable analysis. However, the hardness of the Susie adit mine drainage is already in excess of 1,000 mg/L, and lime addition will only further increase the hardness of the treated water. This maximizes the concentrations calculated for the hardness-based standards since the maximum hardness that can be used in calculating the hardness-based standards is 400 mg/L. The 400 mg/L hardness-based standards are also listed in Table 1.

Table 1. Montana Numeric Water Quality Standards, CircularWQB-7.

Contaminants	WQB-7 Standards (100 mg/L hardness)	WQB-7 Standards (400 mg/L hardness)
As	10 micrograms per liter (μg/L)	10 mg/L
Cd	0.27 μg/L	0.76 mg/L
Cu	9.3 μg/L	30.5 mg/L
Fe	300 μg/L	300 mg/L
Lead (Pb)	3.2 μg/L	18.6 mg/L
Mn	50 μg/L	50 mg/L
Zn	120 μg/L	388 mg/L

The As standard is listed as 10 µg/L, reflecting the new federal maximum contaminant level (MCL). WQB-7 does not list an aquatic standard for manganese; instead, a secondary MCL (aesthetic, taste) of 50 mg/L is listed.

Project Site Discussion

Site Descriptions

The laboratory-scale testing of alternative treatment options to remove heavy metals from the project waters was performed at the MSE Testing Facility in Butte, Montana and at the Susie/Valley Forge Mine in Rimini, Montana. The Susie/Valley Forge Mine water (Susie Water) chemistry is provided in Table 2 and discussed in detail in the following sections. Fig. 2 shows the approximate locations for Rimini Mining District, ASARCO Smelter, and MSE Testing Facility.

Susie/Valley Forge Mine. The Susie Mine is located in the Tenmile Creek near Rimini Subarea and is centrally located in the town of Rimini. The site was reclaimed originally by the state and then EPA conducted a more extensive reclamation in 2000. The adit discharge has been diverted into a 6-inch pipe, which runs under the main road and directly into Tenmile Creek (about 300 feet from the adit). The flow rate from this adit ranges from 3 to 6.4 gpm. The pH ranges from 4.5 to 5.54. Extremely high concentrations of As, Cd, Cu, lead (Pb), Zn, Fe, Mn, and aluminum (Al) have been reported in the adit discharge. These high concentrations along with significant discharge rates rank the Susie Mine as one of the highest sources of adit loading of As, Cd, Cu, Fe, Mn, and Zn in the upper Tenmile Creek watershed (CDM, 2003).

Preliminary results from sampling conducted by CDM in 2003 and 2004 (not yet reported) indicated that the concentrations of As and Zn in the Susie adit discharge have nearly doubled when compared to concentration presented in the 2002 AMD study conducted by CDM.

The described mine sites produced gold, silver, Pb, and Zn. For more detailed historical information on each mine visit www.deq.state.mt.us/abandonedmines/linkdocs/techdocs/103tech.asp.

Table 2. Analytical information for the project waters.

Analytical Data	Rimini Mining District Waters				ASARCO Waters		
	Susie/Valley Forge	Lee Mountain	Red Water	Rimini Combination Water	Plant Stormwater	Well EH-100	ASARCO Combination Water
pH	4.7	3.2	6.9	3.02	6.75	6.11	6.28
ORP [millivolts (mV)]	162	316	10	477	355	100	173
TSS (mg/L)	29	40	18	83			
Metals (μg/L)							
Aluminum (Al)	1,250	18,100	31	1,960	<23.3	42.3	36.4
Antimony (Sb)	<0.5	3.6	0.90	0.9	85.9	<0.5	10.4
As	23,300	26,400	106	2,990	10.5	5,590	4,900
Cd	241	310	51.7	123	3,700	3.6	389
Calcium (Ca)	251,000	121,000	59,600	100,000	61,700	129,000	123,000
Cu	69.7	174	23.7	42.7	791	4	97.1
Fe	228,000	160,000	7,460	45,400	<15.1	<9	168
Pb	3.8	372	0.28	48.5	56	0.32	8.7
Magnesium (Mg)	93,700	36,600	13,100	31,100	10,800	43,100	40,400
Mn	20,500	17,700	5,220	8,950	2,200	12,200	11,000
Nickel (Ni)	55.7	103	<18.1	30	291	<22.1	56
Selenium (Se)	6.1	7	3.3	2.8	54.8	315	228
Thallium (Tl)	0.12	0.66	<0.1	<0.1	229	0.61	26.6
Zn	50,200	51,300	11,300	21,200	8,180	581	1,460

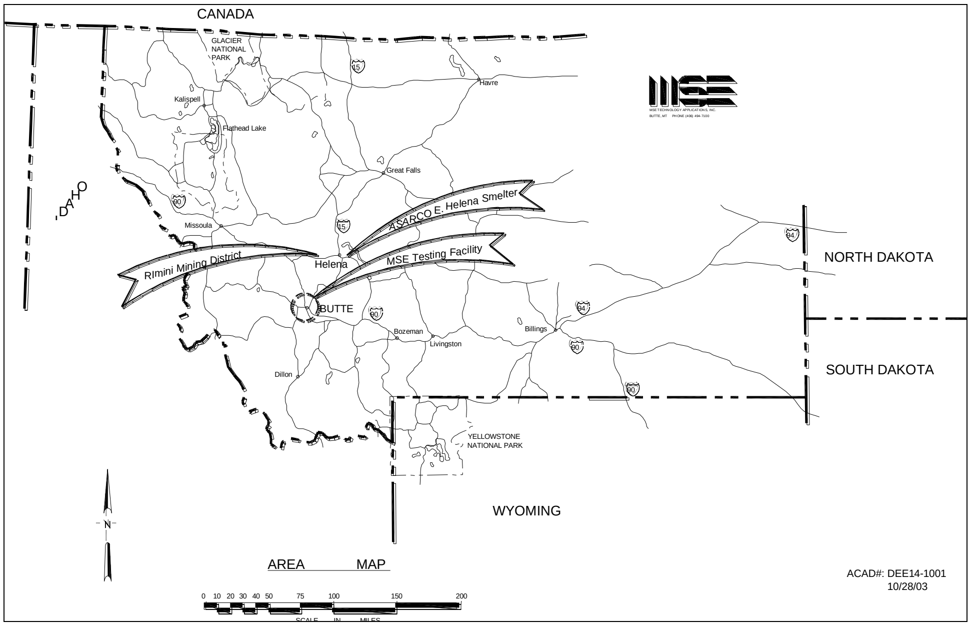

Figure 2. Site map.

Technology Discussion

The tests performed for the treatability studies are discussed below.

Test Set 1 – Filtration.

Test Set 1 consisted of filtering each of the seven project waters with various pore size filters as described below. The goal was to determine the amount of dissolved metals in each project water and determine if simple filtration would be effective in reducing the metal concentrations.

0.45-Micron Filtration. Each project water was filtered through a 0.45-micron filter. Prior to filtration, a head sample was collected and analyzed for TSS and for total recoverable metals (As, Cd, Cu, Fe, Mn, Zn). A sample of the filtered water (i.e., filtrate) was collected and analyzed for total recoverable metals. Both pH and ORP measurements were taken for each project water and associated filtrate.

0.20-Micron Filtration. Each project water was filtered through a 0.20-micron filter. Prior to filtration, a head sample was collected and analyzed for TSS and for total recoverable metals (As, Cd, Cu, Fe, Mn, Zn). A sample of the filtrate was collected and analyzed for total recoverable metals. Both pH and ORP measurements were taken for each project water and associated filtrate.

Test Set 2 – PH Adjustment

Test Set 2 consisted of adjusting the pH of each project water with lime or NaOH and then filtering the pH adjusted water through a 0.45-micron filter. With the exception of Groundwater Monitoring Well EH-100, each of the project waters contained dissolved Fe and had a pH of 6 or below. Increasing the pH of the project waters to 6.5 or higher produced metal hydroxide precipitates that could be filtered. In project waters containing Fe and Al, hydroxides act as an adsorptive media to remove other heavy metals from solution. As stated, test samples were analyzed following 0.45-micron filtration. It was assumed for the preliminary testing that the equivalent of 0.45-micron filtration could be duplicated in the field utilizing equipment (i.e., sand filter) to be specified for the proposed treatment process.

Lime. The pH of the project waters was adjusted to 6.5 and 9.5 using $Ca(OH)_2$. The pH of each of the project waters was adjusted to the appropriate pH value (6.5 or 9.5) and allowed to mix for 30 minutes. A sample of the unfiltered pH adjusted water was collected for TSS analysis prior to settling; the pH-adjusted water was then filtered using 0.45-micron filter media and a sample of the filtrate was analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and after each pH adjustment.

Sodium Hydroxide. The pH of each of the project waters was adjusted with NaOH to the appropriate pH value (6.5 or 9.5) and allowed to mix for 30 minutes. A sample of the unfiltered pH adjusted water was collected for TSS analysis prior to settling; the pH-adjusted water was then filtered using a 0.45-micron filter and a sample of the filtrate was analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and after each pH adjustment. Fig. 3 is a photograph of Susie/Valley Forge Mine water with NaOH added. Fig. 4 is a photograph of the same water with the ferrihydrite precipitate settling.

Figure 3. Susie/Valley Forge Mine water treated with NaOH.

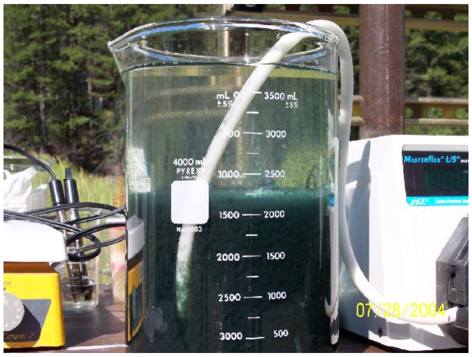

Figure 4. Susie/Valley Forge Mine NaOH treated water showing the ferrihydrite precipitate settling.

Test Set 3 – Oxidation Reduction Potential Adjustment

Test Set 3 consisted of oxidizing the project waters by adjusting the ORP with the addition of hydrogen peroxide (H_2O_2) or sodium hypochlorite (NaHClO). These tests were performed to determine if adjusting the ORP of the project waters that contained Fe and Al would produce metal hydroxides that could be used as an adsorptive medium to remove other heavy metals. The dark green to black color of the Fe hydroxide precipitate in Figs. 3 and 4 is an indication that the water was under reducing conditions. If the Fe precipitate were red, it would be an indication that the water was under oxidizing conditions.

Hydrogen Peroxide. Initially, it was thought that the ORP of the project waters could be adjusted to 200 mV greater than the potential for the ferrous/ferric couple with H_2O_2. However, it was learned during some testing that ORP could not be adjusted and increased to any appreciable levels. In addition, it was found that when the pH of the Susie Mine water increased, the ORP decreased. This is consistent with the information shown in the iron speciation diagram in Fig. 1. In the water stability region, which is the area between the dotted lines, this is shown. The O_2 is being consumed by the H^+ ions. The ORP of each of the project waters was adjusted to the appropriate ORP value and allowed to mix for 30 minutes. A sample of the unfiltered ORP adjusted water was collected for TSS analysis; the ORP adjusted water was then filtered through a 0.45-micron filter and the filtrate was analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and at the end of each test.

Sodium Hypochlorite. The ORP of each of the project waters was adjusted to the appropriate ORP value and allowed to mix for 30 minutes. A sample of the unfiltered ORP adjusted water was collected for TSS analysis; the ORP adjusted water was then filtered with a 0.45-micron filter and a sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and at the end of the test. Approximately 1 liter of each project water was used for each test.

Test Set 4 – Chemical/Precipitation

Test Set 4 consisted of adding reagents to the project waters to produce precipitates that could be used as adsorptive media to enhance or assist with the removal of heavy metals. Two Fe chemistry technologies (ferric and ferrous) and a phosphate chemistry technology were evaluated.

Ferric Chemistry. Ferric (as ferric sulfate) was added to the project waters at one times (1X) and five times (5X) the combined concentration of the heavy metals present. Following the ferric additions and a 30-minute mixing time, one unfiltered sample was collected and analyzed for TSS, and one filtered sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). The pH of the water was then increased to approximately 8 with NaOH and allowed to mix for 30 minutes. One unfiltered sample was collected and analyzed for TSS, and one filtered sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were taken initially and prior to each sample collection exercise.

Ferrous Chemistry. Ferrous (as ferrous sulfate) was added to the project waters. After the ferrous addition and a 30-minute residence time, one unfiltered sample was collected and analyzed for TSS, and one filtered sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). The pH of the water was then increased to approximately 8 with NaOH and allowed to mix for 30 minutes. One unfiltered sample was collected and analyzed for TSS, and one filtered sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and prior to sample collection.

Phosphate Chemistry. Phosphate (as sodium phosphate or phosphoric acid) was added to the project waters at ten times (10X) the stoichiometric requirement to remove all the heavy metals as metal phosphate compounds. After the phosphate addition, the pH was adjusted to approximately 8 with NaOH and allowed to mix for 30 minutes. One unfiltered sample was collected and analyzed for TSS, and one filtered sample was collected and analyzed for dissolved metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and prior to sample collection.

Test Set 5 – Adsorptive Media

Test Set 5 consisted of evaluating the metal adsorption capabilities of GFH. Other adsorption media was not tested during Phase I due to insufficient project funds. The flow rate for each column was set, based on column pore volume, to give a 30-minute retention time in each column. The wet pore volume in each column was measured to be approximately 300 milliliters (mL).

Granular Ferric Hydroxide. Granular ferric hydroxide is a packed-bed adsorption technology that combines the advantages of coagulation/filtration, efficiency, and small residual mass with the simple processing advantages of activated alumina. Arsenic and heavy metals are removed from solution by adsorption onto ferric hydroxide particles. The GFH used for the tests was a marketed product. The GFH vessels used in the treatability tests were vertical fixed bed columns operated with upward-flowing water (see Fig. 5). Samples were collected after the displacement of a predetermined number of bed volumes and analyzed for total metals (As, Cd, Cu, Fe, Mn, Zn). Solution pH and ORP measurements were conducted initially and during sample collection.

Figure 5. Photograph of the Susie/Valley Forge Mine site and testing apparatus.

~~4.~~Test Results and Summary

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Over 150 tests were performed on the seven project waters using the technologies discussed previously. Only the analytical data from the treatability tests for the Susie Water are discussed in this paper. In the majority of tests, the samples were analyzed for (As, Cd, Cu, Fe, Mn, Zn), and in some test samples [Al, antimony (Sb), calcium (Ca), Pb, magnesium (Mg), phosphorus, nickel (Ni), selenium (Se), silicon, and/or thallium (Tl)] were analyzed. For consistency in the technology evaluation, only As, Fe, and Zn analyses will be discussed in the following sections. The Montana Numeric Water Quality Standards, Circular WQB-7 (MDEQ, 2004), for As, Fe, and Zn are 10 μg/L, 300 μg/L, and 388 μg/L, respectively. Other Circular WQB-7 metal standards are listed in Table 1. The treatment goal for the selected process is to reduce As, Fe, and Zn below the Circular WQB-7 standards. The test procedures, sampling procedures, quality assurance objectives, analytical procedures and calibration, and internal quality control checks followed for each test are outlined in the project quality assurance test plan (MSE, 2004). Actual test conditions are summarized in the project logbook (MSE, 2003b). Table 3 lists the critical and noncritical measurements performed during testing of project waters.

Table 3. Critical and noncritical measurements.

Measurement	Matrix	Classification	Sample Frequency	Sample Location
pH	Aqueous	Noncritical	Initially, end of test	Filtration Tests ORP Adjustment Tests Phosphate Chemistry
			Initially, after each pH adjustment	pH Adjustment Tests Ferric Fe Chemistry Ferrous Fe Chemistry
			Initially, after each sample collection	Adsorptive Tests
ORP	Aqueous	Noncritical	Initially, end of test	Filtration Tests ORP Adjustment Tests Phosphate Chemistry
			Initially, after each pH adjustment	pH Adjustment Tests Ferric Fe Chemistry Ferrous Fe Chemistry
			Initially, after each sample collection	Adsorptive Tests
Total Metals (As, Cd, Cu, Fe, Mn, Zn)	Aqueous	Noncritical	Each collection time	Each project water
			Following a predetermined amount of bed volumes	Adsorptive Tests

Table 3. Critical and noncritical measurements.

Measurement	Matrix	Classification	Sample Frequency	Sample Location
Total Metals [Al, beryllium (Be), cobalt (Co), chromium (Cr), Mg, Ni, Pb, Sb, Se]	Aqueous	Noncritical	Each collection time	Each project water
Total Recoverable Metals (As, Cd, Cu, Fe, Mn, Zn)	Aqueous	Noncritical	End of test	0.45-Micron Filtration 0.2-Micron Filtration
Dissolved Metals (As and Zn)	Aqueous	Critical	End of test	Reverse Osmosis Nanofiltration ORP Adjustment Tests Phosphate Chemistry
			After each pH adjustment	pH Adjustment Tests Ferric Fe Chemistry Ferrous Fe Chemistry
Dissolved Metals (Cd, Cu, Fe, Mn)	Aqueous	Noncritical	End of test	Reverse Osmosis Nanofiltration ORP Adjustment Tests Phosphate Chemistry
			After each pH adjustment	pH Adjustment Tests Ferric Fe Chemistry Ferrous Fe Chemistry
TSS	Aqueous	Noncritical	End of test	0.45-Micron Filtration 0.2- Micron Filtration ORP Adjustment Tests Phosphate Chemistry
			After each pH adjustment	pH Adjustment Tests Ferric Fe Chemistry Ferrous Fe Chemistry

Susie/Valley Forge Mine

The Susie/Valley Forge Mine water was subjected to a series of tests utilizing the technologies discussed earlier. The analytical results of the treatability tests are shown in Table 4 and discussed below.

pH Adjustment Tests. The Susie/Valley Forge Mine water pH was adjusted from 2.65 to 6.5 and then to 9.5 using a 5% $Ca(OH)_2$ slurry. Approximately 5.6 mL of 5% lime slurry per 1 liter was required to raise the Susie Mine water pH from 2.65 to 6.5 and another 0.93 mL to raise the Susie Mine water pH from 6.5 to 9.5. The results (SVF-lime-022504-1 and SVF-lime-022504-2) of the tests indicate that the As concentration can be reduced to approximately 400 μg/L raising the pH to 6.5; however, Zn concentration was reduced only to 35,800 μg/L. When the water pH was raised to 9.5, the Zn concentration was reduced to <100 μ/L.

Table 4. Susie/Valley Forge Mine water treatability test analytical results.

		Metals, μg/L					
Test	Sample ID	As	Cd	Cu	Fe	Mn	Zn
Head – Total	Susie 1 Head	23,300	241	69.7	228,000	20,500	50,200
Head – Dissolved	Susie 1 Head	21,300	233	67.1	217,000	19,600	48,400
Head – Total	Susie 2 Head	23,500	255	71.9	230,000	20,600	49,900
0.45-micron filtration	SVF-0.45-021104-1	11,000	299	109	172,000	20,500	49,900
0.20-micron filtration	SVF-0.2-021204-1	10,700	280	104	164,000	20,100	49,300
Lime, pH = 6.5	SVF-lime-022504-1	403	186	1.6	15,200	18,700	35,800
Lime, pH = 9.5	SVF-lime-022504-2	47.4	2.1	<1.5	<15.1	3,550	39.6
NaOH, pH = 6.5	SVF-NaOH-022704-1	363	165	<1.5	10,100	18,000	33,100
NaOH, pH = 9.5	SVF-NaOH-022704-2	92.2	1.9	<1.5	19.2	2,930	107
Oxidation, H_2O_2	SVF-H2O2-031204-1	19	121	2.5	184	16,900	28,300
Oxidation, NaHClO,1	SVF-SH-031804-1	8,890	246	61.6	179,000	18,500	46,200
Oxidation, NaHClO,2	SVF-SH-031804-2	2,340					38,000
Oxidation, NaHClO,3	SVF-SH-031804-3	196					27,800
Ferric, 1X, AR	SVF-Fe+3-032904-1	14,600	255	63.7	291,000	19,200	47,200
Ferric, 1X, pH = 8, 1	SVF-Fe+3-040104-4	410	94.4	2.4	97,100	18,100	20,400
Ferric, 1X, pH = 8, 2	SVF-Fe+3-1	390					14,800
Ferric, 5X, AR	SVF-Fe+3-033004-2	14,100	263	79.4	692,000	20,300	46,800
Ferric, 5X, pH = 8	SVF-Fe+3-033104-3	247	68.8	1.6	102,000	18,300	14,300
Ferrous, 1X, AR	SVF-Fe+2-032404-1	16,500	272	63.8	270,000	19,100	47,500
Ferrous, 1X, pH = 8	SVF-Fe+2-032504-4	486	65.5	1.5	18,200	15,500	3,310
Ferrous, 5X, AR	SVF-Fe+2-032404-2	16,200	262	65.5	547,000	19,500	47,200
Ferrous, 5X, pH = 8	SVF-Fe+2-032504-3	6,090	159	1.5	276,000	18,500	7,840
Phosphate, 1X, 1	SVF-PO4-041304-1	10,100	239	61.4	91,200	19,400	48,500

Table 4. Susie/Valley Forge Mine water treatability test analytical results.

Test	Sample ID	Metals, µg/L					
		As	Cd	Cu	Fe	Mn	Zn
Phosphate, 1X, 2	SVF-PO4-041304-2	7,840					332
NaOH, pH=9.5, GFH – Head	SVF-NaOH-070804-2A	* 2,750					44,900
NaOH, pH=9.5, GFH – Sand Filtration	SVF-NaOH-070804-2B	4.4					23.3
NaOH, pH=9.5, GFH – GFH Column	SVF-NaOH-070804-2C	4.4					17.7

* The As concentration is an order of magnitude lower than previous head samples. No explanation.

The pH of the Susie/Valley Forge Mine water was adjusted from 2.65 to 6.5 and then to 9.5 using a 10% NaOH solution. Approximately 50 mL of 10 mg/L NaOH solution was required to raise the Susie Mine water pH from 2.64 to 6.5 and another 9 mL to raise 1 liter of Susie Mine water pH from 6.5 to 9.56. The results (SVF-NaOH-022704-1 and SVF-NaOH-022704-2) of the tests using NaOH were consistent with the addition of $Ca(OH)_2$ results. At pH 6.5, the As concentration was reduced to 363 µg/L and the Zn concentration was reduced to 33,100 µg/L. When the pH was raised to 9.5, the Zn concentration was reduced to 107 µg/L, while the As concentration decreased to approximately 92.2 µg/L. The later results were confirmed in the tests SVF-NaOH-081604-10A through SVF-NaOH-081604-16A shown in Table 5.

Table 5. Susie/Valley Forge head sample with no ferric added to remove As, Cd, Cu, and Zn by ferrihydrite coprecipitation/adsorption at pH 8.

Element	Predicted Final Concentrations at pH 8, µg/L	Achieved, µg/L
As	2,000	390,410
Cd	<1	94.4
Cu	<1	2.4
Fe(III)	<1	
Fe(II)	2,000	97,100
Zn	10,000	20,400

Stabcal adsorption model used for the above calculation results. The calculations were performed at an added ferric concentration to give an Fe/(As+Ca+Cd+Cu+Mg+Ni+Zn) weight ratio of one.

ORP Adjustment Tests. The pH of the Susie/Valley Forge Mine water was first adjusted from 2.86 to 7.5 using NaOH and then the ORP was increased from 284 mV to 338 mV by adding H_2O_2 followed by 0.45-micron filtration. The H_2O_2 test data (SVF-H2O2-031204-1) shows that the As concentration was reduced to 19 μg/L while the Zn concentration was reduced to 28,300 μg/L. The NaHClO test data (SVF-SH-031804-1) shows that the As concentration was reduced to 196 μg/L, while the Zn concentration was reduced to 27,800 μg/L. The results for these tests did not meet the Circular WQB-7 standards for either As and Zn. However, it did show that if the Fe in solution can be oxidized and precipitated, a significant amount of the As and dissolved metals can be removed from solution either by adsorption onto the ferrihydrite surface or by coprecipitation.

Chemical/Precipitation Tests. Ferric (as ferric sulfate) and ferrous (as ferrous sulfate) were added to the Susie/Valle Forge Mine water at 1X and 5X (as described previously) at approximately 228,000 μg/L and approximately 2,149,000 μg/L, respectively. The pH of each water was raised to 8. Stabcal Modelling (Huang, 1998) results for 1X and 5X are presented in the figures and tables that follow. Fig. 6 and Fig. 7 are solubility diagrams developed using the Stabcal Modelling program. The diagrams show metal solubilities expected in the Susie/Valley Forge Mine water as a function of pH. Table 5 and Table 6 are comparisons of the calculated values from the Stabcal Modelling to actual achieved values.

Table 6. Five times the initial concentration requirement of ferric added to remove As, Cd, Cu, Zn by ferrihydrite coprecipitation/adsorption at pH 8.

Element	Predicted Final Concentrations at pH 8, μg/L	Achieved, μg/L
As	<1	247
Cd	1	68.8
Cu	<1	1.6
Fe(III)	<1	
Fe(II)	150	102,000
Zn	50	14,300

Stabcal adsorption model used for the above calculation results. The calculations were performed at an added ferric concentration to give an Fe/(As+Ca+Cd+Cu+Mg+Ni+Zn) weight ratio of one.

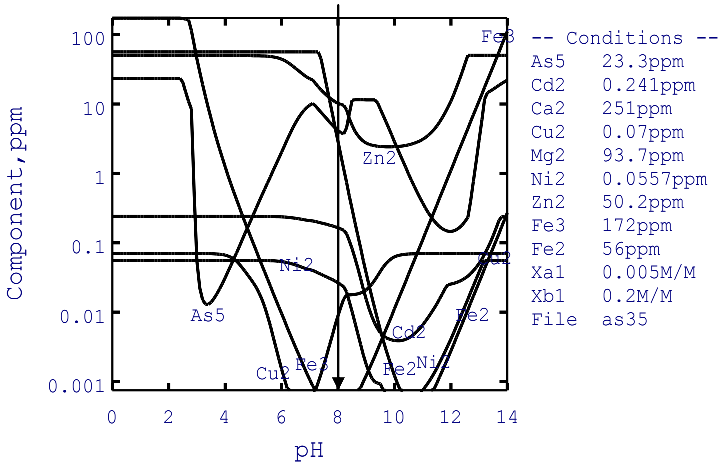

Figure 6. Stabcal Model of metal solubility diagram for Susie/Valley Forge Mine water with no addition of ferric Fe. The water has equivalent to 1X the initial concentration of As, Cd, Cu, Fe, Ni, and Zn.

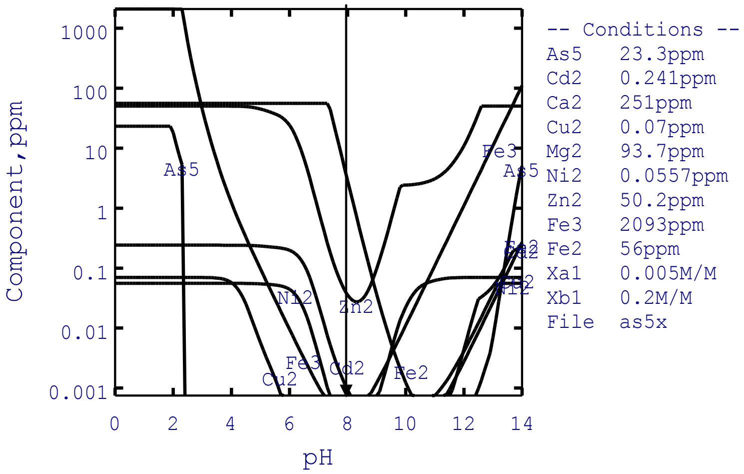

Figure 7. Stabcal Model for metal adsorption and precipitation for Susie/ Valley Forge Mine water with addition of ferric Fe at 5X the initial concentration of As, Cd, Cu, Fe, Ni, and Zn.

The results for these tests did not meet the Circular WQB-7 standard for As and Zn. However, the test data indicate that additional ferric Fe could be beneficial for increased As removal. The data also indicates that Zn will not be reduced to below the Circular WQB-7 levels with Fe chemistry; Zn solubility is pH dependent and the pH must be raised above 9 to reach the desired results.

<u>Adsorption Tests</u>. Adsorption tests using GFH media were performed on the Susie/Valley Forge Mine water. The laboratory apparatus is shown in Fig. 8 and the field apparatus is shown in Fig. 9. The water used for the adsorption tests was the filtrate from the water that was adjusted to pH 9.5 and filtered. Test results (SVF-NaOH-070804-2A through SVF-NaOH-070804-4C) indicate that the As concentration in the Susie/Valley Forge Mine water can be reduced to <18 µg/L, as shown in the data summary Table 7. A number of tests were performed to confirm the results of the preliminary tests shown in Table 4.

Figure 8. Laboratory apparatus.

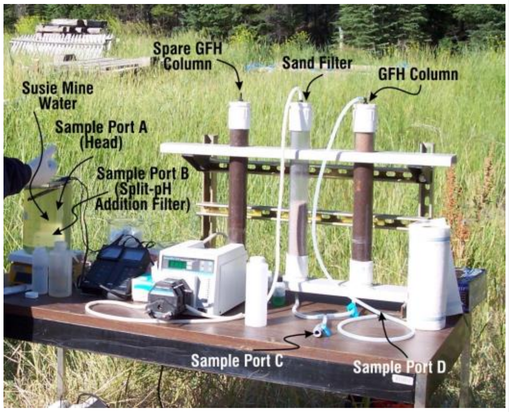

Figure 9. Field apparatus.

Table 7. Susie/Valley Forge confirmatory test analytical data.

Test	Sample ID	Sample Location	Metal, µg/L		Comments
			As	Zn	
Lab Apparatus					
NaOH, pH=9.5, GFH	SVF-NaOH-070804-3B	4	4.4	17.5	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-070804-3C	5	4.4	<8	Sand filter, GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-070804-4B	4	4.4	19.8	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-070804-4C	5	4.4	<8	Sand filter, GFH column
Field Apparatus					

Table 7. Susie/Valley Forge confirmatory test analytical data.

Test	Sample ID	Sample Location	Metal, μg/L As	Metal, μg/L Zn	Comments
NaOH, pH=9.5, GFH	SVF-NaOH-071304-5A	A	18,700	37,500	Head sample
NaOH, pH=9.5, GFH	SVF-NaOH-071304-5B	B	727	25.1	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-071304-5C	D	1.7	78.8	Sand filter, GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-071304-6A	A	18,000	37,200	Head sample
NaOH, pH=9.5, GFH	SVF-NaOH-071304-6B	B	467	<8	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-071304-6C	D	4.3	111	Sand filter, GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-081604-10A	A	17,800	43,900	Head sample
NaOH, pH=9.5, GFH	SVF-NaOH-081604-10B	B	770	13.5	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-081604-10C	C	302	166	Sand filter
NaOH, pH=9.5, GFH	SVF-NaOH-081604-10D-1	D	5.4	10.3	GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-081604-10D-2	D	5.4	11.4	Second sample after GFH column
NaOH, pH=9.5	SVF-NaOH-081604-11A	B	825	14.6	pH adjustment, 0.45-micron filter
NaOH, pH=9.5	SVF-NaOH-081604-12A	B	615	11.1	pH adjustment, 0.45-micron filter
NaOH, pH=9.5	SVF-NaOH-081604-13A	B	775	17.1	pH adjustment, 0.45-micron filter
NaOH, pH=9.5	SVF-NaOH-081604-14A	B	737	11.7	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, H_2O_2	SVF-NaOH-081604-15A	B	706	6.5	pH adjustment, ORP adjustment, 0.45-micron filter
NaOH, pH=9.5, H_2O_2	SVF-NaOH-081604-16A	B	418	9.8	pH adjustment, ORP adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-081704-17A	A	17,700	44,900	Head sample

Table 7. Susie/Valley Forge confirmatory test analytical data.

Test	Sample ID	Sample Location	Metal, μg/L		Comments
			As	Zn	
NaOH, pH=9.5, GFH	SVF-NaOH-081704-17B	B	4.4	8	pH adjustment, 0.45-micron filter
NaOH, pH=9.5, GFH	SVF-NaOH-081704-17C	C	1.7	6.1	Sand filter
NaOH, pH=9.5, GFH	SVF-NaOH-081704-17D	D	1.2	10.4	GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-081704-18A	D	0.99	15.9	GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-081704-18B	D	0.92	9.4	GFH column
NaOH, pH=9.5, GFH	SVF-NaOH-081704-18C	D	1.1	11.8	GFH column

The supplier (USFilter) of the GFH completed an adsorption model of the filtered water following the pH adjustment to determine the adsorption capacity of the GFH for the pretreated water. The adsorption capacity for As used in the simulation process model in Fig. 14 was 1,000 mg of As per kilogram of GFH, assuming an empty bed contact time (EBCT) of 64.83 minutes. The USFilter representative also stated that the optimum pH of the process water for As adsorption is approximately pH 7.6 to 7.8. If required, sulfuric acid could be used to adjust the pH of the process water prior to the GFH reactors.

Fig. 10 is the solubility diagram developed for the GFH column process. The diagram shows the solubility of the metals in the Susie/Valley Forge Mine water over a pH range. Table 8 is a comparison of the calculated values from the Stabcal Model to actual achieved values from the treatability tests. The scenario for Fig. 10 was to show what the As and metals removal would be with excess ferric Fe in the process.

The Susie/Valley Forge Mine water was selected for the process water to be treated in Phase II. Further discussion on the Susie/Valley Forge Mine site and water chemistry is provided in the Site Selection section.

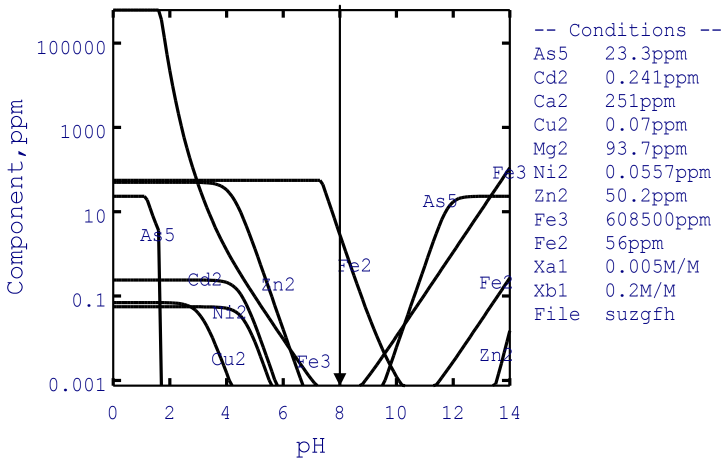

Fig. 10. Stabcal Model of metal solubility diagram for Susie/Valley Forge Mine water simulating the amount of ferric Fe available in GFH columns to remove As, Cd, Cu, Fe, Ni, and Zn.

Table 8. Column tests using GFH packing at pH 9.5.

Element	Predicted Final Concentrations at pH 8, μg/L	Achieved, μg/L
As	<1	0.9-5.4
Cd	<1	
Cu	<1	
Fe(III)	2	
Fe(II)	3	
Zn	<1	6-79 generally <25

Stabcal adsorption model used for the above calculation results. The calculations were performed at an added ferric concentration of 608,500 mg/L based on a column packing of 810 g of GFH and a residence time of 30 minutes. The Fe concentration in the column packing was calculated based on the GFH having a general formula of $Fe_5HO_8.4H_2O$ and 50% water. Only As and Zn were analyzed in the effluent solution.

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~~5.~~Site Selection

Selection Criteria

In May 2004, MSE presented the test results from Phase I of the MWTP Physical Solutions Project to the EPA NRMRL Project Officer, and representatives from the MDEQ, EPA Region 8, and CDM. During this meeting, the Susie/Valley Forge Mine water was selected as the project water for the Phase II demonstration. The criteria used to select the Susie/Valley Forge Mine were: 1) significance to the Tenmile Creek Drainage Record of Decision to determine alternative treatment for AMD; 2) accessibility to the mine site; 3) opportunity for sustainable treatment of the water; and 4) compatibility with future plans (i.e., EPA Region 8 and MDEQ) to treat the water and/or identify source control options in the mine workings. The Susie/Valley Forge Mine site was the only site that satisfied all four criteria. However, it was recommended during the meeting that ASARCO pursue additional testing using adsorption technology (i.e., GFH) to determine the feasibility to treat both the stormwater and groundwater from Groundwater Monitoring Well EH-100. Fig. 5 is a good photo of the landscape around the Susie/Valley Forge Mine adit. Figs. 11 and 12 are photographs of the Susie/Valley Forge Mine water discharge and show the red precipitate and ferric hydroxide sludge in the discharge area prior to entering Tenmile Creek.

Figure 11. Susie/Valley Forge Mine water discharge (looking toward Tenmile Creek).

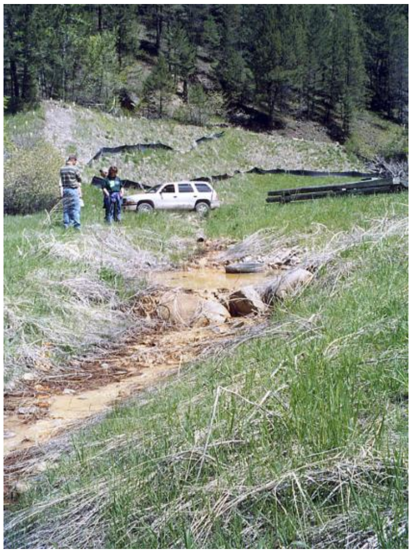
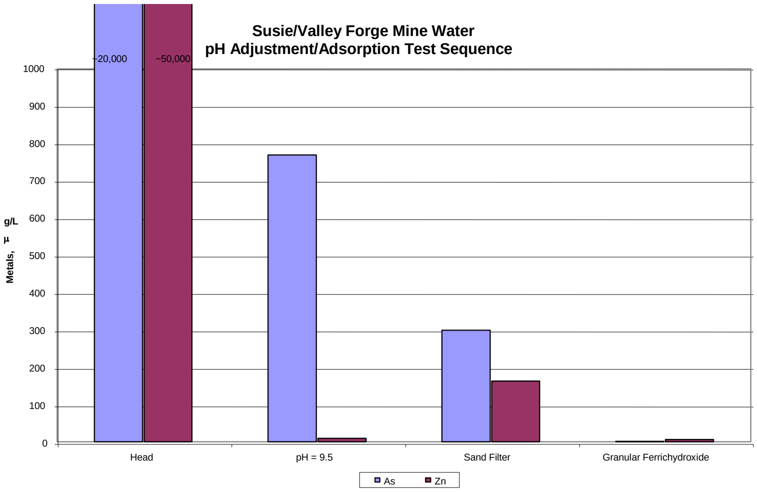


Figure 12. Susie/Valley Forge Mine water discharge (looking toward the mine adit).

Technology Selection

Technology Review

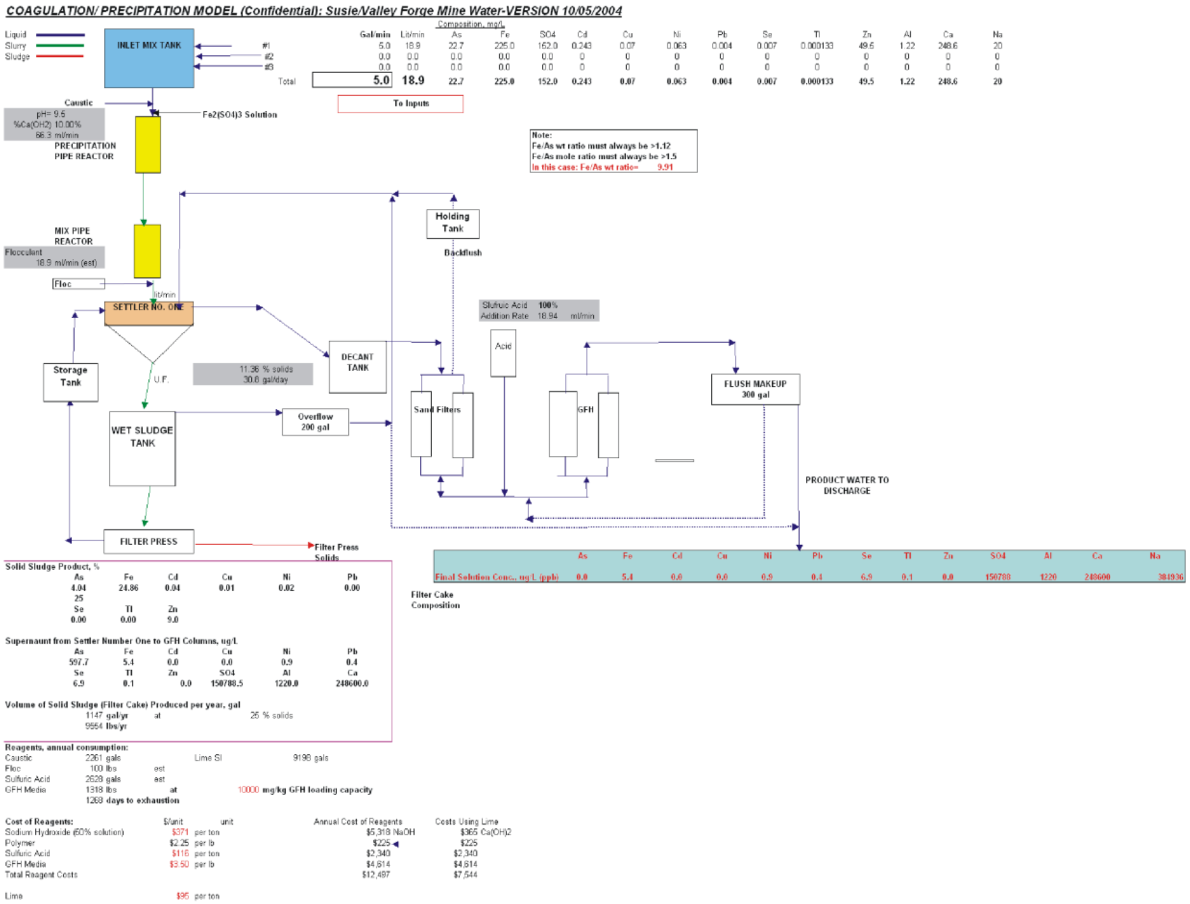
Following the selection of the Susie/Valley Forge Mine site, additional treatability tests were performed on the Susie/Valley Forge Mine water to confirm results from earlier testing and to develop process design information (Table 8). A conceptual treatment process was developed from this information. The proposed process consists of pH adjustment using NaOH and $Ca(OH)_2$; coprecipitation of ferric hydroxide and other metals along with adsorption of As and metals onto the ferric hydroxide precipitate; and a polishing stage using GFH for adsorption of the remaining As. Fig. 13 is a graph showing the reduction in As and Zn. The process will be designed to treat 10 gpm. The additional volume capacity could be necessary should the Lee Mountain Mine water be pumped to the Susie for treatment in the proposed treatment system. The Red Water Mine discharge would be treated separately due to the large discharge volume. A process flow model was developed by the Montana Tech Metallurgical Engineering Department (Dr. Larry Twidwell) to support the design effort. An example of the process flow diagram model is shown in Fig. 14.



Note: The rise in the Zn concentration following sand filtration cannot be explained.

Figure 13. Estimated As and Zn reduction for each process step; only one sample sequence used.

For discussion purposes, the average yearly flow rate for the Susie/Valley Forge Mine discharge is assumed to be 5 gpm. The following discussion uses the 5-gpm flow rate in order to illustrate the annual products production and reagent consumption for the process. Using the analytical data from the treatability testing flowsheet shown in Fig. 14 simulates the process and the products produced. The treatability test analytical data and simulated model data were reviewed and found to be comparable for developing process product(s) information for design purposes.



COAGULATION/ PRECIPITATION MODEL (Confidential): Susie/Valley Forge Mine Water-VERSION 10/05/2004

Composition, mg/L

	Gal/min	Lit/min	As	Fe	SO4	Cd	Cu	Ni	Pb	Se	Tl	Zn	Al	Ca	Na
#1	5.0	18.9	22.7	225.0	162.0	0.243	0.07	0.063	0.004	0.007	0.000133	49.6	1.22	248.6	20
#2	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0	0
#3	0.0	0.0	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0	0
Total	**5.0**	**18.9**	**22.7**	**225.0**	**152.0**	**0.243**	**0.07**	**0.063**	**0.004**	**0.007**	**0.000133**	**49.5**	**1.22**	**248.6**	**20**

pH= 9.5
%Ca(OH2) 10.00%
66.3 ml/min

Flocculant
18.9 ml/min (est)

Note:
Fe/As wt ratio must always be >1.12
Fe/As mole ratio must always be >1.5
In this case: Fe/As wt ratio= 9.91

Slufruic Acid **100%**
Addition Rate 18.94 ml/min

11.36 % solids
30.8 gal/day

	As	Fe	Cd	Cu	Ni	Pb	Se	Tl	Zn	SO4	Al	Ca	Na
Final Solution Conc., ug/L (ppb)	0.0	5.4	0.0	0.0	0.9	0.4	6.9	0.1	0.0	150788	1220	248600	384936

Solid Sludge Product, %

As	**Fe**	**Cd**	**Cu**	**Ni**	**Pb**
4.04	**24.86**	**0.04**	**0.01**	**0.02**	**0.00**
25					
Se	**Tl**	**Zn**			
0.00	**0.00**	**9.0**			

Supernaunt from Settler Number One to GFH Columns, ug/L

As	**Fe**	**Cd**	**Cu**	**Ni**	**Pb**
597.7	**5.4**	**0.0**	**0.0**	**0.9**	**0.4**
Se	**Tl**	**Zn**	**SO4**	**Al**	**Ca**
6.9	**0.1**	**0.0**	**150788.5**	**1220.0**	**248600.0**

Volume of Solid Sludge (Filter Cake) Produced per year, gal
1147 **gal/yr** at 25 % solids
9554 **lbs/yr**

Reagents, annual consumption:

Caustic	2261 gals		Lime Sl	9198 gals
Floc	100 lbs	est		
Sulfuric Acid	2628 gals	est		
GFH Media	1318 lbs	at	10000 **mg/kg GFH loading capacity**	
	1268 **days to exhaustion**			

Cost of Reagents:	$/unit	unit	Annual Cost of Reagents	Costs Using Lime
Sodium Hydroxide (50% solution)	$371	per ton	$5,318 NaOH	$365 Ca(OH)2
Polymer	$2.25	per lb	$225	$225
Sulfuric Acid	$116	per ton	$2,340	$2,340
GFH Media	$3.50	per lb	$4,614	$4,614
Total Reagent Costs			$12,497	$7,544
Lime	$95	per ton		

Figure 14. Susie/Valley Forge Mine water simulation process flow diagram.

At 5 gpm, approximately 2.6 million gallons per year of Susie/Valley Forge Mine water would be treated. The theoretical final solution concentrations are provided in the simulation process flow diagram in Fig. 14. Using the analytical information in Table 2, the Susie/Valley Forge Mine water at 5 gpm contributes over 7,000 pounds of As and heavy metals consisting of Cd, Cu, Fe, Mn, and Zn to the Tenmile Creek. The proposed process will remove these constituents from the water into an environmentally stable form. If the sludge were filtered, approximately 9,500 pounds per year, estimated to be 25% solids, will be produced. Preliminary research indicates the sludge should pass the toxicity characteristic leaching procedure (TCLP) and be suitable for landfill disposal. However, additional testing in Phase 2 will be performed. The actual means of disposal for the sludge will be determined by the MDEQ. The main option is to dispose of the sludge in the Lutrell Repository, which is located at the Basin Creek Mine, approximately seven miles south of the Susie/Valley Forge Mine site.

Four reagents will be used in the process. Hydrated lime will be used to adjust the Susie/Valley Forge Mine water pH. It is estimated that 9,200 gallons per year of $Ca(OH)_2$ at 10% by weight will be required. A cationic flocculant will be used to assist precipitate settling. The amount of flocculant used is very small. It is estimated that 80 pounds of flocculant will be required per year. Sulfuric acid will be required to adjust the pH of the effluent prior to discharge. It is estimated that 1,000 gallons per year of sulfuric acid will be required. Ferric sulfate may be used to increase the Fe concentration in the mine water. This may be necessary to improve As and dissolved metals removal if operating the system at a lower pH range is desired. Additional test work in Phase 2 will be performed to determine optimum Fe additions.

Granular ferric hydroxide media will be used in a polishing step to remove As and other residual dissolved metals of concern prior to discharging to the Tenmile Creek. Approximately 1,607 pounds per year of GFH will be used assuming 8,000 milligrams per kilogram As loading capacity for Susie/Valley Forge Mine water supernate chemistry from Settler one.

Technology Costs and Process Economics

The proposed treatment system can be classified as a small coagulation/filtration system with adsorption of As onto GFH as a polishing system. The proposed system will be designed to treat 10 gpm or 0.014 million gallons per day of Susie/Valley Forge Mine water. The adit flow rate ranges from 3 to 6.4 gpm. Operational costs are calculated for treating an average of 5 gpm. Annual reagent costs are provided in Table 9. The unit price for each reagent was taken from the EPA document, *Technologies and Costs for Removal of Arsenic from Drinking Water* (EPA, 2000). The GFH cost is a quote from USFilter in 2004.

Table 9. Estimated annual reagent costs to treat 5 gpm.

Reagent	Unit	$/Unit	Amount Required	Cost of Reagents
$Ca(OH)_2$	ton	$95.00	3.8	$365
Polymer	pounds	$2.25	100	$225
Sulfuric Acid	ton	$116.00	20	$2,340
GFH Media	pounds	$3.50	1318	$4,614
Total Annual Reagent Costs				$7,544

Table 10 is a preliminary capital cost breakdown for a package coagulation/filtration water treatment plant with 12-square foot (ft^2) filter area. The model was taken from EPA Document 815-R-00-028. The cost model was used because the processes have similar equipment. The costs provide an estimate. An engineering cost estimate of the process will be developed in Phase 2.

Table 10. Water model capital cost breakdown of package conventional treatment [coagulation/filtration, filter area (12 ft^2)].

Cost Component	Cost Breakdown	Percentage Breakdown
Excavation and Site Work	$3,500	3.19%
Manufactured Equipment	$44,900	40.89%
Concrete	$1,000	0.91%
Labor	$14,700	13.39%
Pipes and Valves	$8,300	7.56%
Electrical	$4,500	4.10%
Housing*	$18,600	16.94%
Subtotal	$95,500	
Contingencies	$14,300	13.02%
Total (2000)	$109,800	100.00%
Total (Adjusted to 2004)	$120,780	

* Housing costs are added to the total capital cost after application of the TDP cost approach.

Table 11 is an estimated annual cost breakdown to operate the proposed system. Assumptions used to determine the operational costs are as follows.

- Labor rates for an operator – $48 per hour
- Labor hours per week – 4 hours
- Labor rates for a water treatment engineer – $95 per hour
- Labor hours per week – 1 hour
- Analytical sampling – $500 per quarter
- Electricity – $0.08/kilowatt hour (kWh)
- Building energy use – 102.6 $kWh/ft^2/year$
- Building – 500 ft^2
- Annual safety & health, and hazardous material training will be required

Table 11. Annual operational cost estimate.

Cost Component	Cost Breakdown
Labor (operator hours)	$10,000
Labor (engineer)	$5,000
Analytical	$2,000
Energy	$4,000
Training	$2,000
Total	$23,000

It is estimated that 9,554 pounds of ferrihydrite sludge will be produced annually by the process. In addition, 1,318 pounds of spent GFH will have to be disposed. All solid waste from the process will be sent to the Latrell Repository. To determine a cost for disposing of the process solids, $0.50 per pound will be used for each solid waste. This cost estimate will include all shipping and handling (i.e., labor, vehicle, food, etc.). Table 12 shows annual disposal costs for all solid waste material.

Table 12. Annual disposal cost for solid waste material.

Cost Component	Amount (pounds)	Cost Breakdown
Ferric Hydroxide Sludge	9,554	$4,800
GFH Media	1,318	$650
Total		$5,450

Annual operational costs are estimated to be $36,000.

Conclusions And Recommendations

Treatment for all the project waters (i.e., Susie/Valley Forge Mine, Lee Mountain Mine, and Red Water Mine) for the removal of As and Zn proved to be a difficult task. The test data shows that there were only a few treatment options capable of removing both As and Zn to below the Circular WQB-7 standards for the Susie Mine water.

The Susie/Valley Forge Mine discharge was selected as the project water to be treated in the field demonstration in Phase 2 of the Physical Solutions Project. After evaluation of all the test data developed in Phase 1, it was determined that the Susie/Valley Forge Mine water could be treated to meet the Circular WQB-7 standards for As, Cd, Cu, Fe, Pb, and Zn. The technology selected for Phase 2 to demonstrate the effective treatment of the Susie/Valley Forge Mine water is coagulation/filtration using the mine water's Fe with addition of $Ca(OH)_2$ to produce ferric hydroxide precipitate. Precipitate formation happens in combination with metal adsorption onto and within the ferrihydrite solid structure. Solid/liquid separation is then performed by gravity separation and followed by filtration. The settler supernate requires polishing to remove the remaining dissolved As in solution. This is accomplished using GFH as an effective As adsorption media. There are three products from the process: 1) treated water to be discharged to the Tenmile Creek; 2) sludge to be disposed at the Latrell Repository; and 3) the spent GFH to be disposed of at the Latrell Repository. The preliminary estimate to implement the process equipment is $120,780. The estimated annual operational cost is $36,000.

At the designed flow rate of 10 gpm, the process will eliminate approximately 10,000 pounds of hazardous metals from entering the Tenmile Creek. The use of $Ca(OH)_2$ in the process will result in more favorable discharge pH and added nutrients in the form of $Ca(OH)_2$ and $CaCO_3$ to improve or enhance the crestation population (form of food for the fish population) in the Tenmile Creek. Additional research may have to be performed to justify this statement. Treatment of the Susie/Valley Forge Mine water should provide noticeable improvement of the Tenmile Creek ecosystem and significantly enhance the water quality.

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