Spring 4-21-2023

A GUIDE TO FIFTY YEARS OF RESEARCH AT MONTANA TECH: Part 1-THE TREATMENT OF ARSENIC, SELENIUM, THALLIUM, METAL BEARING SOLUTIONS AND WASTE SOLIDS

Larry G. Twidwell

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L.G. Twidwell
Emeritus Professor of Metallurgical Engineering
Metallurgy/Materials Engineering Department
School of Mines and Engineering
Montana Technological University

ABSTRACT and FORWARD

The removal of arsenic, selenium, and metal species from hydrometallurgical solutions and wastewaters has been and continues to be an important research topic. This presentation includes a discussion of the research conducted at Montana Tech in the Department of Metallurgical and Materials Engineering during the past fifty years. The discussion is focused on removal of arsenic by co-precipitation with Fe(III) and Fe(II), co-precipitation with Fe(III) and Al(III), reduction using elemental iron; the removal of selenium by elemental iron and catalysed iron; and the removal of cadmium, copper, nickel, zinc by co-precipitation with Fe(III) and Al(III).

This presentation is based on the research of Master of Science graduate students, industrial and academic colleagues, at the Montana College of Mineral Science and Technology (which morphed to Montana Tech [1977], then to Montana Tech of The University of Montana [2000], then to Montana Technological University [2019]). The referenced work of each of the graduate students in this presentation is gratefully acknowledged. The following summary does not include other research studies conducted in the Metallurgy/Materials Engineering Department by other teaching and research colleagues (except for some of the work supervised by Dr. Hsin Huang). See Appendix A for a list of the Master of Science research thesis students (11) and their research topics highlighting their contributions to our departments' research efforts (student theses are readily available, on-line in digital format, at the Montana Tech Library).

The referenced research was supported by the U.S. Environmental Protection Agency Mine Waste Treatment Program (EPA-MWTP), the National Science Foundation, and the Center for Advanced Metallurgical and Mineral Processing (CAMP) over a period of ten years.

Because of our extensive arsenic research, I have included a recent detailed annotated literature survey of the topic "Fixation of Arsenic (August 2021)" prior to presenting a summary of the Twidwell group's specific research studies and results at Montana Tech. The reader may bypass the literature survey by going to page 32 for a summary of Montana Tech research studies and results.

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Please note: As a convenience to readers using this presentation as a guide to the subject literature, all references are bolded and highlighted throughout the text.

INTRODUCTION

Prior Research

In addition to our arsenic/selenium research, EPA and NSF supported studies directed toward treating high value electroplating and electromachining hydroxide sludge materials (primarily we investigated ways to selectively recover iron, chromium, cobalt, and nickel from a wide variety of industrial supplied hydroxide source materials. A list of the studies with annotated comments is presented in Appendix B and in Part 2 (available as a separate document).

Arsenic, Selenium, Metals, Thallium Research and Literature Discussion with Annotations

Our interest in arsenic removal from aqueous solutions and fixation/stabilization of arsenic bearing products began in 1974 mainly because of our location near the Anaconda Copper Smelter site in Anaconda, Montana, and the fact that they and other copper smelters needed a means of stabilizing copper smelter flue dust so that arsenic would not be released into the environment. Our first two arsenic studies were conducted during 1974-76 by **Knoepke (1974)** and **Mehta (1976)** who investigated the stabilization of Anaconda and other copper smelter flue dust using lime/dust and ferric compounds/dust mixtures by thermal roasting to fixate the arsenic. The fixated products were then encapsulated in cements and concretes and subjected to long-term water leaching. The ARCO Company ended up encapsulating over 340,000 tons of the smelter arsenic flue dust in a lime/cement mixture and placing it into a permanent repository near the former smelter site. Our interest in arsenic continued during the period 1982-2010 with funding from the USBM Mineral Industry Waste Treatment and Recovery Generic Center, EPA, and the National Science Foundation to identify appropriate arsenic bearing compounds that would remain stable for long-term outside storage. These studies included the formation of arsenic bearing substitution compounds such as lead arsenate phosphate (**Comba 1987; Comba, Dahnke, and Twidwell 1988; Twidwell et al. 1994);** arsenate/phosphate apatite compounds **(Plessas 1992; Miranda 1996; Gale 1998; Saran 1997; Wilson 1998;** and **Orser 2001),** and arsenic loaded slags (**Blaskovich 1982; Downey 1982; Roset 1982;** and **Pande 1993).**

Our interest was further focused on removing arsenic from wastewater solutions, during a semester long visit, by Dr. R.G. Robins, to our department in 1984. Dr. **Robins and Tozawa (1982)** were the first investigators to recognize and to alert the gold industry that arsenic storage as calcium arsenate was inappropriate. Our work has continued until the present and a number of research summaries are available from the EPA Mine Waste Technology Program (MWTP), e.g., arsenic and selenium removal by cementation using elemental iron as the reductant **(MWTP-41 1994; MWTP-191 2001; MWTP-262 2005)** and catalyzed elemental iron reductant **(MWTP-213 2004];** formation and stability of arsenatephosphate apatite **(MWTP-82 1999; MWPT-82R1 1998** and **82R2 1999; MWTP-121 1999; MWTP-305 2008; Twidwell et al. 2004);** ferric and ferrous treatment of mine waters **(MWTP-56 1991; MWTP-240 2005; MWTP-262 2005);** ferrihydrite/arsenic co-precipitation and aluminum modified ferrihydrite/arsenic treatment of waste water and long-term product storage **(MWTP-282 2007; MWTP-293 2008; MWTP-307 2008);** and the influence of anion species on ferrihydrite/arsenic co-precipitation and long-term storage (**MWTP-307 2008).**

Our other interests and studies have included: selenium (**Dahlgren 2000; Dahlgren et al. 2004**; **Twidwell et al. 2000; Twidwell et al. 2005);** thallium **(MWTP-204 2003; MWTP-143 2001; Twidwell and Williams-Beam 2002);** metals (Cu, Cd, Ni, Zn) removal from waste waters and their long-term storage stability **(MWTP-262 2005; Twidwell and Leonhard 2008a, 2008b);** and deep-water sediment in acid mine pits **(MWTP-133 1999, MWTP-81 2000. MWTP-305 2008).**

Literature reviews covering state-of-the-art technologies to remove arsenic, selenium, and thallium were conducted prior to our experimental studies. These reviews are available as follows: **arsenic** (**MWTP-41 1994, MWTP-60 1996, MWPT-90 1996, Twidwell et al. 2002, 2019, 2021); selenium** (**MWTP-106 1999);** and **thallium (MWTP-143 2001, MWTP- 204 2004).**

FIXATION of ARSENIC LITERATURE REVIEW

[Recent additional information on this subject is presented by **Twidwell 2021]**

Past Practice

For decades, the major practice for the disposal of arsenic bearing solutions was lime addition to form calcium arsenate/calcium arsenite with placement in containment ponds or tailings impoundments **(Velenzuela 2006).** R.G. Robins (University of New South Wales) and Tozawa (University of Tohoku) were

the first to alert industry that "*calcium arsenate is unstable when exposed to carbon dioxide in air*" and is, therefore, "*not suitable for storage of calcium As(III) or As(V) compounds*" **(Robins and Tozawa 1982).** Note in Figure 1 that there is a range of pH values where calcium arsenate is stable in the absence of carbon dioxide, i.e., the Environmental Protection Agency (EPA) specified the Toxicity Characterization Leach Procedure (TCLP, discussed later) value must be less than five mg As/L for the product to be designated a non-hazardous product. However, when these compounds are exposed to air, which contains carbon dioxide, they are not stable and calcium carbonate forms releasing arsenic back in the solution phase and the arsenate and arsenite compounds are not thermodynamically stable and the arsenic in the solution phase will exceed the EPA TCLP regulatory standard at >5 mg As/L.

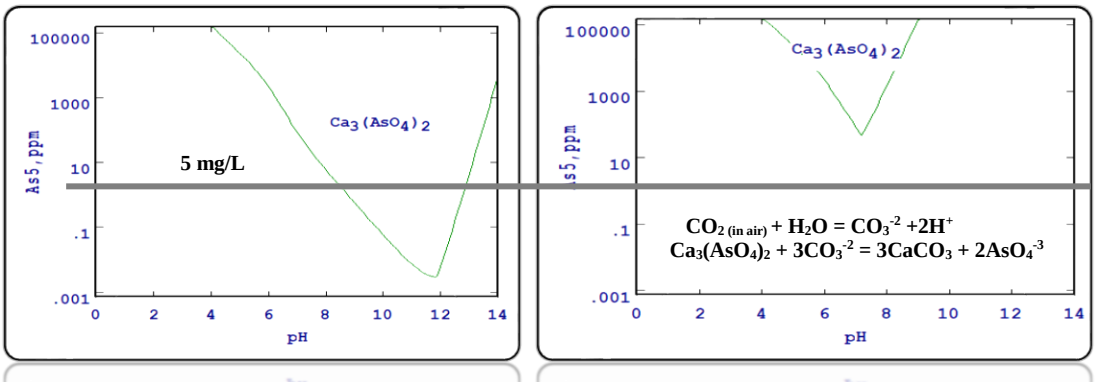


Figure 1. The conversion of calcium arsenate to calcium carbonate by carbon dioxide in air
(Line drawn at the U.S. EPA TCLP required level of <5 mg/L to designate the solid as non-hazardous)
Source: Diagram generated by STABCAL, **(Huang 2021).**

Riveros et al. (2001) have demonstrated that calcium arsenate sludge can leach up to 4,400 mg As/L using the TCLP leach test. **Nishimura and Umetsu (1985)** have shown that crystalline calcium arsenate can be formed by calcination and that its solubility is decreased. Regardless of this, dissolution of arsenic will occur with time. However, **Nazari et al. (2017)** state that two smelters in Chile (Codelco's Chuquicamata and Noranda's Altonorte plant) still (2017) employ lime neutralization to form calcium arsenite/gypsum and calcium arsenate/gypsum products. The resulting residues are stored and monitored in permitted hazardous waste landfills. **Zhang et al. (2019)** evaluated the stability of calcium arsenate solids as a function of pH and aging time, e.g., slurries were formed from arsenate bearing solutions (1,000 and 2,000 mg As(V); Ca/As molar ratios of 1, 2, and 4) at various pH levels (8, 10, 12) and were aged in the presence of atmospheric carbon dioxide for up to 1120 days. The results showed appreciable arsenic leached for all combinations of the studied variables, e.g., approximately 10 to 300 mg/L at 1120 days. **Coudert et al. (2020)** in an extensive literature review concluded: *"Despite the satisfactory efficiency of lime neutralization in As removal from mine waters (>95%), it is now acknowledged that this process is an unsuitable option for As-rich effluents".*

Brief Summary of Current Industrial Practice

Three ferric/arsenic precipitation removal technologies are presently practiced by industry throughout the world: (1) ambient temperature arsenic adsorption/co-precipitation to form arsenical **ferrihydrite (FH)**; (2) elevated temperature and elevated pressure autoclave precipitation of **scorodite** ($FeAsO_4.2H_2O$); and (3) ambient pressure, elevated temperature precipitation of **scorodite**.

The ambient temperature/pressure FH technology (1) is relatively simple and the presence of commonly associated metals (aluminum, copper, lead, zinc) and gypsum have a stabilizing effect on the long-term stability of the outdoor storage of the product. The disadvantages of the adsorption technology are that: a relatively large amount of waste material is created (Fe/As mole ratio varies but is usually approximately three to four but can be as high as ten); the product is difficult to filter (20-25 wt.% solids); the requirement

that the arsenic be present in the fully oxidized state (arsenate); the presence of competitive associated anionic species may negatively influence the adsorption of arsenate; and the question as to long-term stability of the product in the presence of reducing substances in anoxic and/or bacterial environments. However, according to the U.S. EPA the FH/arsenate technology is the Best Demonstrated Available Technology (BDAT) available for removing arsenic from wastewater and storage of the precipitated arsenical FH **(Rosengrant and Fargo 1990).** It is the most utilized treatment procedure throughout the world (greater detail is presented later).

The second technology (2) practiced at several copper smelting facilities is arsenic removal by precipitation of **scorodite**. The advantages of the scorodite process over the FH technology is that less waste is formed (Fe/As molar ratio of one); greater density (better filterability); and better thermodynamic stability (under some conditions). The disadvantages of autoclave scorodite precipitation are that the treatment process is more capital and energy intensive; the compound may dissolve incongruently to form arsenical FH if the pH is >3-4; and its long-term storage may not be stable under reducing and/or anaerobic bacterial conditions.

The third technology (3) is the elevated temperature, ambient pressure **scorodite** process which is likely to be widely adopted in the future **(Fujita et al. 2010, 2012; Demopoulos 2009).** However, the same cautions stated above must be considered. In general, the FH adsorption process is favored for treating relatively low-level arsenic (<1 g/L) bearing waste solutions, while the scorodite precipitation process is more suitable for elevated arsenic bearing solutions.

Ferrihydrite/Arsenic Treatment

The U.S. EPA published regulations for the Best Demonstrated Available Technology (BDAT) to be used for the following Listed and Characteristic waste containing Arsenic or Selenium: K031, K084, K101, K102, Arsenic wastes (D004) and Selenium wastes (D010), and Phosphorus and Uranium wastes (Rosengrant and Fargo 1990). The specified BDAT technology for treatment of effluent solutions is adsorption on FH. This technology has also been selected by EPA as one of the Best Available Technologies (BAT) for removing arsenic from drinking waters and its application is widespread.

What is Ferrihydrite (FH)

FH is a ferric oxyhydroxide. The accepted formulae is $5Fe_2O_3{:}9H_2O$ **(Paktunc et al. 2008a, 2008b**). FH is a large surface area solid phase often referred to as an amorphous material, but it is a metastable nano-crystalline material. Important reviews detailing conditions for formation and the stability of FH are presented by **Jambor and Dutrizac (1998**), **Schwertmann and Cornell (2000), Cornell and Schwertmann (1996, 2003)**, and **Paktunc (2015), Paktunc et al. (2008, 2010).** The reviews by Jambor and Dutrizac (314 references) and **Cornell and Schwertmann** (approximately 1500 references) are, indeed, excellent sources of information on FH occurrence, structure, chemical composition, adsorptive capacity for cations and anion, its transformation rate, and a summary of factors that influence its transformation to hematite (Fe_2O_3) or goethite (FeOOH).

FH is characterized by x-ray diffraction as having a two-line structure, which relates to the number of broad peaks present. Two-line FH is formed by rapid hydrolysis to pH 4-7 at ambient temperature and is the form usually precipitated in industrial treatment systems. Crystallite sizes have been reported to be 2–4 nm. The surface area of freshly precipitated two-line FH is 150-340 m^2/g (**Paktunc et al. 2008a). Hohn (2005)** has demonstrated arsenic-loaded (7% As(V)) FH prepared at pH 4 and 7 self-flocculate to a mean agglomerate size of 5-10 micrometers.

Ferrihydrite Transformation

FH is considered a metastable phase that transforms to hematite or goethite with time. The rate of transformation has been investigated in detail and the rate of transformation is a function of time, temperature, pH, and the presence of adsorbed anions and cations, e.g., conversion of 2-line FH to hematite

at 25°C is half complete in 280 days at pH 4 but is completely converted at 100°C in four hours. Transformation results in a relatively large change in surface area, e.g., freshly prepared 2-line FH showed a surface area of ~150 m^2/g that, when converted to goethite at 25°C, was reduced to 92 m^2/g; when converted to goethite at 90°C the particulate surface area was reduced to 9 m^2/g (**Schwertmann and Cornell 2000).** The fact that conversion occurs reasonably rapidly and that the conversion results in a significant decrease in surface area may hold important negative consequences for long-term outdoor storage stability for adsorbed arsenic. However, in real industrial systems, the FH conversion rate may be mitigated (changed from days to years or decades) by the presence of other species and solution conditions during precipitation and subsequent storage. General factors that have been shown to decrease the rate of conversion to more crystalline forms include lower pH; lower temperature; presence of adsorbed arsenate, silicate, aluminum, manganese, heavy metals, and organics.

Ferrihydrite/Arsenic (Arsenical FH)

The structural relationships for FH adsorption of arsenate are via the formation of inner-sphere complexes rather than simple surface adsorption. The exact nature of the adsorption is controversial, but the use of EXAFS spectroscopy has shown that the adsorption is by bidentate corner-sharing surface complexes without the formation of monodentate corner sharing **(Sherman and Randall 2003).**

The terms **scorodite, ferric arsenate, and arsenical FH** are often used throughout the arsenic literature; sometimes incorrectly**. Paktunc et al. (2010)** and **Paktunc (2015)** experimentally investigated the structure of scorodite, ferric arsenate, and arsenical FH and they have clarified the distinction between the three forms, e.g., scorodite is a fully crystallized phase containing a Fe/As molar ratio of one ($FeAsO_4$:$2H_2O$); ferric arsenate is a microcrystalline product ($FeAsO_4$:4-7H_2O); and arsenical FH is arsenate absorbed within the FH ($5Fe_2O_3$:$9H_2O$) structure. Ferric arsenate forms at low pH and is transformed rapidly to scorodite at pH levels below ~1.7. Above that pH ferric arsenate and arsenical ferrihydrite form up to approximately a pH of 4.5 for Fe/As ratios from one to ten. See also **Paktunc (2015**) for further information on the formation and stability of scorodite and arsenical FH.

Removal of Arsenic from Aqueous Solutions

A relatively wide range of arsenic removal results, by FH precipitation/adsorption, are reported in the literature; this is to be expected because there are several experimental factors that influence the removal process. The influencing factors include: **the method of FH/arsenic contact, the iron/arsenic molar ratio, pH, time, initial concentration of arsenic, arsenic valence, and the presence of other anionic** species **(Twidwell et al. 2011**; **Twidwell 2018; Twidwell 2019a; Twidwell 2019b;** and **Twidwell 2021**).

Arsenic Speciation-Thermodynamic stability regions for arsenic species at ambient temperature as a function of solution potential and pH is illustrated in Figure 2. Arsenate As(V) species are stable under the more oxidizing potentials while, arsenite As(III) species exist under more reducing potentials. The effectiveness of FH removal of arsenic depends on the arsenic being present as As(V) species.

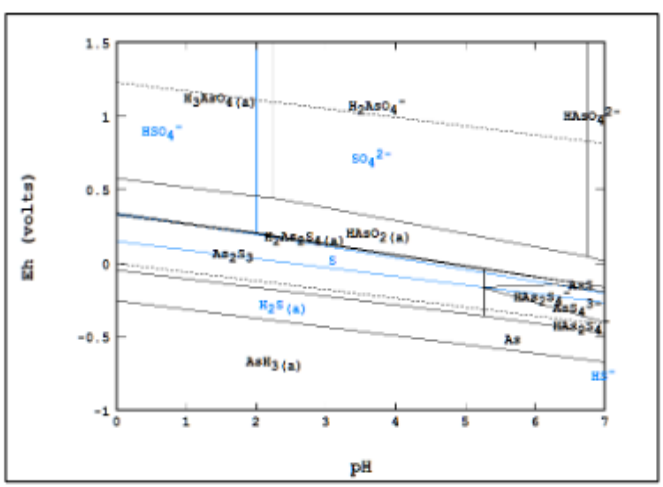
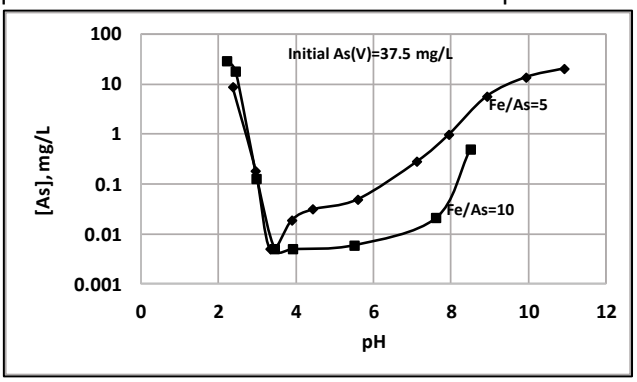


Figure 2. Potential/pH diagram for the As-S-water system (Arsenic concentration 10 mg/L. *Source:* Diagram generated by STABCAL **(Huang 2016).**

Method of Contact-Two approaches are currently used in industry: Co-Precipitation or Adsorption**.** ***Co-Precipitation*** occurs when iron and arsenic are present as dissolved species in the solution phase. When the solution pH is raised FH precipitates insitu throughout the solution with intimate contact between the solid and the arsenic in the solution phase. The second approach is termed **Adsorption.** Adsorption is promoted when a ferric containing solution is added to an arsenic solution at the desired pH. Upon addition of the dissolved ferric, FH forms and supplies surfaces for arsenic adsorption. The arsenic loading densities achieved by the two approaches are very different, e.g., co-precipitation results in a greater loading density (mole As/mole Fe is 0.7-1.0); whereas adsorption results in a loading density of 0.3-0.5.

Fe/As Molar Ratio, pH, Initial Arsenic Concentration-The influence of Fe/As molar ratio as a function of pH is illustrated in Figures 3-5. However, it is important to restate that the actual Fe/As molar ratio requirement for effective arsenic removal depends on the several experimental factors stated above.



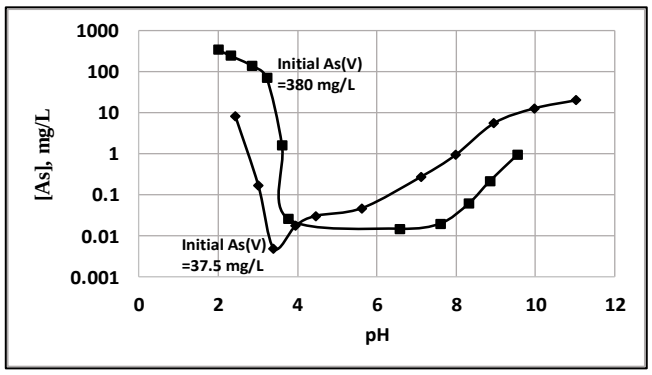


Figure 3. The influence of Fe/As molar ratio and pH on the removal of arsenic, As(V), by FH co-precipitation (left figure) and **Figure 4. The influence of initial arsenic concentration and pH on the removal of arsenic by FH co-precipitation** (right figure). *Source:* Adapted from **Wang, Nishimura and Umetsu (2000).**

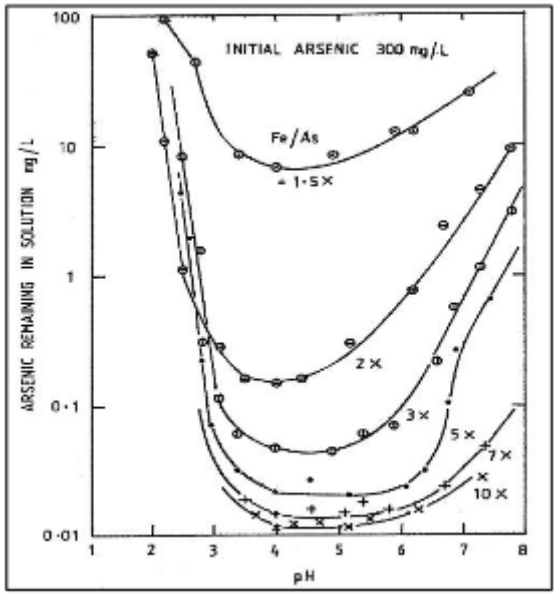


Figure 5. The influence of Fe/As molar ratio, and pH on the removal of arsenic by FH co-precipitation. (The Fe/As molar ratio is showen by 1.5x, 2x, 3, etc) *Source:* **Robins et al.**

(1988 p 104)

Valence State-The presence of arsenite, As(III), and other dissolved aqueous species are important aspects that need to be considered when selecting an appropriate FH technology. The normal approach when considering FH removal of arsenic is to consider ways to oxidize the As(III) to As(V). It is often stated that As(V) is much more effectively removed by FH than As(III). However, the relative removal of As(V) and As(III) depends upon the Fe/As ratio, pH, and whether the arsenic species are present individually or as mixtures. As(III) is often found in appreciable concentration in ambient temperature metallurgical operation flue dust leaching solutions, acid blowdown solutions, wastewater, groundwater, and surface waters. In fact, **Borho et al. (1996)** state that "*approximately thirty percent of the arsenic present is often As(III)".* The influence of Fe/As molar ratio, arsenic valence state, and pH is illustrated in Figure 6.

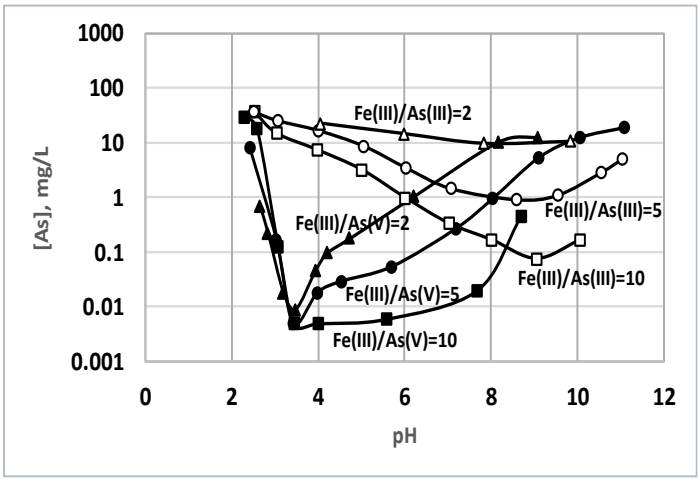


Figure 6. The influence of Fe/As molar ratio, arsenic valence, and pH on the removal of arsenic by FH co-precipitation. (Initial As(V) or As(III)=37.5 mg/L, 25°C, 30 minutes (Source*:* Adapted from **Wang, Nishimura, Umetsu (2000)**

Oxidation of As(III)-The oxidation of As(III) has been the focus of many studies. **Nazari et al. (2017)** present detailed discussions concerning what oxidants have been studied and a summary of the application conditions. The reader is referred to that publication. With respect to industrial applications the authors state that: *"As(III) bearing streams obtained from hydrometallurgical and pyrometallurgical processing frequently consist of a high concentration of As(III*). *Hydrogen peroxide, permanganate, ozone and SO_2/O_2 gas mixture have been typically employed in industrial scale to oxidize As(III) to As(V)".* The oxidation of As(III) is an important consideration because successful removal of arsenic by FH adsorption or scorodite precipitation requires that the arsenic be present as arsenate. This is especially true when forming scorodite.

Presence of Associated Ions-The presence of associated ions such as phosphate, sulfate, carbonate, and dissolved organic species can greatly influence the removal of arsenic and the relatively long-term stability of FH. A review of the effect of associated ions is beyond the scope of the present presentation and the reader is referred to the following publications: **Jain et al. (1999**); **Jain and Loeppert (2000); Appellos et al. (2002); Grafe et al. (2002); Violante et al. (2003);** and **Frau et al. (2008).** The presence of cations, such as Al(III), has been shown to enhance the removal of arsenic and to increase the long- term stability of FH **(De Klerk et al. (2012); Twidwell and McCloskey (2011);** and **Twidwell et al. (1999. 2000, 2002, 2005). Krause and Ettel (1989)** have shown that the presence of divalent cations; Zn, Cd, Pb, Ca, and Mg, extend the FH formation and stability range from pHs of 4-7 to ~4-10.

Stability of Ferrihydrite and Example Industrial Applications

Many investigations have focused on the formation and stability of **FH (Ford (2002); Riveros et al. (2001); Harris (2000a, 2001, 2003; Harris et al. (2003b); Hohn (2005); Twidwell et al. (2007); Twidwell (2021),** and many more). A few examples are presented here:

Ford (2002) investigated the storage stability of 2-line FH and arsenate-loaded FH for periods up to 112 days at 40 °C and pH 6. He found that the stability with respect to rate of conversion to hematite (Fe_2O_3) was a function of arsenate loading and that for some lower-level arsenate loadings the arsenic release from the solid phase did not occur even though appreciable FH was converted to Fe_2O_3 as a function of time. Ford also demonstrated, for arsenate loadings less than the maximum loading capacity of FH, that a significant fraction of the retained arsenate was lost from the originally co-precipitated FH but was not released to the solution phase. That is, the arsenate transferred to the crystalline Fe_2O_3 phase that was created during the aging process.

Twidwell et al. (1996-2008) investigated the stability of FH and aluminum modified FH (AMF, Al/Fe molar ratio of one) under a variety of conditions, including the [Al+Fe]/As molar ratio, temperature (25 and 70°C), initial As(V) concentration (0.1 to 10 mg/L), and aging time (30 minutes to 500 days). The partitioning of arsenate after 500 days at 70°C to the AMF formed hematite was significantly greater than for the FH solid, whereas the extent of conversion for the As-loaded AMF solids was much lower (17%) than for the As-loaded FH (73%) solids, showing that greater arsenic loading to the hematite conversion product occurred. Partitioning of arsenate from the amorphous solids to hematite or to the solution phase at ambient temperature did not occur over 500 days for either AMF or FH, i.e., the initial amorphous solids did not convert to crystalline ferric oxide. The influence of pH on arsenic solubility by formation of AMF and FH initially and at 367 days is presented in Figure 7. For additional information on this topic (FH/AMF) refer to the EPA Mine Waste Technology Program [MWTP] studies **(MWTP-282 2007; MWTP-293 2008);** and **MWTP-307 2008).** See also **Mohapatra et al. (2005)** for the effect of citrate, oxalate, acetate, silicate, and phosphate on stability of synthetic Arsenic-loaded Ferrihydrite and Al-Ferrihydrite.

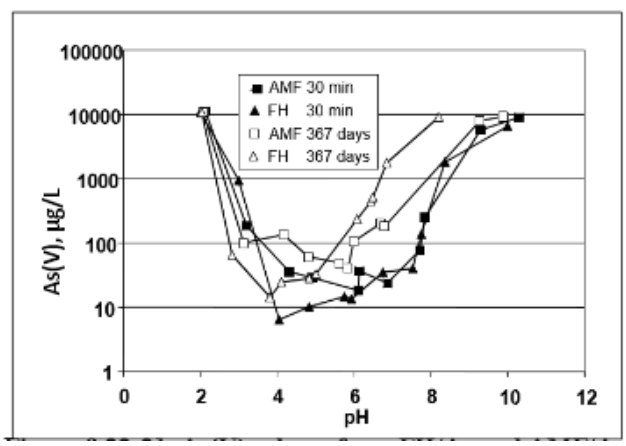


Figure 7. As(V) release from FH/As and AMF/As at 30 minutes and 367 days. (Conditions: initial As(V) = 10,000 µg/L; Fe/As or [Al+Fe]/As molar ratio = 5, ambient temperature). *Source:* **Twidwell et al. (2007).**

Removal of arsenic from solution by ferric precipitation has been or is practiced at numerous extractive metallurgical facilities, e.g., the Xstrata's Horne smelter; the Giant Mine, the Con Mine, and the Teck-Corona mine; the Kennecott Utah Smelter; Placer Dome Lonetree and Getchell mines (on a periodic basis);

Barrick's gold mining operations in Nevada; and the Saganoseki and Kosaka copper smelters in Japan, **Valenzuela (2000). Harris (2000)** has tabulated worldwide industrial operating practice (as of 2000/2001) for removal and stabilization of arsenic by the FH, autoclave, lime neutralization processes or by production of copper arsenate. **Harris (2003)** states that: "*by far the most popular approach is arsenical ferrihydrite, although possibly not always with the requisite level of understanding. INCO's CRED plant in Sudbury has been operating for close to thirty years, with no sign of ferrihydrite breakdown, or of arsenic release. As noted earlier, it is however, well known that the incorporation of small amounts of cations and anions into the ferrihydrite matrix appreciably slows down any crystallization process to the formation of goethite/and or hematite, and hence the consequent release of adsorbed ions. To all intents and purposes, it appears that recrystallization in these ferrihydrite materials in these situations is virtually non-existent. Certainly, the EPA regards the arsenical ferrihydrite process as the BDAT, and operations applying it correctly (molar Fe(III)/As(V) ratio >4 have not reported any contamination of local groundwater"*.

Nazari, et al. (2017) noted several industrial facilities that control their arsenic removal by arsenical FH adsorption and/or ferric arsenate formation. Examples presented include: the Xstrata Horne smelter (data from reference **Godhehere et al. (1995)** and **Peacey et al. (2010);** a uranium mill in northern Saskatchewan, Canada **(Demopoulos 2014),** and the Boliden Harjavalta plant in western Finland **(Salokannel et al. 2013).** The arsenic disposal practices are briefly paraphrased here: Xstrata's product included ferric arsenate, arsenical FH, and ferric arsenite. The products were mixed with smelter slag and were placed in their smelter slag tailings impoundment. Arsenic release was < 1 mg/L as required by the province of Quebec. The uranium mill product was ferric arsenate which was placed in their tailings facility. Arsenic release was below Saskatchewan regulations of 2 mg/L. The Boliden products were ferric arsenate and metal hydroxides; placement was not specified.

A comprehensive survey of *"Arsenic Management in the Metallurgical Industry"* **(Valenzuela, 2000**) is a recommended reference. This review includes identification of industrial applications throughout the world for both copper and gold processing and their arsenic removal and storage practices, at least up to the year 2000.

Additional data are presented in several publications. Please refer to SME Mineral Processing and Extractive Metallurgy Handbook; Chapter 10.9. For further information concerning the long-term stability of arsenical FH refer to publications presented by **Welham et al. (2000 Review); Paktunc et al. (2008a, 2008b); Riveros and Dutrizac (2001);** and **Drahota and Fillppi (2009a, 2009b Review);** and **Paktunc (2015).** Several conclusions taken from these publications follow:

A detailed review of the stability of scorodite, ferrihydrite, and ferrihydrite arsenate adsorption is presented by **Welham et al. (2000 Review**). The authors state that: *"there are significant problems with the use of jarosite and scorodite as phases for the disposal of iron and/or arsenic from metallurgical systems. Neither phase is stable under typical atmospheric weathering conditions with transformation to goethite predicted to occur. The currently permitted discharge level of arsenic is only achieved due to the slow kinetics of the transformation releasing arsenic over time. Crystalline scorodite is two orders of magnitude less soluble than amorphous iron (III) arsenate precipitates often formed in low temperature systems."* See also **Fuller, Davis, and Waychunas (1995)** and **Waychunas et al. (1995, 1996).**

Paktunc et al. (2008) concluded from their extensive study of phase transformations of arsenic bearing solids that: "*Industrial practice to stabilize arsenic in metallurgical circuits is to form precipitates having Fe/As molar ratios greater than 3 or 4. Despite its important implication, the meaning of this ratio in terms of controlling arsenic releases has remained unknown. As described above, the precipitates with different Fe/As ratios, invariably referred to as ferric arsenate or arsenical ferrihydrite, are not composed of a single phase. Instead, they are mixtures of ferric arsenate and ferrihydrite. Following the precipitation of ferric arsenate from arsenic-rich solutions, ferrihydrite forms at pH 2 and above. Its formation drives the solution*

composition to undersaturation with respect to ferric arsenate and promotes dissolution of ferric arsenate. With this, the ferrihydrite would impose control on the ferric arsenate. The increasing relative abundance of ferrihydrite would impose control on the As concentration in solution by providing additional sites for arsenate adsorption. Accordingly, formation of ferrihydrite coupled with ferric arsenate dissolution would be considered as an efficient process in terms of maximizing As releasee."

Riveros and Dutrizac (2001 Review) concluded from their review of the literature that *"for practical purposes, arsenical ferrihydrite can be considered stable provided the Fe/As molar ratio is greater than 3, the pH is slightly acidic and that it does not come in contact with reducing substances such as reactive sulphides or reducing conditions such as deep water, bacteria or algae".*

Conceptual Flowsheet for forming Arsenical Ferrihydrite

A conceptual Flowsheet for Forming Arsenical Ferrihydrite is presented in Figure 8.

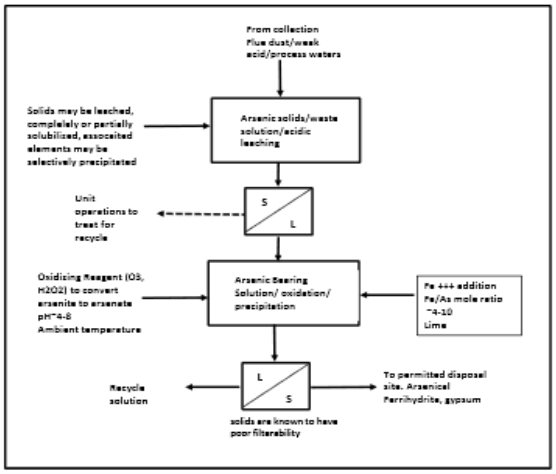


Figure 8. Conceptual flowsheet for forming Arsenical FH

Ferrihydrite Stability Concerns

In general, arsenical FH passes the U.S. EPA TCLP (Method 1311) toxicity test and the waste products do not have to be subjected to further stabilization as required by the U.S. LBR (Land Ban Restrictions). However, an important unknown at this time is whether the product from FH adsorption of arsenic will be stable if storage conditions are anaerobic or may become anaerobic or contain microbial agents. Many investigations have considered FH stability under oxic conditions. However, is FH stable when mixed with sulfide tailings and the mixture becomes reducing and are buried where the local environment may be anoxic?

Anoxic Conditions-**Doerfelt et al. (2016)** have considered the stability of FH and aluminum containing ferrihydrite (AMF) in the presence of sulfide as a reducing agent at anoxic conditions at relatively high pH levels. Their investigation focused on molar ratios of Fe(III)/As(V)=4 and Fe(III)/Al(II)/As(V)=2/2/1 co-precipitated products. The products were subjected to *"excess"* sulfide (molar ratio of sulfide/Fe(III)=1) at *"extremely reducing"* conditions in a nitrogen protected environment. The results of the study were very encouraging and demonstrated that FH and aluminum FH were stable under these severe treatments. Their stated results were: *"It was found that the ferric-arsenate co-precipitates could retain up to 99% of its arsenic content despite the high pH (10.5) and extremely reducing (E_H<-200 mV) environment. There was no significant reduction of arsenate and only 45% of ferric iron was reduced by 50% (down to 15 mg/L) hence mixed Fe(III)/Al(III)-arsenate co-precipitates may offer better resistance to reductive destabilization over the long term than all iron co-precipitates".*

Additional example study results follow: **Erbs et al. (2010)** demonstrated that induced reduction conditions using hydroquinone resulted in arsenic and iron reduction and that coprecipitated FH/As(V) showed less arsenic release than adsorbed arsenic on previously precipitated FH. **Brannon et al. (1987)** have demonstrated that anaerobic lake sediments convert As(V) to As(III) (pH 5-8). However, when the anaerobic conditions were shifted by aerobic leaching the previously reduced As(III) was reconverted to more immobile As(V) which was associated with aluminum and iron oxyhydroxides. **Chatain et al. (2005 a, b)** investigated the effect of controlling the solution redox potential (E_H) and pH using sodium ascorbate (–7 to 345 mV) and sodium borohydride (–500 to 140 mV) to treat an arsenic bearing gold mining soil (2.8 % As, 1.8% on FH). The release of arsenic from the soil under oxidizing conditions (410 mV) showed the normal FH release of arsenic (V) (i.e., ~0.3 mg/L); whereas the treatment with 0.046 mole/L sodium ascorbate at an $E_H = -7$ mV (pH ~6) released ~80 mg/L As(III).

Also, it is known that the effect of bacterial reduction of FH and arsenate can be extensive. **Kocar et al. (2010)** found that the effect of sulfate reducing bacteria (that produces dissolved sulfide species) was to reduce FH to other iron solids along with the reduction of arsenate to arsenite. **Chatain et al. (2005b)** investigated the influence of anaerobic conditions (at pH ~ 7) with indigenous bacterial activity on the release of arsenic (and other metals) from a contaminated mining soil (3% As, 0.3% on FH). The results showed <4 mg/L arsenic release from baseline soil/ water leaches (80 days) and ~100 mg/L As(III) for nutrient fed indigenous bacteria. **Langner and Inskeep (2000)** have investigated the possible reduction of As(V) to As(III) on FH. They adsorbed arsenate onto previously precipitated 2-line FH solids, added a reducing fulcose fermenting microorganism to a suspended slurry containing the precipitated arsenate and arsenate species in solution at pH 6.8 and aged for 24 days. The solution arsenate was reduced to arsenite in less than one day but precipitated As(V) and FH were not reduced.

Scorodite Formation

The second technology practiced at several copper and gold facilities is arsenic removal by precipitation of scorodite.

What is Scorodite?

Scorodite is a naturally occurring iron-arsenic mineral, $FeAsO_4.2H_2O$. It has a low solubility in a water environment and has one mole of arsenic/mole of iron, i.e., it contains 25-30% arsenic, whereas the maximum arsenic that FH can contain is 0.5 to 7%, depending on the required Fe/As molar ratio (usually 3-10). *"Scorodite is found in hydrothermal deposits and as a secondary mineral in gossans worldwide. Scorodite was discovered in the Schwarzenbert Saxony district, Erzgebirge, Sacony, Germany. Named from the Greek Scorodion, garlicky. When heated it smells of garlic, which gives it the name."* (Wikipedia 2017). Scorodite thermodynamic standard free energy of formation (ΔG^o_f) has been determined to be -1,284.8 kj/mole **(Majzlan et al. 2012):** orthoarsenate ($FeAsO_4 \cdot 0.75\ _2O$) standard free energy of formation $\Delta G^o_f = -993.15 \pm 2.57$ kJ/mol and $\Delta H^o_f = -1140.38 \pm 2.59$ kJ/mol (however, synthesis of this compound requires an elevated temperature >200C). the solubility of orthoarsenate is lower than the solubility of scorodite (at pH 3), 29 and 92 μg/L, respectively **(Majzlan et al. 2016 a, b).** Natural scorodite is often associated with arsenopyrite and enargite and is found in copper and gold bearing deposits. It is relatively stable at pHs of 2.8-5.3 (Riveros et al. 2001) and passes the EPA TCLP Method 1311 solubility test of <5 mg As/L.

There are several technologies that can be used to form scorodite:

- Autoclave hydrothermal precipitation of scorodite from acidic solutions (pH ~1, ~150°C) containing Fe(III) and As(V) (**Gomez et al. 2011a; 2011b, and many others)**
- Elevated temperature, ambient pressure precipitation from acidic solutions (pH ~1, 90-95°C) containing Fe(III) and As(V) or As(III) **(Demopoulos 2005, 2008, and many others)**
- Intermediate temperature, ambient pressure precipitation by insitu oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70°C, 95°C) **(Fujita et al. 2008a, 2008b, 2009, 2012, and others)**

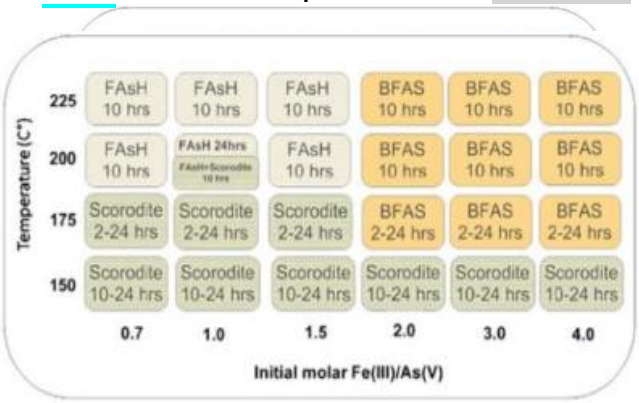
- Intermediate temperature, ambient pressure precipitation by biogenic insitu oxidation of Fe(II) in the presence of As(V) from acidic solutions (pH ~1, ~70°C) **(Okibe et al. 2013, 2014; Gonzalez-Contreras et al. 2012a, 2012b, 2014).**

Autoclave Applications

There have been many autoclave studies demonstrating the successful formation of scorodite and scorodite-like phases. **Gomez et al. (2011a)** present a brief comparison of the phases formed and identified by past research efforts. Detailed laboratory studies indicated that several Fe(III)-arsenate type compounds may be formed under typical conditions of autoclave treatment of refractory gold ores **(Swash & Monhemius 1994; Dutrizac & Jambor 2007; Gomez et al. 2011a, 2011b***)*. The basic ferric arsenate (BFAS) phase (Gomez et al. 2008), also known as Type II ferric arsenate **(Swash and Monhemius 1994)** or Phase 3 **(Dutrizac and Jambor 2007)** is one of the most common arsenic bearing products **(Harris 2003; Dutrizac & Jambor 2007).** BFAS precipitation is viewed as one of the best routes for arsenic stabilization and performed equally well to scorodite during environmental stability test **(Harris 2003; Swash & Monhemius 1994; Dutrizac & Jambor 2007; Gomez et al. 2011a). Swash and Monhemius (1994)** have shown that scorodite-like phases may form during autoclave ferric precipitation (especially in a sulfate bearing solution). They have designated the products Type I and Type II: e.g., Type 1 [$(Fe_2HAsO_4)_3$:xH_2O]) and **BFAS** (also referred to by **Swash and Monhemius (1994)** as Type II [$Fe_4(AsO_4)_3(OH)_x(SO_4)_y$]. Type I does not pass the U.S. EPA TCLP test for arsenic (5-85 mg/L) and Type II does (<5 mg/L). Information is not available concerning the long-term stability of these compounds.

The results of an extensive study of the formation and characteristics of three phases formed during the hydrothermal precipitation of Fe(III) and As(V) are presented by **Gomez et al. (2011a).** The phases formed included: Sulfate substituted **Scorodite** [$(FeAsO_4)_{1-0.67x(}SO_4)_x$:$2H_2O$] x≤0.16; **FASH** (also referred to by Swash and Monhemius as Type I [$FeAsO_4)_{0.988}(SO_4)_{0.01}0.72H_20$]; and **BFAS** (also referred to **by Swash and Monhemius (1994)** as Type II) [$FeAsO_4)_{1-x}wH_20$ x=0.3to 0.7]. The conditions for temperature and initial molar ratio of Fe(III)/As(V)) to form the various products are summarized by the authors in a table designated the GBD Precipitation Diagram (Gomez-Becze-Demopoulos) shown here as Table 1. The authors also report that TCLP stability tests were conducted on the products during short and long-term aging. The results follow: Short term (multiple TCLP solution contacts for 24 hours at pH ~5) results were: **FASH** was slightly more soluble than scorodite and **BFAS;** all gave <1 mg/L after 7 contacts. Long-term (>**8 months** at pH 3, 5, and 7.5) test results were: **BFAS** and scorodite about equivalent; **FASH** had a higher release. At pH 3 all were < 1 mg/L; at pH 5 **FASH** was 2.5 mg/L; **BFAS** was ~0.1 mg/L; sulfate substituted scorodite was 0.6 mg/L. At pH 7 all were relatively high, >>1 mg/L. The authors recommend that the **BFAS** may be the best form for storage at pH<7.

Table 1. GBD diagram for the conditions required to form various autoclave products *Source*: **Gomez et al.**



A recent autoclave scorodite formation (205°C, 5 bar O_2, 50 minutes) study has been reported by **Strauss, Yahorava, and Gomez (2017)** and **Strauss et al. (2021).** The authors investigated the stability of the BFAS product before and after cyanidation. *"BFAS precipitates, as well as their cyanidation residues were found to pass the respective environmental tests in terms of arsenic release".* The stability tests were short term studies using exposure to the **U.S. TCLP (EPA Method 1311**) and **SPLP (EPA Method 1312**, a water leach test at a pH of ~4.8) test procedures. The results were: before cyanidation 0.55 mg/L (SPLP) and 0.56 mg/L (TCLP); after cyanidation 0.16 mg/L (SPLP) and 0.16 mg/L (TCLP). Long-term test work was not reported.
Autoclave production of scorodite has been investigated by **Nazari et al. (2017)**. This treatment is referred to as HTPO (High Temperature Pressure Oxidation) and has been applied to gold refractory ores containing arsenopyrite. The specific treatment conditions were: 150-230°C, 2000 kPa, Fe/As molar ratio ~1. Ferric sulfate was added as an iron source and arsenopyrite was reacted to form As(III) which was then oxidized to As(V) and scorodite was precipitated. The residue containing scorodite and gold was leached in cyanide: scorodite was not solubilized in the cyanide solution. The scorodite residue can be stored in a permitted disposal site.

Autoclave /POX production of ferric arsenate compounds and other products have been reported on by **Strauss et al. (2021).** The group produced autoclave products by solution precipitation from controlled Fe/As mole rates experienced in pyrite/arsenopyrites treatment in the gold industry; and they investigated autoclave/POX treatment of gold industry concentrates containing similar Fe/As ratios as present in the synthetic solutions. The products formed from the synthetic solutions included "*basic ferric sulphate (As-BFS), basic ferric arsenate sulfate (BFAS) and ferric arsenate sub—hydrate (FAsH)".* However, the *"major Fe-As's generated in the POX residues form the concentrates were As-BHS and BFAS".* This work points out that great care must be taken when evaluating and comparing actual treatment parameters.

Atmospheric Pressure Formation of Scorodite

Atmospheric scorodite formation has been investigated for more than twenty years and has now advanced to industrial application. **Filippou and Demopoulos (1997)** and **Demopoulos (2009)** have described the process (paraphrased as follows): ferric ions are fed to a reactor at ~80-95°, at ambient pressure, containing arsenate at a pH of ~0.9 to form amorphous ferric arsenate; crystallization is accomplished by slow addition stepwise neutralization over a pH range of 0.9-4 in the presence of scorodite seed crystals with the result being that the ferric arsenate formed crystalline scorodite. The ambient pressure process also requires relatively high initial arsenic bearing solutions, e.g., 1 to 10 g/L. **Fujita et al. (2008a, 2008b, 2009, 2010, 2012b)** have shown that scorodite can be formed at ambient pressure at lower temperatures, e.g., 50-70°C, by insitu oxidation of ferrous ions in arsenate solutions. **Su and Ma et al. (2021)** have recently reported on their studies using ferrous carbonate (siderite) to treat concentrated waste sulfuric acid with the formation of scorodite. Their conditions were like that quoted by **Fujita et al.,** i.e., pH 1.1, Fe/As molar ratio 2, 95°C, 10 hours. Their products were scorodite with >99.6% arsenic containment for solutions containing 5.7-32 g/L As. The studied process was pH adjustment with lime to ~1 (gypsum formation), H_2O_2 oxidation of As(III) and Fe(II) with subsequent precipitation of scorodite. The product passed the U.S. EPA TCLP test, 0.19 mg/L, but longer stability test work was not reported.

It is often stated in the literature that scorodite can only be formed at ambient pressure from elevated arsenic containing solutions (>10 g/L; however, **Caetano et al. (2009)** have demonstrated that scorodite can be formed from dilute arsenic bearing solutions, e.g., 0.1 to 1.1 g/L under ambient pressure, elevated temperature treatment. The advantage of non-autoclave processing is that it is less costly, more energy efficient than the autoclave process and produces less waste material to be disposed of when compared to the FH process.

Rong et al. (2020a, 2020b) have investigated the conditions to transform arsenical ferrihydrite to scorodite. "*A series of experiments were carried out to investigate the optimal reaction conditions and applicable scope of initial arsenic concentration for this process. The results indicated that 99.9% of arsenic was removed from aqueous solution and immobilized as stable scorodite at reaction time of 6 h, pH 1.5, Fe/As molar ratio of 1.1 and reaction temperature of 90◦C. This process is applicable to the solution with initial arsenic concentration ranging from 1 to 10 g/L, which shows great potential for practical applications".* All the scorodite products were subjected to the TCLP conditions and less than 0.1 mg As/L was leached. Long-term aging tests were not preformed. **Rong et al. (2020b)** also discuss the ferrihydrite to scorodite pathway and they note that the transformation is dependent on the initial arsenic concentration, e.g., crystalline scorodite is formed (six hours required) for solutions initially containing 20--30 g/L arsenic but not at concentrations below 10 g/L or above 30 g/L. "*At 10 and 20 g/L initial arsenic concentration, the oxidation of ferrous ions produces ferrihydrite. The transformation of ferrihydrite into scorodite goes circularly through four stages: (i) surface complex of arsenate and ferrihydrite, (ii) release of ferric ion by the dissolution of ferrihydrite, (iii) the adsorption of ferric ion on adsorbed arsenate, and (iv) re-adsorption of arsenate on adsorbed ferric ion [29,30]. This cycle ensures the transformation of ferrihydrite into scorodite".*

Stability of Scorodite

Scorodite formed by all the processes listed above pass the short-term EPA TCLP test. Example longer-term test results are summarized in Table 2.

Note that the EPA TCLP test is not considered (by most investigators) a reasonable measure of stability by many investigators. The test is an acetate pH buffered environment (pH~5) designed to simulate co-disposal conditions in a municipal landfill. It is a test used to determine if a solid waste should be considered hazardous (for arsenic the measured concentration must be <5 mg/L to be considered non-hazardous). It is a test conducted under oxidizing conditions at only one pH, one solid/liquid ratio, one temperature, and one reaction time. However, an industrial waste may be stored under reducing conditions, under microbiological conditions, changing pH conditions, changing oxidation/reduction potentials and temperature. The TCLP results are biased by not considering reaction kinetics, particulate size, time and susceptibility to reagent complexation and valence state.

Ma et al. (2021) demonstrated that hydrous ferric arsenate HFA (Fe(III)/As(V) molar ratio of ~1) transforms to symplesite and parasymplesite in anaerobic and circumneutral leaching conditions in the presence of added Fe(II). Significant transformation occurred within a fifteen-day period (aging was evaluated to 72 days) at pH 6-8. The authors summarized their results: *"HFA is stable at pH 2 in the presence of Fe(II). At pH 4, HFA can react with Fe(II) and form a Fe(II)-bearing semi-crystalline phase. At pH 6, crystalline symplesite and parasymplesite were formed and constituted the major As-bearing phases in the host solids, regardless of the amount of Fe(II) added. At pH 8, parasymplesite became the dominant crystalline phase in the host solids with the input of Fe(II)".* Symplesite and Parasymplesite are both Fe(II) and As(V) compounds.

Zidan et al. (2020) in a follow up paper **(Ma et al. 2021)** investigated the stability of scorodite under reducing conditions. Their study demonstrated significant transformation of the scorodite to parasymplesite. The reduction of scorodite after 134 days at pH 6 to7 released approximately thirty percent of the arsenic. The test environment was maintained reducing by enolic hydroxyl groups (AH_2) common to natural organic matter. The author's presented summation was: *"scorodite, therefore, was unstable during its long-term storage in an Fe-reducing environment at (slightly) circum-neutral pH".*

Coudert et al. (2020) reported on their extensive review of the literature for the treatment of As-rich mine effluents and produced residues stability: *"An extensive literature review showed that Fe(III)-As(V) precipitates, especially bioscorodite and (nano)scorodite, appear to be the most appropriate forms to*

immobilize As due to their low solubility and high stability, especially when encapsulated within an inert barrier such as hydroxyl gels". See also, **Langmuir et al. (2006).**

Zhu et al. (2019) have recently reported on their re-evaluation of the thermodynamics and kinetics of scorodite dissolution. Their evaluation is not good news for using scorodite as a stable secure waste disposal procedure. A few of their conclusions follow: ***"****Assuming scorodite (grain size > 5microm) is the main storage of As in a porous geological medium (e.g., aquifer) that has an average water content of 15% (w/w) and a background As concentration of 15 ppm* ***(Smith et al., 1998),*** *dissolution at this rate (log rn = 11.3 mol/m2/s at* 25oC*) would render initially As-free water to one with arsenic concentration surpassing the 10 ppb threshold value within 17 h".* Also *"On the other hand, calculated ambient condition scorodite dissolution rate is one to two orders of magnitude higher than that of common rock-forming minerals, indicating that previously assumed low solubility may not be a solid rationale for treating scorodite as a safe storage for As in natural environments or industrial settings".*

Table 2. Examples of long-term stability test work for scorodite

Reference	Study Period	Results, mg As/L	Comments
Demopoulos 2005; Bluteau 2004 (Thesis). Bluteau and Demopoulos 2007	20-weeks at 75°C 66-weeks at 22°C	For the 22°C 66-week water solubility tests, the results were: pH 5, 0.35 mg/L; pH 6, 0.97 mg/L; pH 7, 5.89 mg/L. The 66-week tests showed that scorodite "*undergo slow incongruent dissolution yielding a highly metastable nano-sized 2-line ferrihydrite phase*" *(2004, 2005*). "The *growth and re-crystallization of ferrihydrite was apparently retarded by arsenate adsorption"* (2007).	At pH levels above ~4 incongruent dissolution of scorodite will slowly form nano-size FH. After 20-weeks at 75°C or 66- weeks at 22°C the authors did not observe any signs of growth or transformation of the amorphous arsenical FH.
Gomez et al. 2011a	>8-months at pH 3, 5, and 7	Short term (multiple TCLP solution contacts for 24 hours at pH ~5), FASH slightly more soluble than scorodite (SR) and BFAS-all gave <1 mg/L after 7 contacts. Long-term (>8months) pH 3 all were <0.1 mg/L pH 5 SR 0.6 mg/L; FASH 2.5 mg/L; BFAS ~0.1 mg/L pH 7 all high >>1	Tested the short and long-term stability of Scorodite (SR), FASH (Type I); BFAS (Type II), autoclave products in TCLP.
Lagno et al. 2010 (See also Katsarock 2011)	10-days, 6-weeks	Results: Oxic-the coating was protective (reduced As release from 1.5 mg/L to ~0.15 mg/L at pH 4; 45 mg/L to 1.5 mg/L at pH 8). Anoxic-pH 7, 100mV, not as protective, Fe(III) and As(V) partially reduced to Fe(II) and As(III). Uncoated scorodite showed ~200 mg/L As at six-weeks (pH 8); coated showed <10 mg/L (values not given by authors, data from their Figure 13).	Scorodite was encapsulated with aluminum phosphate and then subjected to oxic and anoxic water aging. Oxic aging was conducted for 10-days; anoxic aging for 6-weeks. Four materials were evaluated: scorodite; one, two, and three layers of aluminum phosphate on scorodite.
Bluteau et al. 2009	Up to 57-weeks	The gypsum saturated equilibrium arsenic concentration was 3.6 mg/L at pH 7; without gypsum the value (as reported by	Scorodite dissolution tests were conducted in deionized water saturated with gypsum

Reference	Study Period	Results, mg As/L	Comments
		Bluteau and Demopoulos, 2007) was 5.9 mg/L	(4-8 g/200 mL) at 22°C, pHs 5, 7, 9 for up to 57 weeks.
Gonzalez-Contreras 2012a Gonzalez-Contreras et al. 2012b	Up to 1-year	Aging time after formation was 10 or 22-days. The TCLP exposure was for 1-year: the 10-day aged product leached 1.5-2 mg/L; the 22-day aged product leached 1 mg/L to 0.16 µg/L. The most stable crystals were formed at pH 1.2, aged 22-days and when exposed to synthetic landfill conditions for 1-year leached 16 µg/L	Bioscorodite stability tests were conducted using EPA TCLP Method 1311 test conditions.
Salomon-de-Friedberg et al. 2017 (CESL)	3-years	Water leachability was less than the British Columbia limit of <2.5 mg/liter for 3-year aging. TCLP was applied to many residue samples during the pilot studies; results were always <0.15 mg/L	Stability of scorodite was evaluated by contacting the residue with twenty times its weight in water and observing the dissolution of arsenic as a function of time.
Leetman et al. 2016	169-days 900-days	A sulfate gel/scorodite system (at a low Al(III)/As(V) molar ratio of 0.1 and 0.2) was aged in a water environment at a pH of ~7 for up to 900 days. The reported results were that arsenic dissolution was <2 mg/L for unwashed gel/scorodite and <0.5 mg/L for washed (TCLP solution). Also, the authors state "There was only 0.2 mg/L of As released from the sulfate gel sample/scorodite system (Al/As=1 equilibrated at pH 7.3 for 169-days; that is 50 times lower than the solubility of the control scorodite".	Aluminum hydroxide gel encapsulated scorodite was evaluated by long-term aging in a water leach environment.

Example Industrial Applications that Produce Scorodite

Blanchard et al. (2017) investigated arsenic speciation in the JEB Tailings Management Facility (TMF) at McClean Lake, Saskatchewan to verify that atmospheric precipitated scorodite is stored in their repository. The facility uses an oxidizing sulfuric acid leach of uranium ore that contains appreciable arsenic (as nickel arsenide), e.g., ~300 to 50,000 µg/g. The arsenic is leached as As(V) and As(III) in concentrations of ~100 mg/L to ~10,000 mg/L. The arsenic removal process is performed on their process raffinate solution: ferric sulfate is added to provide a Fe(III)/As molar ratio of at least 3; conditions are E_H +680 mV, pH ~1; pH is adjusted with lime to pH 4 then to 7.5. The precipitated product is thickened along with other residues and pumped to their tailings disposal site. Laboratory studies showed that poorly crystalline scorodite formed up to a pH of 3.2. Excess iron then precipitates as amorphous arsenical FH during the near neutral pH adjustment. Prior to this study scorodite had not been identified in the TMF. However, using XANES spectroscopy showed the following: the tailings samples consisted of *"scorodite and poorly crystalline iron-containing arsenates".* The iron-containing arsenates were assumed to be FH, *"arsenate adsorbed on ferrihydrite is likely present given the abundance of ferrihydrite in the TMF".*

CESL (Cominco Engineering Services Limited), have patented and pilot plant demonstrated their POX process to treat copper-gold-arsenic sulfide concentrates **(Salomon-de-Friedbert et al. 2017).** The CESL process is an intermediate temperature autoclave treatment applied to over 18 high arsenic-copper concentrates (up to 18% As). Autoclave conditions included: ~150°C, ~14 bar pressure, 60-90 minute

reaction time to oxidize copper sulfides and As(III) with the precipitation of scorodite. The process consists of autoclave formation of Type II scorodite; atmospheric leaching the residue to recover copper; multiple washing stages; and disposal of scorodite by impoundment. The TCLP test was applied to many residue samples during the pilot studies and the results were always <0.15 mg/L. Stability of the scorodite has been evaluated by contacting the residue with twenty times its weight in water and observing the dissolution of arsenic as a function of time. The results have shown leachability of less than the British Columbia limit of <2.5 mg/L over a three-year period.

Outotec provides POX technology for treating copper-arsenic and gold-arsenic-pyrite concentrates **(Ruonala et al. 2011; Haavanlammi 2017).** The process is based on atmospheric oxidation/precipitation of amorphous ferric arsenate with subsequent recovery of the ferric-arsenate residue and treatment to convert the ferric arsenate to crystalline scorodite in an autoclave using the following operating conditions: 160-200°C, pH 1.5-4.5, and an Fe/As molar ratio 1-1.5. The stated advantage of this treatment is that only the ferric arsenate residue need be treated in an autoclave and not the entire solution. A smaller autoclave operating at a lower temperature than conventional HTPO processes should give it an economic advantage.

EcoMetales Copper Flue Dust Treatment Plant (PTPA) and the Arsenic and Antimony Abatement Process (PAAA) near Calama, Chile treat smelter flue dust, refinery effluent and other solid hazardous waste from Codelco's Chuquicamata, Potrerillos and Ventanas smelters and refinery complexes (MI 2017). Dusts are acid leached and leach residues are recycled to the smelters. The As(III) bearing leach solutions are oxidized, ferric reagent (Fe/As mole ratio ~1) is added pH (1-1.2) at ambient pressure and elevated temperature (80-85°C) to form scorodite (Demopolous et al. 2014). The product is disposed of in an authorized/permitted nearby site.

Monhemius and Swash (1999) have applied an autoclave process that allows bleed streams from copper electrorefining to be treated to produce scorodite. The electrolyte solution builds up the arsenic content to 20 g/L which must be treated to prevent contamination in the smelters copper product. The operating conditions used in their study were: bled solution containing 13 g/L as, ~21 g/L F, ~150-190°C, 2500 kPa O_2, free acid <60 g/L, Fe/As molar ratio of 1/1 to 2/1, residence time 2 hrs. Arsenic removal was >90-95% as scorodite.

Nazari et al. (2017) state that an atmospheric scorodite plant is operated at the DOWA plant in Osaka, Japan. The Dowa plant uses the conditions: 95°C and the iron source is ferrous which is oxidized insitu to react with As(V) **(Abumiva et al. 2012).**

Plaque's **(Huismann et al. 2011)** ASENOTEQ process illustrates that scorodite can be formed using a biological oxidation process. As(III) solutions are oxidized to As(V) by H_2O_2 prior to being fed into a reactor at ~70°C, pH 1.2 and an Fe/As molar ratio of 1.5. Ferrous ions are oxidized biologically to ferric ions insitu and scorodite forms **(Gonzalez-Contreras 2012**). The preferred application is to solutions containing arsenic concentrations >1000 mg/L.

BIOX is a well commercialized example of bacteria biohydrometallurgy applied to oxidize refractory gold ores containing pyrites, arsenopyrite and arsenical pyrites, and copper sulfides. The process is currently being used at twelve sites. The bacteria are mesophilic (40-45°C) and acidophile (pH 1.2-1.8) microorganisms that can function in arsenic concentrations up to 20 g/L As(V) and 6 g/L As(III). Scorodite is formed as the disposable product **(Gonzalez-Contreras 2012b; Van Aswegen et al. 2006).**

Biogenic scorodite or bioscorodite formation has also been described by Gonzalez-Contreras (2012a) in her doctorate thesis and in related publications **(Gonzalez-Contreras et al. 2012b, 2014).** The process is based on the biological oxidation of ferrous ions in the presence of arsenate and the formation of scorodite was demonstrated in a continuous stirred two tank reactor system (CSTR). The conditions were: 72°C, 2.8g/L As(V), and 2.4 g/L ferrous were fed to the reactor system at a pH 1.2. A 10% by volume

biomass (thermoacidophile microorganisms) oxidized the ferrous to ferric insitu with the As(V). The reported rate of As(V) removal was 1 g/L/day and the formation of scorodite was 3.2 g scorodite/L/day. The study conclusion was that the effluent contained ~30 mg/L arsenic, and that 99% of the incoming arsenic was removed and that bioscorodite formed. Testing in TCLP solutions showed good stability, e.g., only 0.4 mg/L As(V) was leached in one hundred days of exposure. When jarosite was present the stability test resulted in a solution As(V) concentration of 0.8 mg/L. **Gonzalez-Contreras et al. (2012b)** note that the relative stability of the bioscorodite is dependent on several factors including the rate of precipitation and aging time. They present aging stability data, e.g., in a leaching test (conditions not given) showed 0.1 mg/L of dissolved arsenic after 40 days. The authors suggest that the process could be utilized "*for treating acid plant effluents, copper electrorefining electrolyte bleed streams, leach solutions from treatment of arsenic oxide dusts and contaminated soils"*. Plaques has commercialized the process as Arsenoteq (Huisman et al. 2011).

Conceptual Flowsheets for formation of arsenical FH and scorodite

Conceptual flowsheets for forming arsenical FH and scorodite are presented in Figure 9.

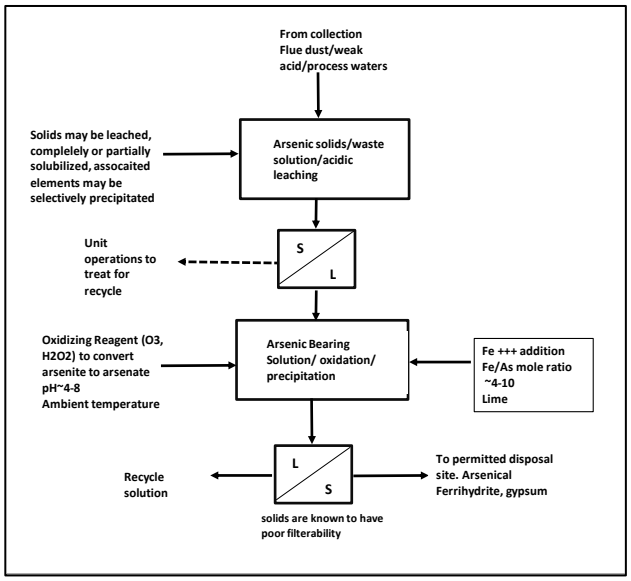
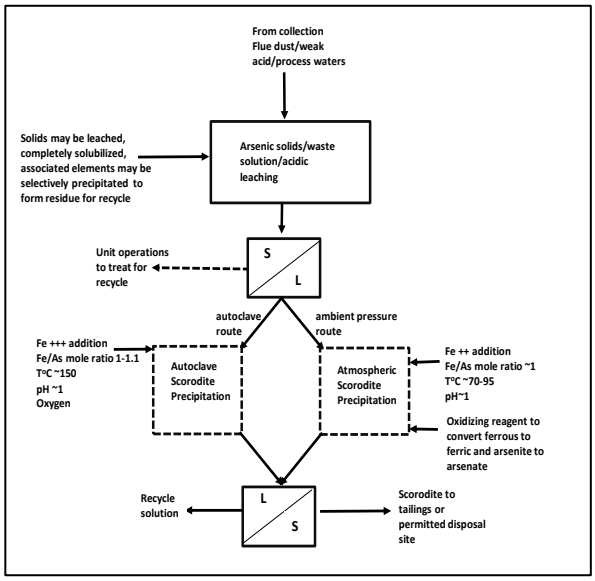


Figure 9. Conceptual flowsheet for forming arsenical FH



Conceptual flowsheet for forming scorodite by autoclave or ambient pressure, elevated temperature treatment

Other Fixation Possibilities

Encapsulation Possibilities

Scorodite is unstable in a variety of conditions including alkaline solutions. There have been several studies designed to increase scorodite stability at high pH levels, e.g., the use of surface coatings to encapsulate and provide a protective barrier. Encapsulation of scorodite particles with hydroxyapatite (HAP, $Ca_{10}(PO_4)_6(OH)_2$) and hydroxyfluoapatite (FAP) showed arsenic leachability of <1 mg/L for HAP and ~8 mg/L for FAP when exposed to an anoxic environment at pH 9 for 40 days **(Katsarou 2012).** Uncoated scorodite released 22 mg/L in the same environment. However, chemical, and mechanical stability was not sufficient to protect the scorodite (**Demopoulos 2014**; **Lagno et al. 2010).**

Leetmaa et al. (2016) have investigated the use of an aluminum hydroxyl gel made from aluminum sulfate salts (chloride salts were also investigated) that appear to have protective properties. The gel procedure was applied to ambient pressure formed precipitated scorodite. Several variables were investigated, e.g., type of gel, Al(III)/As(V) molar ratio, liquid/solid ratio, prewashing technique, etc. The sulfate gel/scorodite system (at low Al(III)/As(V) molar ratios of 0.1 and 0.2) was aged in a water environment (initially at a pH of 8 and allowed to drift to 7) for up to 900

days. The reported results were that arsenic dissolution was <2 mg/L for unwashed gel/scorodite and <0.5 mg/L for washed (TCLP solution). Additional data are presented and discussed in the investigator's publication.

Ke et al. (2019) have reported on their studies using polyferric sulfate as an agent to facilitate the formation of ferrihydrite particle coatings on scorodite to enhance its stability. The coating procedure utilized the conditions: pH 1.5, 90°C, PFS mass ratio was controlled at 0-30%. The coating technique resulted in decreasing the TCLP leach result from 10-30 mg/L to below 0.01 mg/L. No long-term aging test-work was performed.

Wang et al. (2019) coated scorodite to form a core-shell structure of first ferrihydrite particles on the surface of the scorodite which then grew with time to shield the scorodite core with goethite (FeOOH) and thereby protecting underlying arsenide material. *"Through analysis of the synthesized core-shell materials using XRD, SEM, XPS and EDS techniques, it was confirmed the core was $FeAsO_4{:}2H_2O$, and the shell was FeOOH, TCLP tests at pH 4.93 and leaching time tests were carried out in alkaline solutions with pH of 9.30 and 10.0. The results indicated that S@F (pH 1, 6 h) had significant stability on both weak acid and alkaline solution, the concentrations of As extraction liquid were all below 0.01 mg/L".* See also **Ma et al. (2019).**

Orgon et al. (2019) also investigated the stabilization of scorodite by precipitating ferrihydrite onto scorodite surfaces. Their procedure was to form scorodite first then to precipitate ferrihydrite to form a complex mixture of scorodite and ferrihydrite. They treated 5 g/L As(III) with ozone, pH 3, for 3 hours. Then ferrous sulfate was added and reacted at 90°C for 2 hours. The pH was then raised and ferrihydrite was precipitated. "*The effects of Fe/As molar ratio and pH were evaluated. The TCLP tests demonstrate that the solids generated under these conditions (Fe/As ratio 4, final pH 3 and 4) are stable and no arsenic can be detected in leaching tests for 72 hours".*

Coudert et al. (2020 Review) conducted a review of treatment processes that emphasized product stability. Their conclusion was *"An extensive literature review showed that Fe(III)-As(V) precipitates, especially bioscorodite and (nano)scorodite, appear to be the most appropriate forms to immobilize As due to their low solubility and high stability, especially when encapsulated within an inert material such as hydroxyl gels. Research is still required to assess the long-term stability of these As-bearing residues undermine-site conditions for the sustainable exploitation of refractory gold deposits".*

An extensive review of acid mine drainage literature by **Park et al. (2019)** is highly recommended for its microencapsulation information. The paper deals with stabilization of pyrites and other sulfide minerals to limit their dissolution to form acid mine drainage waste solutions. However, their review includes encapsulating techniques and successes that may lead the reader of this review to capture appropriate techniques for stabilizing arsenic bearing processing products. The authors present references for studies that lead to passivation by organic coatings *(formation of hydrophobic coatings on sulfide mineral surfaces to inhibit mineral-water interactions*), microencapsulation (ferrihydrite, *apatite, iron phosphate, silica coatings*) and silane-based coatings (for forming *coatings composed of both and inorganic components).*

Arsenic Trisulfide

Arsenic (III) trisulfide, As_2S_3, has a very limited solubility in water, e.g., <1 mg/L at pH <4 and is relatively stable under anoxic and reducing conditions. It contains a very high arsenic content, ~60% which makes it a desirable storage product. However, it is susceptible to atmospheric and bacterial oxidation. Therefore, it cannot be stored in landfill disposal sites. An example of the production of arsenic trisulfide is sulfidation of As(III) solutions practiced at the Saganosseki copper smelter; the arsenic bearing solution is treated by lime neutralization and NaHS to form arsenic trisulfide. The arsenic trisulfide is then stabilized by treating it in a non-oxidative autoclave at 200°C, 20-atm to polymerize and densify the product. The product is compact, contains ~60% arsenic, 1% water and is stored in concrete **(Nazari et al. 2017; Valenzuela et al. 2006**). Another example of a treatment that produces arsenic trisulfide is described by **Gabb and Davies (1999)** at the Kennecott Utah smelter. Leach solutions are treated to control the distribution of copper, arsenic, and cadmium. Copper is first selectively precipitated by pH and E_H control (at 40-60°C) into a residue solid that is recycled to the smelter. Arsenic and cadmium are then precipitated as sulfides by addition of either H_2S gas or NaHS. The solids are recovered and are routed to their EPA permitted hazardous waste disposal facility.

Plaques **(Huismann et al. 2011)** has developed and patented the THIOTEQ process for forming arsenic trisulfide. The process has two stages, one chemical and the other biological. Bisulfide (HS-) is produced in a biological reactor external to the chemical reactor. Elemental sulfur and ethanol are fed to the biological reactor to form bisulfide. The reaction is: $6S^o$ + ethanol (electron donor) + $3H_2O = 6HS^- + 2CO_2$ (reaction in presence of bacteria). The HS- solution

is fed to the chemical reactor at pH 1-2, 60-90°C, to precipitate As(III) as orpiment (As_2S_3). Very acidic solutions in the biological reactor are desirable, e.g., pH <3 is required to attain a final arsenic concentration of <0.2 mg/L. Orpiment must be stored in suitable permitted repositories. The authors state that the THIOTEQ technology is used at more than ten industrial plants for the reduction of sulfur compounds. The preferred application is to solutions containing high arsenic concentrations but <5 g/L.

Hu et al. (2019) proposed *"a safe treatment of arsenic-containing acid wastewater, a new process was proposed, including arsenic removal via sulfide precipitation and hydrothermal mineralization stabilization*". Arsenic trisulfide was precipitated using sodium sulfide, the conditions were: pH 4, S^{-2}/As molar ratio 3, 25°C, 60 minutes; mineralization conditions were: 240°C, filling rate 70%, glucose mass fraction 5%, hydrothermal duration 12 hours. The resulting TCLP test result was 4.8 mg/ L (for untreated arsenic sulfide the TCLP leached 212.97 mg/L). Long-term aging was not reported.

Mirazimi, M., J. Fan, and W. Liu (2021) have recently published the results of their studies to delineate the characteristics of the effect of pH, dissolved oxygen, and temperature on the release of arsenic and sulfur from arsenic trisulfide. This paper is a valuable contribution to understanding the leachability of arsenic trisulfide. The authors present their rate equation and have identified that the leaching results are controlled by surface chemical reaction rather than by diffusional transport. The authors present the TCLP leach test results for arsenic trisulfide reported by Lehimura (2007) e.g., 25 mgAs/L.

Shakya and Ghosh (2019) evaluated the stability of biogenic arsenosulphides (mainly orpiment and realgar) generated under reducing conditions. Biosolids were formed in a sulphidogenic growth reactor using a mixed bacterial culture containing sulphate, nitrate, and arsenic. Recovered biosolids were subjected to the TCLP tests (for 24 and 84-hours), including samples containing (or not containing) various amounts of dissolved oxygen (to study the effect of an oxic environment) on the TCLP result. The TCLP results for the 24-hour tests were 21µg/L (anoxic) and 14 µg/L (oxic). Kinetic evaluations were also performed in column exposure tests (with aerated DI water at pH 7 for 90 days). "*For all protocols tested, leachate arsenic concentrations were always below 300 µg/L, which was far below than the current maximum Australian TCLP leachate limits for arsenic of 700 µg/L".* The authors concluded: *"that the biogenic arsenosulphides formed under reduced environment is stable and do falls under the category of hazardous waste".*

Wang et al. (2019) coated scorodite to form a core-shell structure of first ferrihydrite particles on the surface of the scorodite which then grew with time to shield the scorodite core with goethite (FeOOH) and thereby protecting underlying arsenide material. *"Through analysis of the synthesized core-shell materials using XRD, SEM, XPS and EDS techniques, it was confirmed the core was $FeAsO_4{:}2H_2O$, and the shell was FeOOH, TCLP tests at pH 4.93 and leaching time tests were carried out in alkaline solutions with pH of 9.30 and 10.0. The results indicated that S@F (pH 1, 6 h) had significant stability on both weak acid and alkaline solution, the concentrations of As extraction liquid were all below 0.01 mg/L".*

Arsenate Phosphate Hydroxyapatite (APHAP)

Formation and long-term stability of aluminum/arsenate/phosphate hydroxyapatites [APHAP; $Ca10(As_xP_yO_4)_6(OH)_2$] have been investigated by **Twidwell, et al. (1994-2015)** and his research graduate students. These compounds were investigated because they are produced by utilizing a lime-based precipitation process; and it is known that apatite compounds are thermodynamically stable in the presence of carbon dioxide in air (which is not true for the various calcium arsenate compounds). The studies (Figures 10 and 11) demonstrated excellent stability for arsenate-apatite containing a PO_4/AsO_4 molar ratio greater than seven, e.g., the APHAP compounds showed an arsenic release of less than five micrograms/liter using the water-based EPA SPLP Method 1312 and the EPA TCLP Method 1311. The aging solubility results in the SPLP tests were <1.4 µg/L and <0.8µg/L (at pH 12.3) after 4 years and 8 years of exposure to air, respectively.

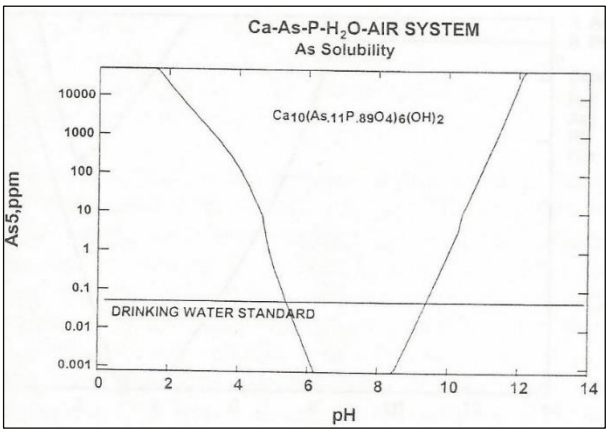


Figure 10. Stability of APHAP (PO_4/AsO_4 mole ratio=7) mineral-like precipitated product exposed to air. *Source:* Generated by **Huang Stabcal (2015).**

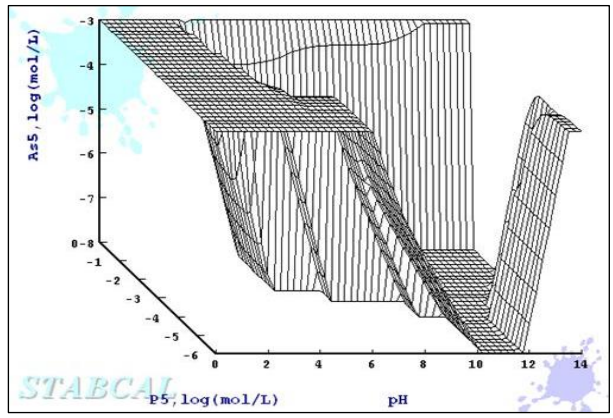


Figure 11. 3-D illustration of the solubility of APHAP (PO_4/AsO_4 mole ratio=7) as a function of pH (Initial arsenic 0.01 mole/L) ***S****ource:* Generated by **Huang Stabcal (2015)**.

Symplesite

McCloskey and Twidwell (2008b) and **McCloskey et al. (2010)** designed and conducted a full-scale operation using a two-stage treatment system at an industrial site in Emeryville, California to lower As(V) concentrations from 100 mg/L to <25 µg/L. The plant was operated for a four-year period to clean contaminated water to less than the drinking water standard. The first stage of treatment was precipitation of symplesite [$Fe_3(AsO_4)_2{:}8H_2O$] by the addition of lime and ferrous sulfate (at pH at 7). The arsenic was lowered to <6 mg/L. The resulting water was then treated by FH precipitation using hydrogen peroxide as the oxidant for Fe(II) conversion to Fe(III) at an Fe/As molar ratio of 4. The residues from the two stages were mixed, dried, and sent to a permitted disposal facility. Symplesite does not pass the TCLP test requirement and must, therefore, be subjected to stabilization as required by the RCRA-LDR regulations.

Ma et al. (2021) demonstrated that hydrous ferric arsenate HFA (Fe(III)/As(V) molar ratio of ~1) transforms to symplesite and parasymplesite in anaerobic and circumneutral leaching conditions in the presence of added Fe(II). Significant transformation occurred within a fifteen-day period (aging was evaluated to 72 days) at pH 6-8. The authors summarized their results: *"HFA is stable at pH 2 in the presence of Fe(II). At pH 4, HFA can react with Fe(II) and form a Fe(II)-bearing semi-crystalline phase. At pH 6, crystalline symplesite and parasymplesite were formed and constituted the major As-bearing phases in the host solids, regardless of the amount of Fe(II) added. At pH 8, parasymplesite became the dominant crystalline phase in the host solids with the input of Fe(II)".* Symplesite ($Fe_2^{+3}(AsO_4)_2.8H_2O$) and Parasymplesite are both Fe(II) and As(V) compounds.

Zidan et al. (2020) in a follow up paper **(Ma et al. 2021)** investigated the stability of scorodite under reducing conditions. Their study demonstrated significant transformation of the scorodite to parasymplesite. The reduction of scorodite after 134 days at pH 6 to7 released approximately thirty percent of the arsenic. The test environment was maintained reducing by enolic hydroxyl groups (AH_2) common to natural organic matter. The author's presented summation was: *"scorodite, therefore, was unstable during its long-term storage in an Fe-reducing environment at (slightly) circum-neutral pH".*

Yukonite

Bluteau et al. (2009) and **Gomez et al. (2010)** have proposed that the mineral Yukonite [$Ca_2Fe_3(AsO_4)_3(OH)_{4-10}:xH_2O$ where x=2-11] likely forms from poorly crystalline scorodite with aging time, especially at pH levels of seven and above. Yukonite has been identified in mine waste and cyanidation tailings, and near neutral pH in natural environments **(Drahota and Filippi 2009;** D**rahota et al. 2018 Review)**. Stability studies have shown positive results such as an arsenic solubility of <5 mg/L at pH 5-10 in an oxidizing, gypsum containing environment for 66 days, e.g., values were pH 5, 3.1 mg/L; pH 7, 8, 10 were 0.4, 0.45, 1.12 mg/L, respectively **(Bohan et al. 2014, 2017). Jia and Demopoulos (2008)** demonstrated that a poorly crystalline ferric arsenate (Fe(III)/As(V) molar ratio of 2), formed by lime neutralization at 22°C, pH 8, does, indeed, transform to Yukonite [$Ca_2Fe_3(AsO_4)_4(OH).12H_2O$] when aged at 75°C for seven weeks. **Coudert et al. (2020 Review)** present the formula for Yukonite to be [$Ca_3Fe(AsO_4)_2(OH)_3.5H_2O$].

Tooeleite (As(III) containing mineral)

Tooeleite ($Fe_6(AsO_3)_4SO_4(OH)_4:4H_2O$) is a ferric arsenite oxyhydroxysulfate hydrate nano-crystalline compound found in waste at the U.S. Mine Gold Hill in Tooele County Utah **(Opio 2013).** *It is the only known ferric arsenite sulfate mineral and has environmental significance for arsenic remediation* (**Li et al. 2020).** Tooeleite has been found in acid mine drainage (AMD) areas and is thought to be formed via bacterial oxidation of Fe(II) **(Morin et al. 2007; Egal et al. 2009).** Tooeleite is similar to scorodite and is known as the trivalent arsenic form of scorodite **(Nazari et al. 2017).** It has been proposed to be an As(III) storage compound **(Nishimura and Robins 2008; Li et al. 2020).** However, **Raghav et al. (2013)** showed appreciable leachability in the TCLP test (which is conducted at a nominal pH ~5) *"tooeleite and silica amended tooeleite often was as least an order of magnitude higher than the TC (toxicity concentration)".* **Opio (2013)** noted that preparation of tooeleite can be formed at ambient temperature at pHs in the range 2-3.5 but is rapidly converted to poorly crystalline ferric arsenite at pH>4. Calcination at 600°C produced a ferric arsenate calcine with a TCLP solubility of <5 mg/L. Synthesis at 95°C showed no improvement for arsenic extraction in TCLP solutions. Their conclusion was *"the resultant precipitation of tooeleite from an As(III)-bearing weak acid and calcination of the resultant precipitate may offer a new process for As(III) fixation from copper smelter weak acid effluents*". Long-term stability testing was not reported. **Choi et al. (2017)** suggests that Tooeleite forms from FH using conditions; pH 1.8-4.5, initial As(III) concentration >0.75 g/L, an Fe/As mole ratio of 0.8-2, and ambient temperature. The authors report that they tested the short-term stability of tooeleite in TCLP solutions as a function of pH (1.8-9). The authors present a figure but did not provide the numerical values for the leach results except in the graph. The arsenic concentration values for pHs 1.8 to 4.5 appear to be greater than 5 mg/L and at pHs of five and above show hundreds of mg/L arsenic.

Wang et al. (2021) studied the biotransformation of As(III) to tooeleite via the oxidation of Fe(II) using Acidithioibacillus ferrooxidans. Optimized conditions were pH 2, 30 °, initial As(III) of 500 mg/L. 95.4% of the arsenic was removed as tooeleite. Stability testing was not reported.

Yuan et al. (2020a, b) reported on the formation of a chloride tooeleite-like compound ($Fe_5(AsO_3)_3Cl_2(OH)_45H_2O$). Conditions for the effective removal of arsenite were established, e.g., Fe(III)/As(III) molar ration 1.7 in a chloride solution at pH 2.3. However, the leachability of the precipitated solids resulted in relatively high arsenic leach results in the EPA TCLP static test procedure, e.g., 32mg/L (about the same as compared to tooeleite, i.e., 30mg/L). Long-term aging stability was not evaluated.

Majzhan et al. (2016a, b) determined the thermodynamic properties of tooeleite, e.g., the standard free energy of formation was determined to be -5,376.3 kj/mol. Their evaluation as to whether tooeleite is an appropriate compound for outdoor long-term storage follows: "*Tooeleite has stability field only at very high activities of aqueous sulfate and arsenate. As such, it does not appear to be a good candidate for*

arsenic immobilization at polluted sites. An inspection of speciation diagrams shows that the predominance field of Fe^{3+} and As^{3+} overlap only at strongly basic conditions. The formation of tooeleite, therefore, requires strictly selective oxidation of Fe^{2+} to Fe^{3+} and, at the same time, firm conservation of the trivalent oxidation state of arsenic. Such conditions can be realized only by biological systems (microorganisms) which can selectively oxidize one redox-active element but leave the other ones untouched. Hence, tooeleite is the first example of an "obligatory" biomineral under the conditions prevailing at or near the Earth's surface because its formation under these conditions necessitates the action of microorganisms.

Chai et al. (2018) reported on their study of the hydrothermal formation of tooeleite at elevated temperatures (105-120°C). The *optimized tooeleite* was reported to be formed at 120°C, pH 1.6, Fe(III)/As(III) molar ratio 1.5. The short-term stability was evaluated in TCLP test solutions to be 9 mgAs/L. They also investigated the use of a silica coating (siloxane bonding) to enhance the stability of the compound: *"this decreased the arsenic leaching concentration to 4 mg/L".*

Other Possible Storage Compounds

Majzhan et al. (2018) suggest that *"If some of the less common arsenate minerals have been shown to be less soluble than the currently used options for arsenic disposal (especially scorodite and arsenical iron oxides), they should be further investigated as promising storage media".* The authors studied several possible storage compounds but suggested that Kamarizaite ($Fe_3(AsO_4)_2(OH)_3.3H_2O$) may be such a compound *"Kamarizaite is predicted to have aa very similar solubility to scorodite, making it a phase of potential interest for further study".* The mineralogical makeup is presented by **Chukanov et al. (2010).**

Wang et al. (2021) have investigated the removal and stabilization of As(III) by the formation of Layered Double Hydroxides (LDH, e.g., ZnFe-As LDHs). Under optimized conditions of pH (8), molar ratios of Zn/Fe (2), Fe/As 3) the following transformations occurred *"The non-crystalline ferric arsenate was firstly formed. And then the phase transferred to amorphous ferrihydrite, followed by incorporating of zinc ions and intercalating of arsenic oxyanions and SO4. Finally, the "stone-like" LDH was obtained"*. Arsenic in initial solution was lowered from 100 mg/L to 0.13 mg/L and the TCLP test results applied to the solid products were always < 5 mg/L (for the optimized conditions the result was 1.87 mg/L). The products contained a mixture of arsenite and arsenate compounds (55% of the arsenite was oxidized to arsenate).

Li et al. (2020) have investigated the anoxic reduction of adsorbed AsO_4 using Layered Double Hydroxides of Mg(III), Al(II) and Fe(III). The reader is referred to this publication. *"A 2-stage release and re-adsorption mechanism of total As(aq) occurred following the order: $MgAlFeCO_3SO_4$ >MgAlSO4 >$MgFeCO_3$ >$MgAlCO_3$ >$MgFeSO_4$. A significant portion of the solid surfaces (30–90%) was found as As(III) for all reacted LDHs. This work provides a guideline for the environmental behavior of As(V) adsorbed LDHs where relevant underwater cover TMF abiotic reducing conditions may exist".*

Layered Double Hydroxide containment of arsenic is presently a very active research area. A review of this topic has not been considered in this paper. The reader may be interested in the publications **Wang et al. (2021), Lu et al. (2020), Majzhan et al. (2018), Gomez et al. (2014), (2013).**

ARSENIC, SELENIUM, THALLIUM, METALS RESEARCH at MONTANA TECH

FERRIHYDRITE/ARSENIC and ALUMINUM MODIFIED FERRIHYDRITE/ARSENIC RESEARCH STUDIES

Arsenic studies conducted at Montana Tech and the Center for Advanced Mineral and Metallurgical Processing (CAMP) are summarized as follows:

1) Arsenic Adsorption by Ferrihydrite (FH) and Aluminum Modified Ferrihydrite (AMF).
2) Long-term Aging Stability Studies.
3) Influence of Anionic Environment on Removal of Arsenic by FH and/or AMF.

Arsenic Adsorption Studies

Ferrihydrite/Arsenate

This topic has been summarized and presented in considerable detail in the previous literature review section "Fixation of Arsenic Treatment". The reader is referred to that section.

Aluminum Modified Ferrihydrite/Arsenic (additional study results are available: **(MWTP-282 2007; MWTP-293 2008; MWTP-307 2008; Twidwell et al. 2000, 2004, 2007).**

Studies completed by **R.G. Robins et al. (2005**) have previously shown that aluminum modified ferrihydrite (AMF) significantly improved arsenate removal (Figures 12, 13). As a result of Robin's work, Hohn **(2005; Hohn et al. 2006**) focused on evaluating the use of an AMF (Fe/Al mole ratio of one) as the adsorbent for arsenate. The purpose of the study was to evaluate the influence of three variables on the final [As] concentration, i.e., [Al+Fe]/As mole ratio (5-10), pH (4-8), and initial [As] concentration (1-10 mg/L, 10-100 and 100-500 mg/L). A comparison was also made to ferrihydrite (FH). This work was conducted for the EPA Mine Waste Technology Projects (MWTP) and all test work was conducted under EPA Quality Assurance Quality Control (QAQC) procedures.

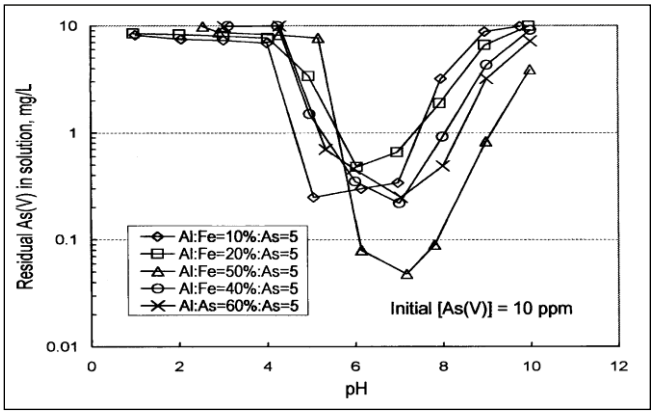


Figure 12. The removal of As(V) from solutions of Al(III)+Fe(III) by adjusting the pH. Compositions are in mole percent. [Robins et al. 2005].

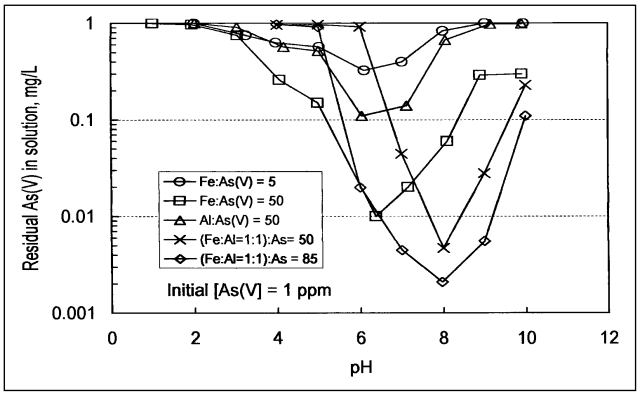


Figure 13. The removal of As(V) from a solution initially at 1 mg/L As by adjusting the pH. Compositions are mole ratios. [Robins et al. 2005]

Design of Experiments (DE)-**Hohn (2005)** conducted two-level full factorial Design of Experiments (DE). DE modeling studies were used to establish the As(V) adsorption characteristics of FH and AMF (DE studies were formulated and analyzed using the StatEase Design-Expert Version 7.01 software package).

Each FH or AMF study was conducted to evaluate the influence of three variables: pH, [Al+Fe]/As(V) mole ratio, and initial As(V) concentration. Each variable was evaluated at two levels with additional tests at midpoint levels: pH 6, 7 and 8; Fe/As or [Al+Fe]/As of 5, 7.5 and 10 mole fraction. AMF initial [As(V)] concentration was evaluated over four levels: 0.1 to 1.0, 1.0 to 10.0, 10.0 to 100, and 100 to 500 mg/L. FH was tested at an initial arsenate concentration of 1 and 10 mg/L for comparison purposes. All design experiments were performed using 1-liter of solution in a 2-liter glass resin kettle with a 4-port lid. The reactor kettle was suspended in a regulated temperature bath set at 25.0 ± 0.1°C. All tests were conducted for 30 minutes prior to solution sampling.

Summary of Adsorption Study Results-The detailed statistical analysis of the results for the adsorption of As(V) by AMF and FH are summarized elsewhere **(Hohn 2005; Hohn et al. 2006; Twidwell et al. 2000, 2004, 2007).** The AMF and FH data sets covered the initial As(V) concentration over the range 0.1 to 500 mg/L. Both data set results (AMF and FH) were dependent on the loading ratio, pH, and the interaction between these two factors. Figures 14 and 15 are presented to illustrate that AMF offers adsorption advantages over FH especially at the lower loading ratios to achieve the project goal of [As(V)] <10 μg/L. A comparison between the adsorption effectiveness for AMF and FH is further illustrated by Figures 16 and 17. Specific combinations of loading ratio/pH are required to achieve the project [As(V)] goal level for the FH adsorbent but all combinations, within the ranges studied, results in achieving the goal level for AMF. These results agree with **Robins et al. (200),** who showed that AMF is more appropriate for As(V) removal at higher pH levels than is normally quoted for FH application. A composite overlay diagram is presented in Figure 18 to illustrate the loading ratio/pH combinations required to lower the arsenic concentration to <5 μg/L (EPA Drinking Water Standard is 10 μg/L) for both AMF and FH.

Both FH and AMF have effective adsorption capabilities. The present EPA Maximum Concentration Level (MCL, drinking water standard) is 10 μg/L. Conditions of loading ratio/pH can be specified to achieve much lower than the MCL arsenic concentration; refer to Figure 17. FH is a more effective adsorbent than AMF at lower pH values and conversely AMF is more effective at higher pH values.

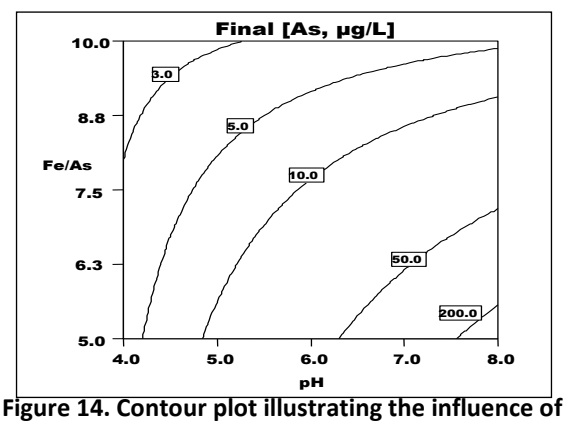


Figure 14. Contour plot illustrating the influence of FH loading ratio and pH on the removal of As(V).
Initial As(V)=10 mg/L.

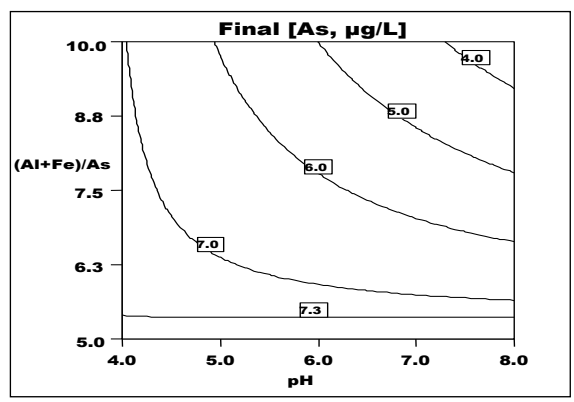
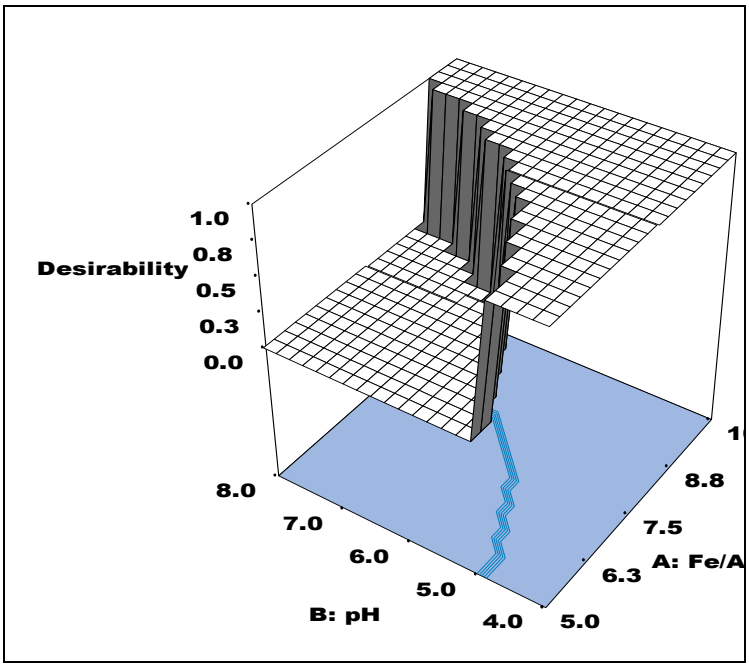
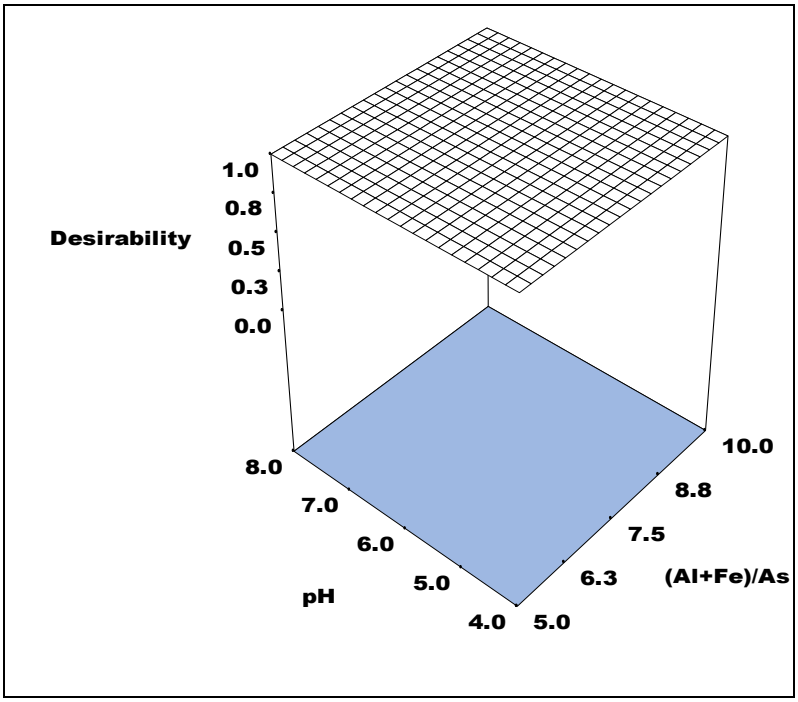


Figure 15. Contour plot illustrating the influence of AMF loading ratio and pH on the removal of As(V).
Initial As(V)=10 mg/L)



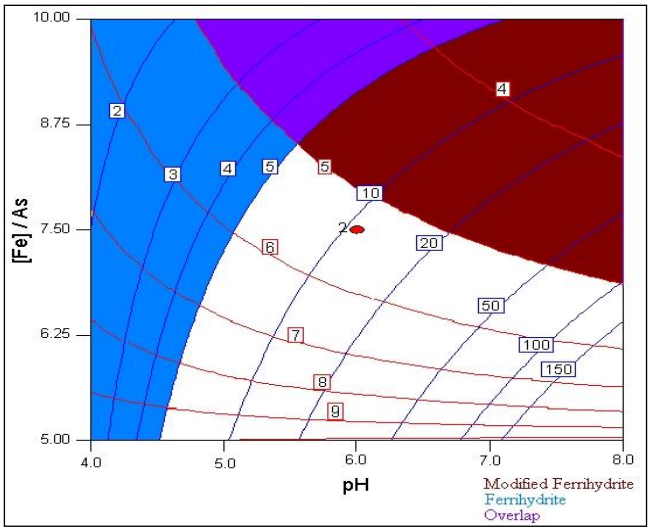
(Desirability of 1 indicates the loading ratio/pH combinations that will achieve As(V)<10 μg/L)

Figure 16. FH: Desirability conditions to attain final As(V) =10 μg/L (initial As(V)=10 mg/L).



(Desirability of 1 indicates the loading ratio/pH combinations that will achieve As(V)<10 μg/L)

Figure 17. AMF: Desirability conditions to attain final As(V)<10 μg/L (initial As(V)=10 mg/L).



[Colored regions indicate final [As(V)] concentration remaining in solution. The blue color represents the combination of loading ratio/pH for **FH** where the final arsenic concentration [As(V)] will be <5μg/L. The red color represents the combination of loading ratio/pH for **AMF** where the final arsenic concentration will be <5μg/L. The purple color defines the conditions where both adsorbents meet the project goal arsenic concentration].

Figure 18. Overlay of AMF and FH charts

Long-term Aging Stability of FH and AMF

Long-term storage stability is important for arsenic fixated products. Aging was studied for extended times for both FH and AMF, e.g., ambient temperature and accelerated aging at 70°C.

Ambient Temperature Aging

To establish long-term aging characteristics of arsenic-loaded **FH** and **AMF** samples were prepared at two levels, i.e., [pH at 2 and 10], [loading mole ratios of Fe/As and [Al+Fe]/As of five] and were aged in their respective solutions for 367 days. The aging characteristics are illustrated by 3-D plots Figures 19 and 20, and by contour plots in Figures 21 and 22. An additional comment is that the Final As(V) concentration was observed to be less than 5 μg/L (at 500-days) when aged at ambient temperature for a Fe/As or [Al+Fe]/As loading ratio of ten.

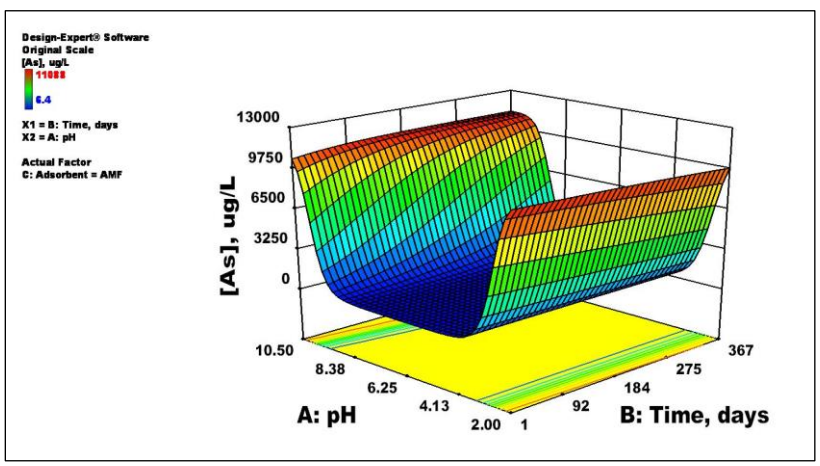


Figure 19. 3-D illustration of the influence of pH and ambient aging time on the final solution concentration of As(V) for the AMF adsorbent at a [Al+Fe]/As(V) mole ratio of five, Initial As(V)=10 mg/L.

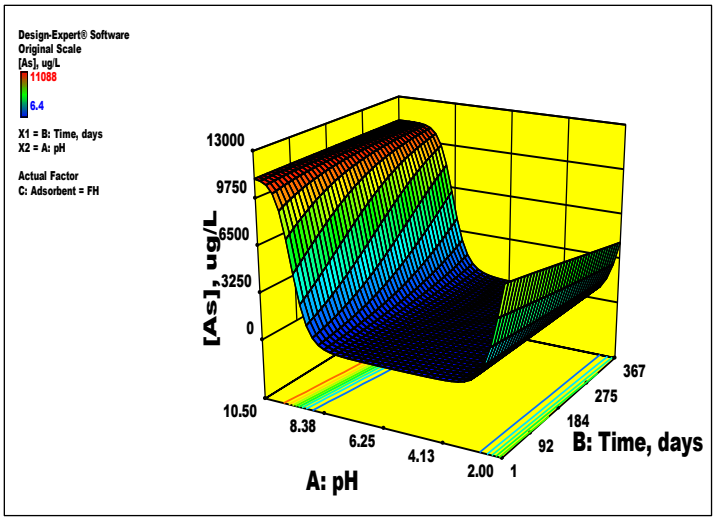


Figure 20. 3-D illustration of the influence of pH and ambient aging time on the final solution concentration of As(V) for the FH adsorbent at an Fe/As mole ratio of five, Initial As(V)=10 mg/L).

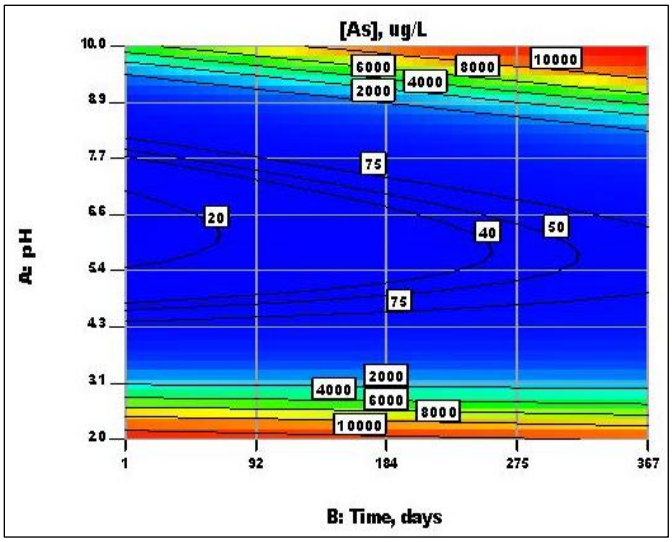


Figure 21. Contour illustration of the influence of pH and Ambient aging time on the solution concentration of As(V) for the AMF adsorbent at a [Al+Fe]/As(V) mol ratio of five, Initial As(V)= 10 mg/L.

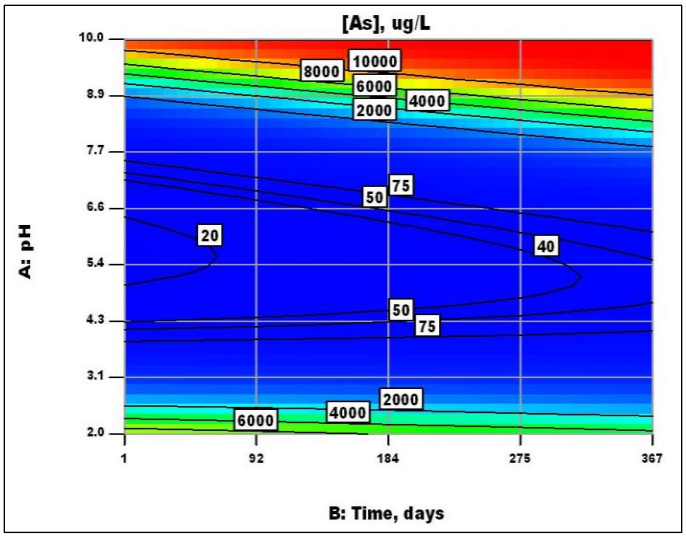


Figure 22. Contour illustration of the influence of pH and ambient aging time on the solution concentration of As(V) for the FH adsorbent at an Fe/As mol ratio of five. Initial [As(V)] = 10 mg/L.

Elevated Temperature Aging

To establish the long-term aging characteristics of FH and AMF samples were aged at 70°C. **Ford (2002)** stated that conducting aging tests at 70°C provides results equivalent to aging for twenty-five times the result conducted at 25°C; therefore, conducting experimental aging tests at 70°C for approximately one year should provide results equivalent to approximately twenty-five years of aging at 25°C.

Four series of test samples were evaluated; FH (no arsenic), AMF (no arsenic), As(V)-loaded FH (designated FH/As) and As(V)-loaded AMF (designed AMF/As). The loading ratio for Fe/As and [Al+Fe]/As was ten and the aging was conducted at pH 7. Ten bottles for each sample set were placed in a Reciprocating Shaking Water Bath at 70°C. Temperature and pH were monitored for each bottle every other day for the first two weeks and then periodically throughout the rest of the test period. The pH remained constant within the range 7.0±0.2. The initial arsenic concentration prior to adjusting the solution pH and thereby precipitating the adsorbent in-situ was 10 mg/L. The arsenic concentration prior to raising the temperature was 1209 µg/L for AMF/As and 1260 µg/L for FH/As.

Samples were aged for up to 16-months. Solution samples were removed from the test series to determine the solution arsenic concentration released during the aging period and to provide solid samples for x-ray diffraction. Samples (50-mL) were subjected to a buffered oxalate leach following the procedure developed by **Schwertmann and Cornell [1996, 2000]** and the solutions were analyzed for arsenic, aluminum, and iron. The oxalate-soluble iron was taken to represent the amount of amorphous FH and AMF present at each specific time. The following information was calculated from the analytical data: the release of As(V) from the solids, the fraction of FH or AMF that was converted to oxalate-insoluble solids (taken in this study to represent a more stable solid, which from x-ray diffraction studies was hematite), and the amount of As(V) in each product.

Aging Study Results

A comparison of the 70°C aging results for FH and AMF are presented in the following figures.

Conversion Rates- Figure 23 is presented to illustrate the relative conversion rates of the aged solids in the 70°C test series. The conversion rates for FH and AMF (no arsenic present) were similar, however, the presence of As(V) in the solids significantly decreased the conversion rate, especially for AMF/As. Under the conditions of this study AMF/As was significantly more stable to conversion than was FH/As.

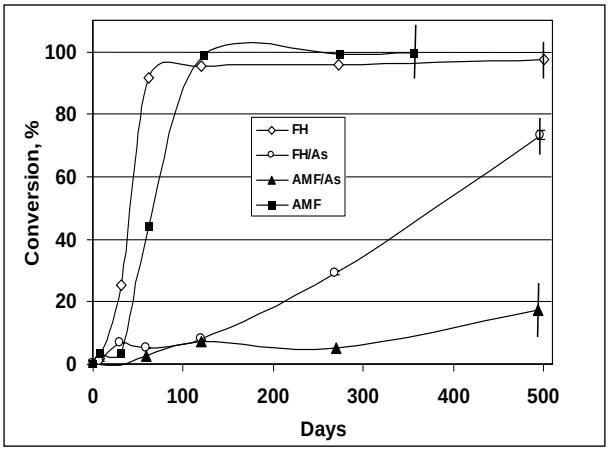


Figure 23. Conversion rate of oxalate-soluble iron solids at 70°C, pH 7, FH/As and AMF/As mole ratios=10.

Partitioning of Arsenate-The partitioning of As(V) to the FH/As and AMF/As solids as a function of aging time is illustrated in Figures 24 and 25. The partitioning of As(V) into the various aged products show similar trends. However, the partitioning of As(V) at 500-days to the oxalate-insoluble AMF/As was greater than for FH/As whereas the extent of conversion for the AMF/As system was much lower (17%) than for the FH/As (73%) system, indicating that greater loading of As(V) in the oxalate-insoluble solids occurred.

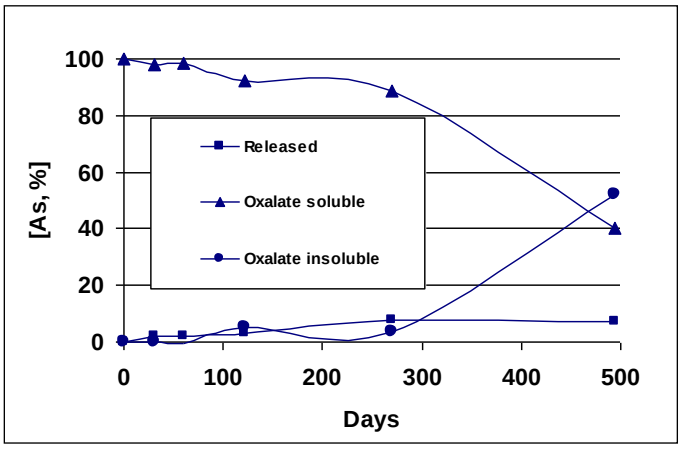


Figure 24. The partitioning of As(V) for AMF/As as a function of aging time at 70°C, pH 7

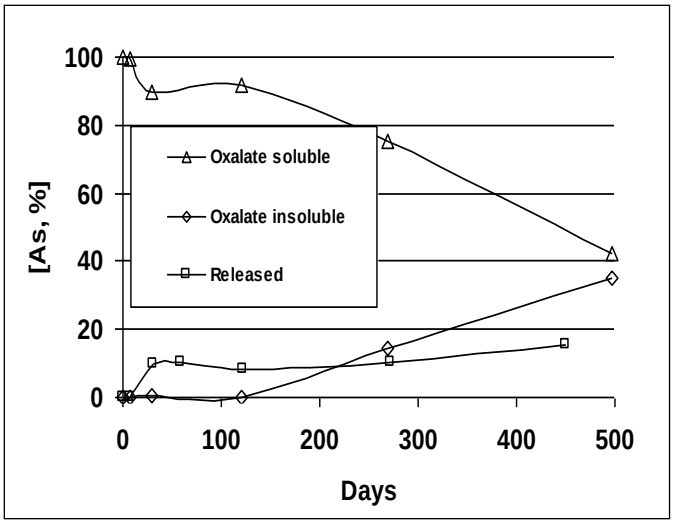


Figure 25. The partitioning of As(V) for FH/As as a function of aging time at 70°C, pH 7

Summary-The general characteristics of FH and AMF with respect to loading capacity, surface area, minimum particle size, and zero point of charge for As(V)-bearing solids have been reported to be similar **(Hohn 2005; Hohn et al. 2006). The distinguishing characteristic of AMF over FH is that As(V) adsorption by AMF is more effective at lower loading ratios and at higher pH levels. Therefore, the use of AMF may be preferred for the applications of final solution polishing or use in the treatment of drinking waters.** However, in this work all the solutions were prepared using deionized water and only the ions of interest. Ferric sulfate was used as the iron reagent so the initial sulfate mole concentration was three times the initial iron(III). There are many other aqueous ions that occur in real systems and, interactions and competitive adsorptive effects should be investigated. Further research in this area is encouraged.

Both FH/As and AMF/As show partitioning of As(V) at 70°C, pH 7 between the solution, the original co-precipitated solids, and the oxalate-insoluble solid. The relative partitioning trends were similar. The partitioning of As(V) at 500-days to the oxalate-insoluble AMF/As solid was greater than for FH/As solid, whereas the extent of conversion for the AMF/As co-precipitated solids was much lower (17%) than for the FH/As (73%) co-precipitated solids, showing that greater loading of the oxalate-insoluble solids occurred.

Partitioning of As(V) at ambient temperature did not occur over the time period studied, i.e., the iron precipitates were completely oxalate-soluble up to 502-days. Release of As(V) was, as expected, a function of the loading mole ratio. At a loading mole ratio of five, for a variety of pH levels, small concentrations of As(V) were released. The release of As(V) from adsorbents aged at ambient temperature was also evaluated at a loading ratio of ten at pH 7. The results showed essentially no release for AMF/As over a 502-day aging period; at time=0 the As(V) was 1209, at 322-days 1262, at 502-days 1217 µg/L. For FH/As the results showed a decrease in arsenic concentration with time, e.g., time=0 As(V) was 1260, at 322-days 160, at 502-days 194 µg/L.

Influence of Anionic Environment on the Removal of Arsenic by FH or AMF

Further research at Montana Tech for the MWTP was directed toward optimizing arsenic removal from waste and minewater **(MWTP-307 2007; Glasgow 2007; Twidwell and Glasgow 2008).** Hohn's previous research showed that modification of FH by co-precipitating aluminum into FH, under some conditions, improved arsenate adsorption and long-term stability characteristics in a sulfate environment. **Hohn [2005]** discovered that the adsorption characteristic of FH was significantly different if the ferric reagent source was chloride or nitrate instead of sulfate, Figure 26. **Glasgow [2007]** initiated a study to investigate

and compare the effect of using various iron reagent sources, e.g., ferric chloride, ferric nitrate, or ferric sulfate on the adsorption of arsenate. Her results for AMF are presented in Figure 27. Compare the two figures to observe the differences in the two adsorbents.

Glasgow [2007] performed the anionic study in two parts: an adsorption study and a long-term stability study. The objectives of these studies were:

- Evaluate the influence of anion type on the adsorptive removal of arsenate from wastewater. The variables considered were pH, Fe/As or [Al+Fe]/As mole ratio, and initial arsenic concentration. Time, agitation rate, and temperature were held constant. Chloride, nitrate, sulfate, and sulfate/chloride systems were studied for both AMF and FH.
- Determine if there are important differences with respect to long-term aging stability in outside storage reservoirs for solids produced from the different reagent anion sources. All influencing factors were held constant except time. The stability study samples were aged at 70°C, pH 7.0 for approximately 0, 30, 120, or 270 days. The Fe/As or [Al+Fe]/As mole ratio was ten. Upon completion of aging, the samples were subjected to an oxalate leach. The leach preferentially dissolved amorphous solids and allowed for the determination of how much of the originally precipitated solids remained and how much was converted to crystalline hematite [Schwertmann and Cornell 1996]. The partitioning of arsenate between the solution, amorphous, and crystalline phases were also calculated.

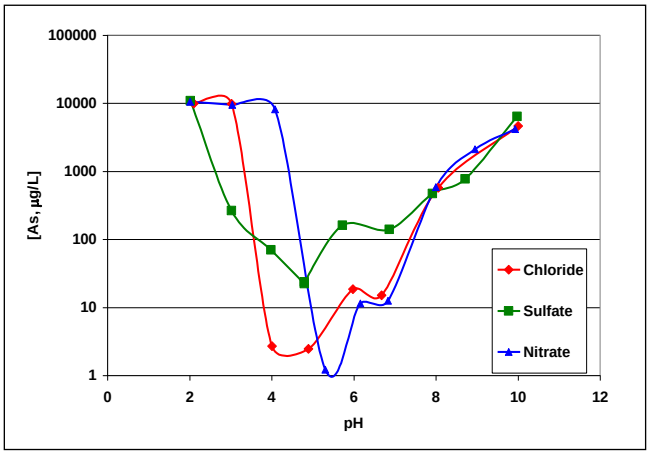


Figure 26. An illustration of the influence of anionic environment and pH on final arsenic concentration for FH (Initial As(V]=10 mg/L, Fe/As mole ratio = 5, 30-minute rest time at each pH) [Hohn 2005].

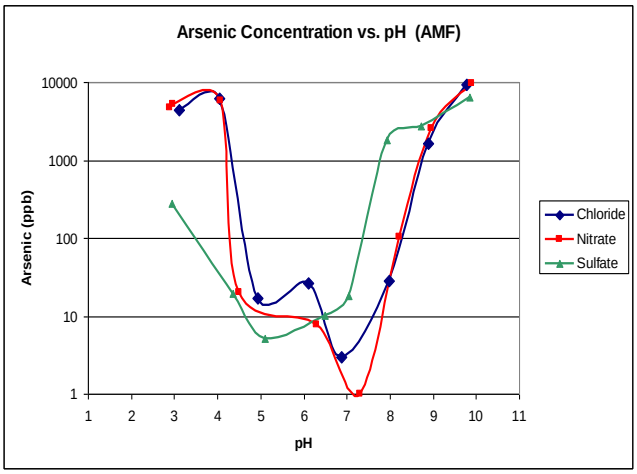


Figure 27. An illustration of the influence of anionic environment and pH on final arsenic concentration for AMF (Initial As(V) = 10 mg/L, [Al+Fe]/As mole ratio = 5, 60-minute rest time at each pH) [Glasgow 2007].

Anionic Adsorption Studies Conclusions

The research objectives as presented above were accomplished and the conclusions resulting from the adsorption studies are briefly summarized below. Detail results are available in the MWTP **(MWTP-307 2008)** report and Glasgow's Master of Science Dissertation **(Glasgow 2007).**

The following conclusions are based on eight Design of Experiment (DOE) studies. Interpretation of the results were based on statistical evaluations using the software program Design-Expert (StatEase 2007). Detailed results are presented in Glasgow's thesis.

In general, combinations of loading ratio for Fe/As or [Al+Fe]/As, pH, and initial [As] concentration can be chosen within the studied design space that results in attainment of the project goal final [As] concentration of ≤10 µg/L regardless of the anionic environment and the type of adsorbent.

Achievement of project goal final arsenic concentration, <10 µg/L at **Midpoint** conditions (pH 6.0, loading ratio 7.5, and initial arsenic concentration 5.0 mg/L) in all environments for AMF and FH adsorbents is demonstrated in Table 3.

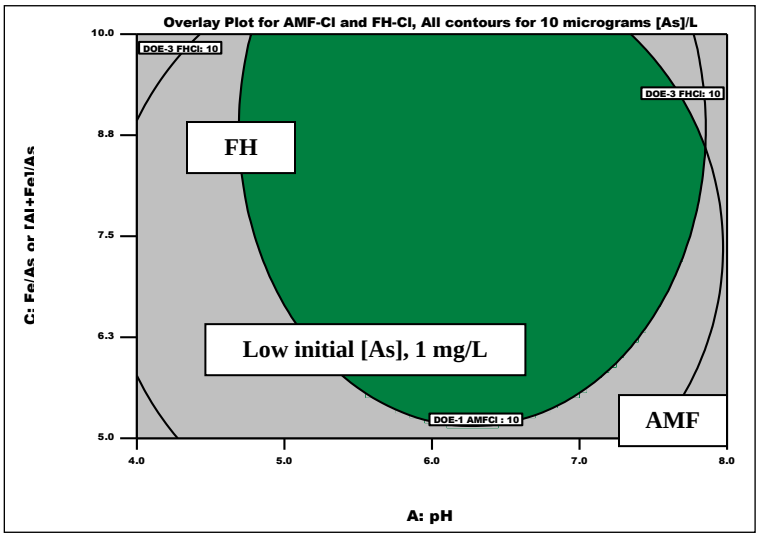
Table 3. Final Arsenic concentration for midpoint conditions

		95% Confidence Level	
	[As] Prediction, µg/L	**Low, µg/L**	**High, µg/L**
DOE-1 AMF-Cl	1	0.2	5.0
DOE-2 AMF-N	1	0.5	2.4
DOE-3 FH-Cl	2	0.7	6.6
DOE-4 FH-N	1.8	0.9	3.5
DOE-5 AMF-S	1.5	1.3	1.8
DOE-6 FH-S	3.6	1.5	8.7
DOE-7 AMF-Cl/S	1.4	0.4	6.2
DOE-8 FH-Cl/S	3.1	2.7	3.5

Midpoint values: pH 6, loading ratio 7.5, initial [As] 5.0 mg/L

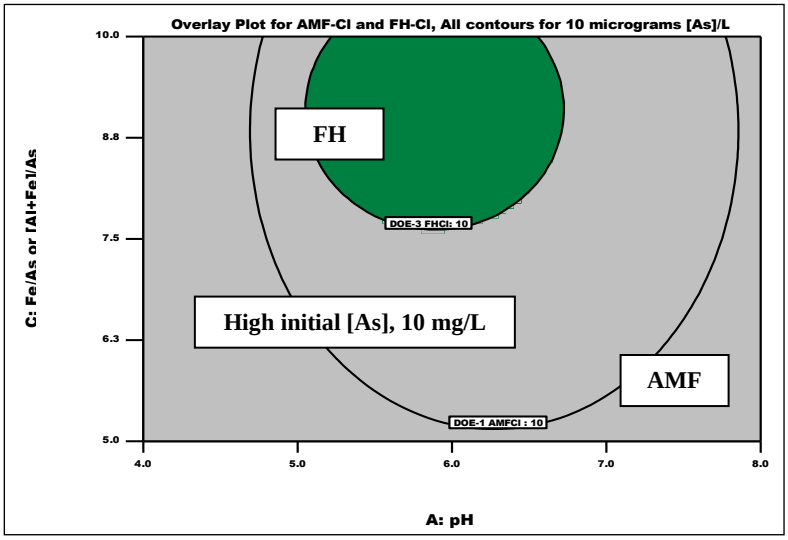
Chloride Environment-The project arsenic goal concentration can be attained by using **FH** rather than **AMF** over a wider range of loading ratio/pH combinations at low initial [As] concentrations (Figure28). FH is more appropriate in acidic conditions at low loading ratios. However, at higher initial [As]

concentrations AMF is more appropriate for many combinations of loading ratio/pH; neither adsorbent attains the project goal for acidic solutions less than pH 4.8 (Figure 29).



[All combinations of loading ratio/pH that lie within each contour result in the attainment of the arsenic project goal concentration. The region outlined in the dark color represents the common combinations of loading ratio/pH where the project goal concentrations are achieved when using either adsorbent].

Figure 28. Comparison of the loading ratio and pH on arsenic adsorption by AMF or FH for a low initial [As] concentration (1 mg/L in a CHLORIDE environment).



[All combinations of loading ratio/pH that lie within each contour result in the attainment of the arsenic project goal concentration. The region outlined in the dark color represents the common combinations of loading ratio/pH where the project goal concentrations are achieved when using either adsorbent].

Figure 29. Comparison of the loading ratio and pH on arsenic adsorption by AMF or FH for a high initial [As] concentration (10 mg/L in a CHLORIDE environment)

Nitrate Environment- The project arsenic goal concentration can be attained by using **FH** rather than **AMF** over a wider range of loading ratio/pH combinations at low initial arsenic concentrations (Figure 30). This conclusion holds for high initial arsenic concentration except a higher loading ratio is required at the lower pH levels (Figure 31).

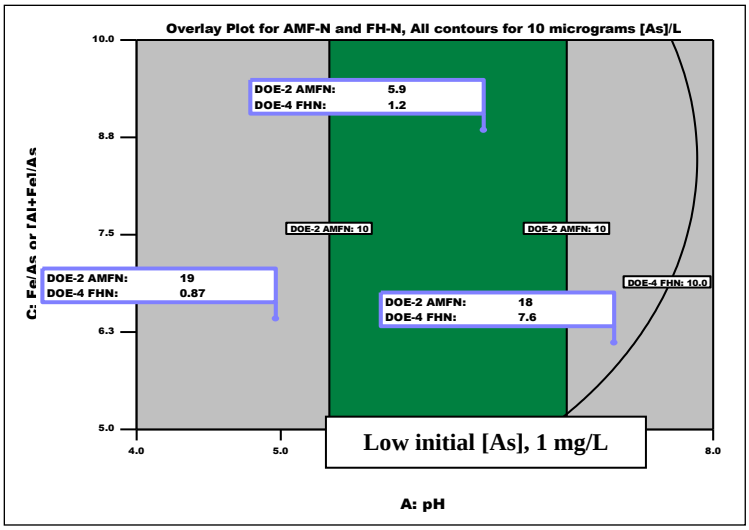


Figure 30. Comparison of the loading ratio and pH on arsenic adsorption by AMF or FH for a low initial [As] concentration (1 mg/L in a NITRATE environment).

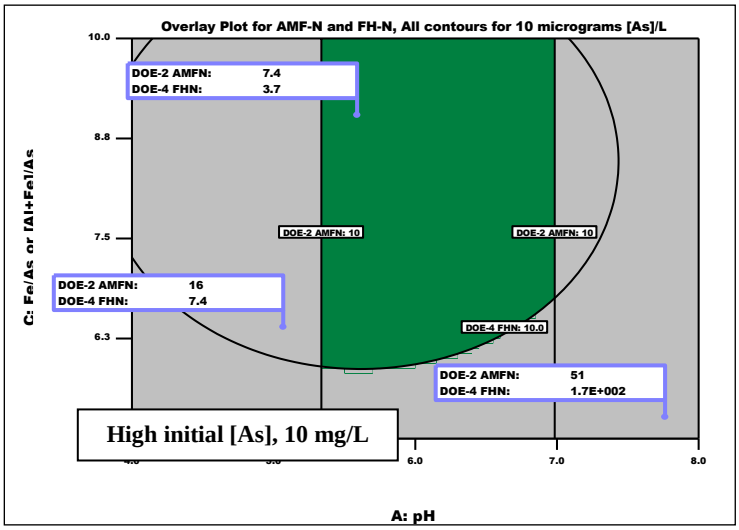


Figure 31. Comparison of the loading ratio and pH on arsenic adsorption. by AMF or FH for a high initial [As] concentration (10 mg/L in a NITRATE environment)

Sulfate Environment- The project goal arsenic concentration can be attained by both adsorbents in acidic solutions at low initial arsenic concentrations for a wide range of loading/pH combinations (Figure 32). **AMF** is more appropriate at neutral and higher pH levels. At high initial arsenic concentrations AMF is preferred over approximately the whole pH range at the lowest loading ratio of five (Figure 33).

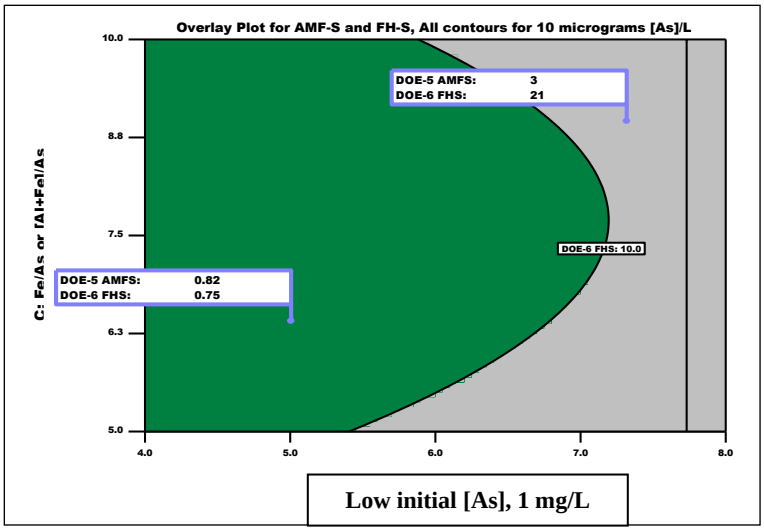


Figure 32. Comparison of the loading ratio and pH on arsenic adsorption by AMF or FH for a high initial [As] concentration (1 mg/L in a SULFATE environment)

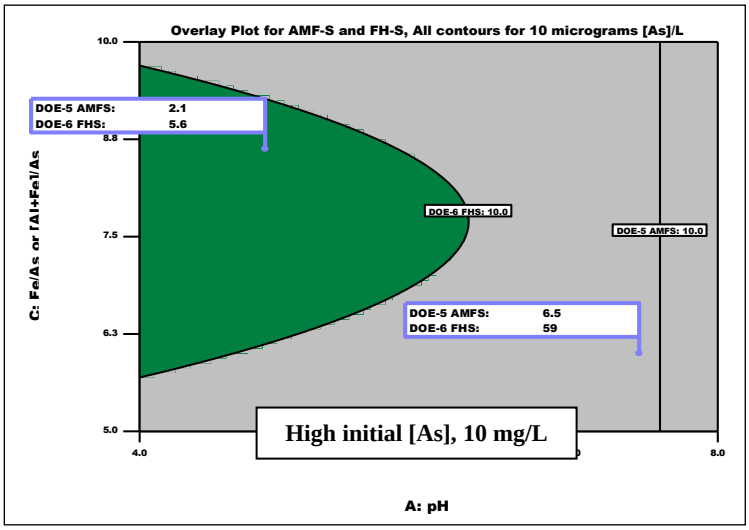


Figure 33. Comparison of the loading ratio and pH on arsenic adsorption by AMF or FH for a high initial arsenic concentration (10 mg/L in a SULFATE environment

Illustrations of the effectiveness of arsenic removal from solutions when using sulfate, nitrate, or chloride iron reagents are presented in Figures 34-37.

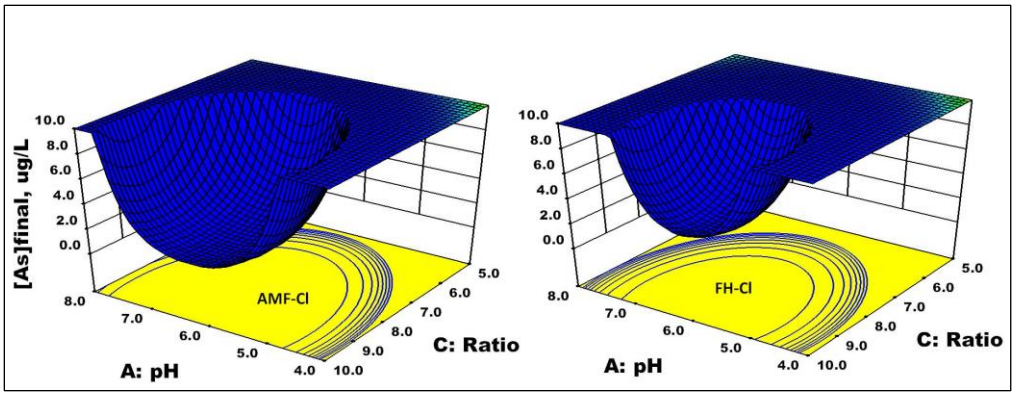


Figure 34. 3-D illustration of the influence of loading ratio and pH on the final arsenic concentration achieved when using FH or AMF adsorbents in a CHLORIDE system. Initial arsenic=10 mg/L **[Glasgow 2007]**

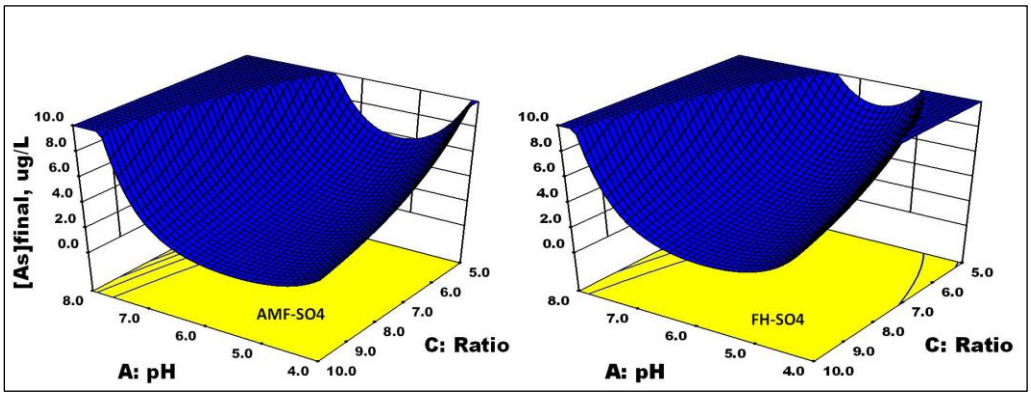


Figure 35. 3-D illustration of the influence of loading ratio and pH on the final arsenic concentration achieved when using FH or AMF adsorbents in a SULFATE system (Initial arsenic=10 mg/L) [Glasgow 2007]

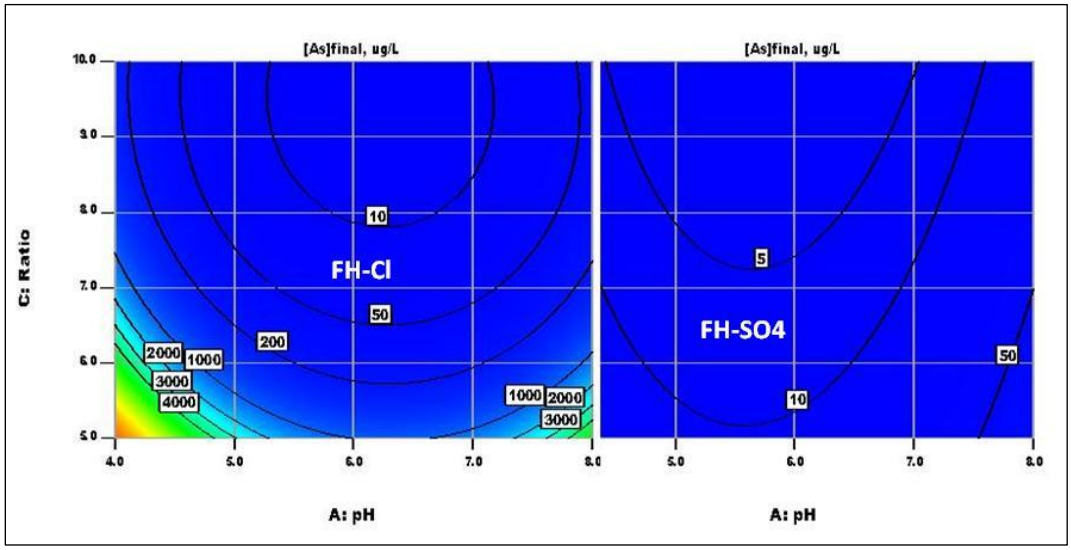


Figure 36. Contour illustration for FH as function of pH and loading ratio in CHLORIDE and SULFATE solutions. (Initial arsenic=10 mg/L) [Glasgow 2007]

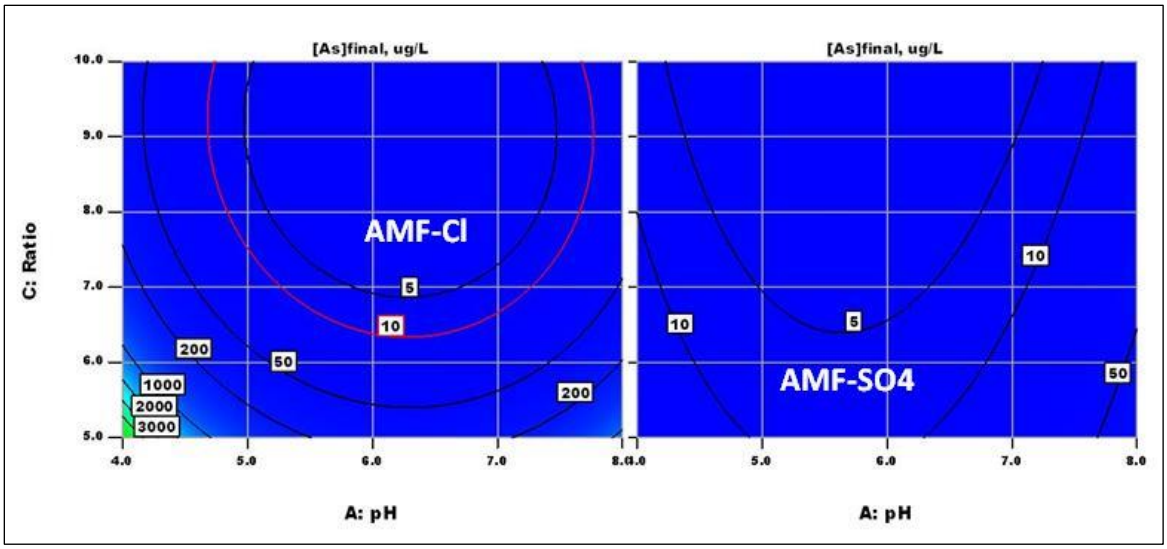


Figure 37. Contour illustration for AMF as function of pH and loading ratio in CHLORIDE and SULFATE solutions (Initial arsenic-10 mg/L) [Glasgow 2007]

Summary of Anionic Environment on Long-term Aging Stability

Stability test work was conducted at 70°C, pH 7.0 to accelerate the rate of conversion of the initially precipitated amorphous solids to more thermodynamically stable crystalline products. The use of elevated temperatures makes it possible for the experimenter to observe the effects of the conversion process in a relatively short period of time, i.e., months instead of years.

The specific research objective as presented above has been accomplished and the conclusions resulting from the elevated temperature aging studies are briefly summarized here. The study was conducted using solids prepared using an Fe/As or [Al+Fe]/As mole ratio of 10, an aging temperature of 70°C, an initial [As] concentration of 500 mg/L, and a pH of 7.0.

The extent of conversion for the control systems (arsenic not present) are presented in Figures 38 (FH) and 39 (AMF). FH converted rapidly in all the anionic environments, i.e., essentially complete conversion occurred within 30-60 days. AMF converted rapidly in a sulfate environment **[Hohn 2005],** the conversions in the chloride and nitrate environments were approximately twenty percent **(Glasgow 2007).** The aging of these two systems ended at 122 days and it is unknown whether significantly greater conversion would have occurred with further aging time.

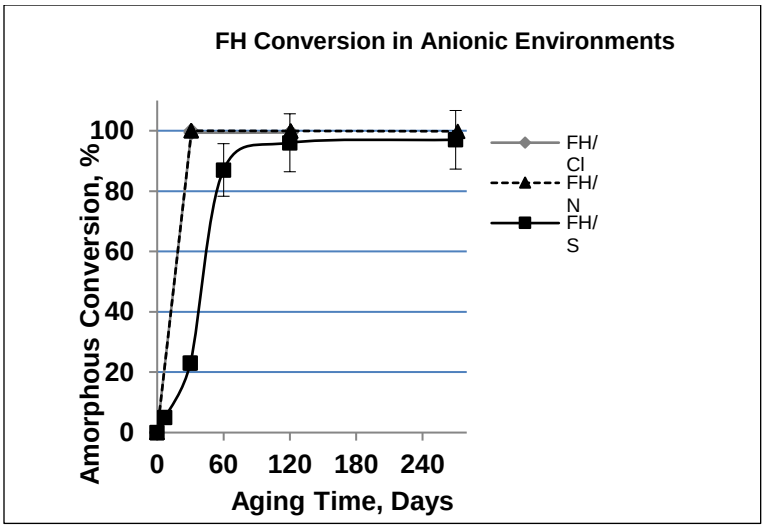


Figure 38. The influence of aging time on the conversion of amorphous FH to crystalline hematite at 70°C, pH 7.0, FH/Sulfate (data from **Hohn [2005]).**

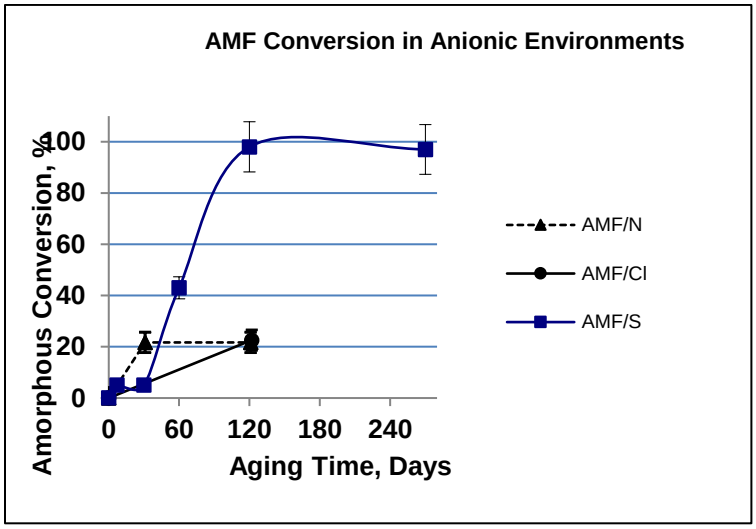


Figure 39. The influence of aging time on the conversion of amorphous AMF to crystalline hematite at 70°C, pH 7.0. AMF/Sulfate (data from **Hohn [2005]).**

The extent of conversion for the adsorbent/arsenic loaded systems are presented in Figures 40 and 41. The presence of arsenic in the solids decreased the rate of conversion of FH in both the chloride and nitrate environments (Figure 40), e.g., FH in the absence of arsenic showed essentially complete conversion in thirty to sixty days but in the presence of arsenic the extent was less than thirty percent over the 276 day study period. The order of conversion of the amorphous FH at 276 days was FH/N < FH/Cl < FH/S. The presence of arsenic in the AMF solids decreased the conversion rate (Figure 41) as compared to the controls. The conversion at 276 days for all three environments was less than twenty percent. There doesn't appear to be much difference in the extent of conversion, at 276 days, for FH and AMF.

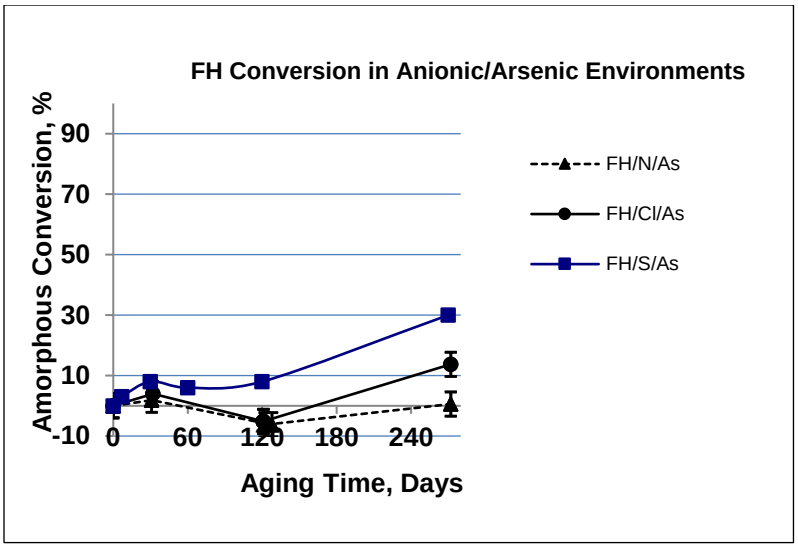


Figure 40. The influence of aging time on the conversion of amorphous FH/As to crystalline hematite at 70°C, pH 7.0. FH/Sulfate (data from **Hohn [2005**]).

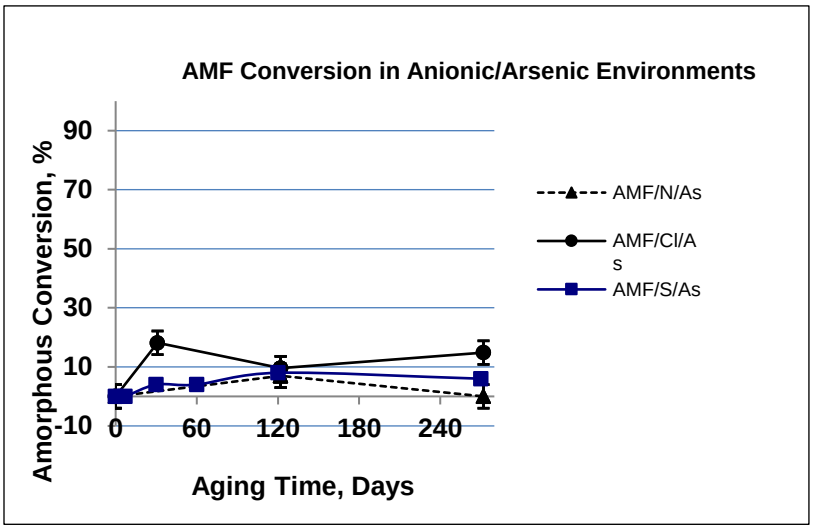


Figure 41. The influence of aging time on the conversion of amorphous AMF/As to crystalline hematite at 70°C, pH 7.0. AMF/Sulfate (data from **Hohn [2005];** Chloride and Nitrate (data from **Glasgow [2007]**

APATITE ARSENIC COMPOUNDS

Introduction

Twidwell and his graduate students investigated the possible formation of arsenate/phosphate apatite solid solution minerals. The graduate student thesis presentations are listed below **[Plessas (1992); Saran (1997); Gale (1998); Wilson (1998);** and **Orser (2001)]** The detailed study characteristics and experimental results are also available in MWTP reports **(MWPT-82R1 1998 and 82R2 1999; MWTP-121 1999; MWTP-305 2008).**

Plessas, K., Recovery of Arsenic from Process Wastewaters, M.Sc. Thesis, **1992**.

Saran, J., Removal of Arsenic from wastewater solutions as storable, stable, mineral-like precipitates, M.Sc. Thesis, 1997, 89 p.

Gale, M., Removal of Arsenic from wastewaters by Calcium/Arsenic/Phosphorous and Iron/Arsenic/Phosphorous precipitation, M.Sc. Thesis, 1998, 75 p.

Wilson, S., Removal of Arsenic from ASARCO blow-down water as stable storable precipitates, M.Sc. Thesis, 1998, 102 p.

Orser, T., Removal of Arsenic from Wastewaters as Storable Stable Precipitates, 2001, 84 p.

The removal of dissolved arsenic from mine waste waters utilizing a lime/phosphate precipitation technique has been studied on a laboratory scale at Montana Tech and on a pilot scale at MSE Technology Applications as a wastewater treatment process potentially capable of removing dissolved arsenic to <10 µg/L. Also, the long-term stability of arsenic bearing lime and lime/phosphate slurries has been investigated in laboratory extended-time air-sparged aging studies, i.e., solution arsenic concentration was monitored for over four years. The lime slurries released their arsenic back into solution in a relatively short period of time, whereas the lime/phosphate slurries showed limited release of arsenic. The developed process has been pilot scale tested by MSE-TA for the EPA Mine Waste Technology Program **(MWTP-121 1999)** on three waters, ASARCO smelter blowdown water, ASARCO thickener overflow water, and Mineral Hill Mine groundwater. The results are summarized here.

Robins and Tozawa (1982) demonstrated that lime precipitation of calcium arsenate with subsequent storage in a tailings pond environment is unacceptable because at pH levels above approximately 8.2 calcium arsenate will be converted to calcium carbonate (by carbon dioxide in air) resulting in the release of arsenic into the aqueous phase. The present studies explored the possibility of sequestration of arsenic in an apatite structure. **Hydroxyapatite [HAP, [$Ca_{10}(PO_4)_6(OH)_2$],** is thermodynamically stable in the natural environment (exposed to carbon dioxide in air) and the premise for the investigation was that arsenate ions, AsO_4^{3-}, could be substituted into the apatite structure in place of phosphate ions, PO_4^{3-}, thereby providing a thermodynamically stable compound suitable for long-term storage.

Preparation and Characterization of AHAP and APHAP Compounds

Arsenatehydroxyapatite **[AHAP, $Ca_{10}(AsO_4)_6(OH)_2$]**, arsenatephosphatehydroxyapatite **[APHAP, $Ca_{10}(As_xP_yO_4)_6(OH)_2$]** and hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] all have similar structures. They are hexagonal and belong to the space group p63/m **(Elliott 1994)**. AHAP (containing arsenate but no phosphate) was successfully prepared and characterized by **Mahapatra (1987).** His results have been successfully reproduced in the Montana Tech laboratory. APHAP compounds (containing both arsenate and phosphate) have been prepared in the Montana Tech laboratory using the Mahapatra technique for solutions containing both arsenate and phosphate at 95°C. The final solid compounds produced depends on the initial P/As mole ratio in the starting solution. To ensure that crystalline AHAP and APHAP were formed, the precipitation was conducted by titrating arsenic solutions, phosphate solutions, and calcium solutions at prescribed rates into an elevated temperature solution.

Structure determinations were conducted using x-ray diffraction (XRD) and X-ray photoelectron spectrometry (XPS). Chemical characterization was performed using EPA SW-846 (Method 3050A) digestions (in triplicate). The digestates were analyzed by EPA SW-846 (Method 6010A) using a Varian ICP. Arsenic concentrations were determined using pre-concentration by the hydride evolution technique. The instrument detection limit (DL) for arsenic was either 1.4 or 0.5 µg/L. All studies following EPA QA/QC protocols.

Long-Term Stability Test Work

Ambient temperature (25-28°C) precipitated solids were prepared utilizing a "recipe" developed during preliminary studies **[Miranda 1996; Orser 2001].** An elevated temperature was not needed. Then to determine the response to long-term aging, a series of slurry samples were exposed to air-sparging for up to four years. Slurries containing various P/As mole ratios were produced from three waters, i.e., arsenate-

doped deionized water, Berkeley Pitlake water and ASARCO blowdown water. Precipitated slurry samples were prepared in one-liter high density polyethylene (HDPE) bottles and were continuously exposed to bubbling air. Solutions were monitored for pH as a function of time. Bottles were withdrawn from the test series at specific times for up to four years. Slurries of precipitated solids were also aged in the absence of air for periods of up to eight years.

Formation and Characterization of AHAP and APHAP

AHAP-AHAP has the chemical formula, $Ca_{10}(AsO_4)_6(OH)_2$. The compound exists in nature, and the mineral form is called Johnbaumite. AHAP has been prepared in the laboratory by only one group of investigators, i.e., **Mahapatra et al. [1987]**. These researchers prepared the compound by precipitation from a slightly supersaturated solution at 100°C and pH 10. They then determined the solubility product of the solid as a function of temperature. AHAP has also been produced in the Montana Tech laboratory using the precipitation procedure described by **Mahapatra.** The procedure consisted of precipitation from a nitrogen-sparged boiling solution at elevated temperature (95°C) and pH 10 from a slightly supersaturated solution. An example XRD pattern for the compound formed is presented in Figure 42. An expanded view of the 2-theta region from 30 to 36 degrees (the region where the most intense predominant peaks are present) is presented in Figure 43. The pattern is similar whether produced by the **Mahapatra** or the Montana Tech technique. The pattern is in reasonably close agreement with the mineral-phase Johnbaumite. The patterns presented in Figures 42 and 43 are for AHAP precipitated from elevated temperature solutions. However, the same compound is formed by ambient temperature precipitation and ambient temperature long-term aging. For example, the XRD trace for ambient temperature precipitated sample solids shows a rather poorly developed pattern (with a cluster of poorly defined peaks at 2-theta values within the 30–36° range). The poorly developed peaks are the result of the solid being a very fine particulate size (the mean diameter is a few nanometers). These solids do form crystalline AHAP with time, i.e., **Plessas [1992]** presented XRD patterns for the ambient temperature precipitated product and for four-year ambient temperature aged samples that showed Johnbaumite crystallinity in the four-year aged product (Figure 44).

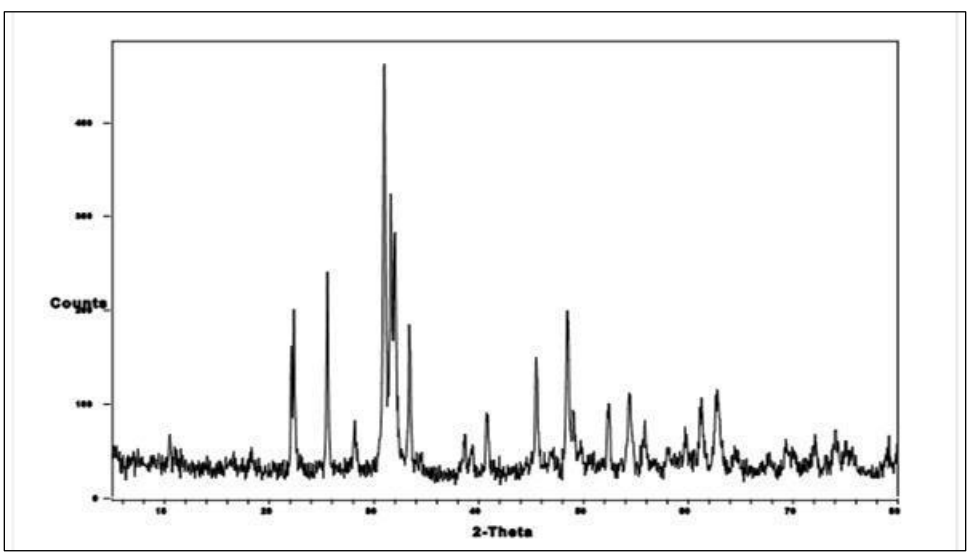


Figure 42. X-ray diffraction pattern for arsenatehydroxyapatite (AHAP) formed from a 95°C solution at pH 10

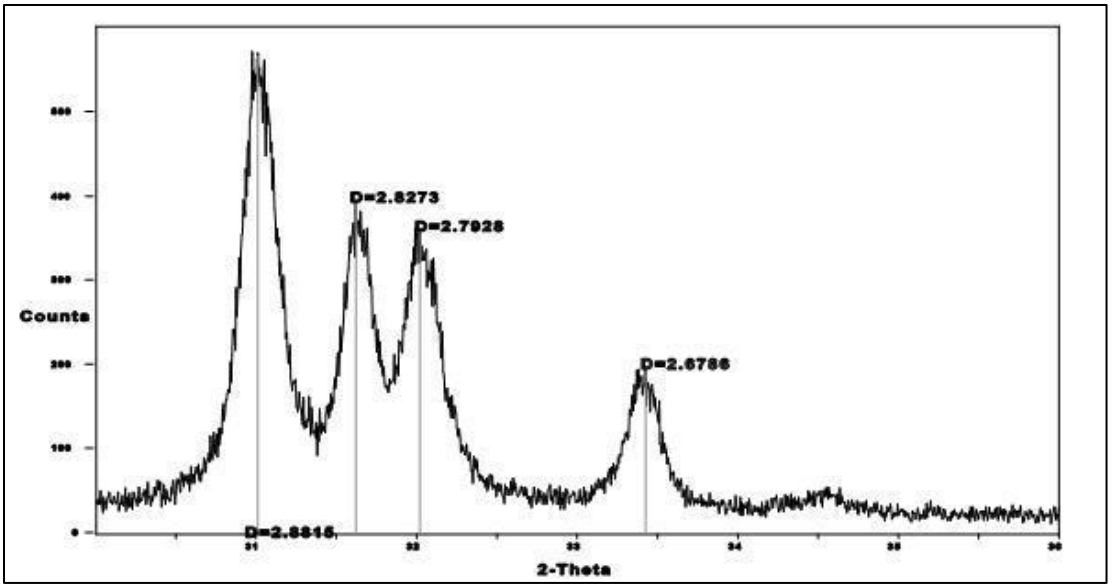


Figure 43. X-ray diffraction pattern for arsenatehydroxyapatite (AHAP) formed at 95°C over the 2-theta range 30-36° (expanded view)

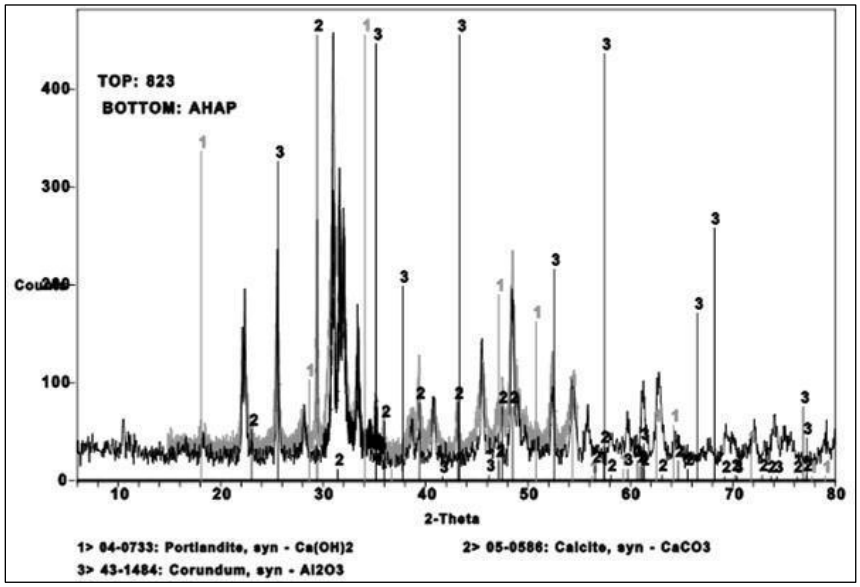


Figure 44. X-ray diffraction pattern for ambient temperature precipitated AHAP Aged at ambient temperature for four years (top grey pattern) compared with the elevated temperature (95°C) AHAP precipitated sample pattern superimposed (bottom black pattern)

APHAP-Many precipitations have been performed to verify that APHAP does, indeed, form. Precipitation from 95°C solutions produces crystalline products. The P/As ratio in the solid products depend on the P/As mole ratio in the initial solution. Several P/As ratios have been studied in this research program, e.g., P/As mole ratios (in the initial solution) of 0, 0.2, 0.7, 3, 5, 7, 10, and no arsenic.

AHAP and HAP are the two end members of a structural family series, i.e., they are both hexagonal and belong to the same space group ($P6_3/m$). When subjected to XRD they produce the same peaks but the peaks exist at different two-theta values, i.e., the reflective planes are the same but "d" spacings are different. This effect is illustrated in Figure 45. The patterns displayed in Figure 45 were produced from

solids formed by the elevated temperature technique described above. Corundum was added to the samples as an internal standard so that true alignment could be attained for the superimposed patterns.

APHAP compounds have also been formed by the same elevated temperature precipitation technique described previously. The starting solutions contained mixtures of arsenate and phosphate. The formation of substitutional compounds was expected because the ionic radii of arsenate and phosphate are similar. The lattice parameters for HAP and AHAP are for HAP a=9.4176 A°, c=6.8814 A°; for AHAP a=9.72 A°, c=6.98 A° **(Mahapatra et al. 1987).** The APHAP compounds have lattice parameters between HAP and AHAP. An illustration of the effect of substitution of arsenate into the phosphate structure on the relative "d" values is depicted in Figure 46. A photomicrograph of APHAP is presented in Figure 47 showing the crystallinity of the product. The precipitated APHAP products all showed very crystalline patterns. APHAP compounds have been loaded up to 28.6±0.7 percent arsenic and structural parameters are presented in Table 4.

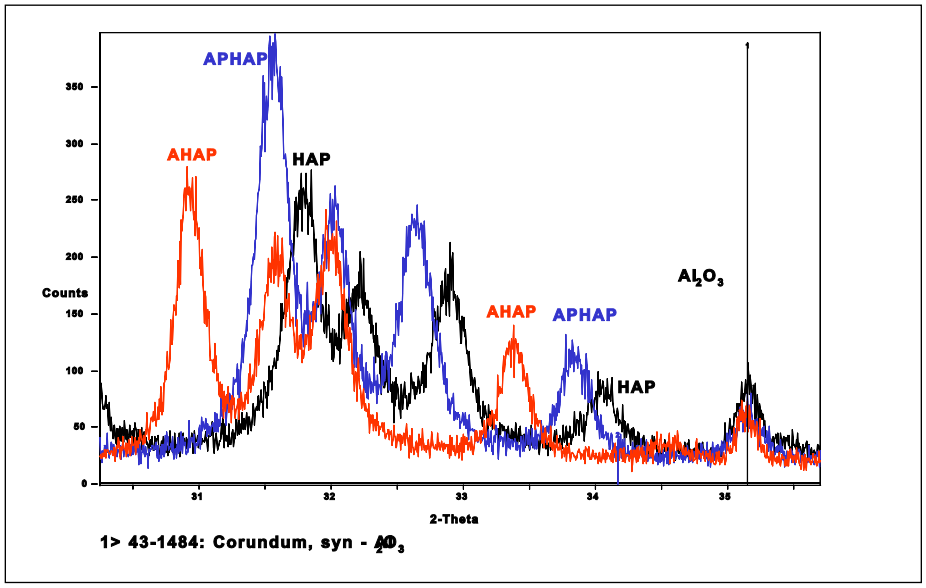


Figure 45. X-ray diffraction patterns for AHAP (no phosphate), APHAP (P/As mole ratio in solids=1.9), and HAP (no arsenate)

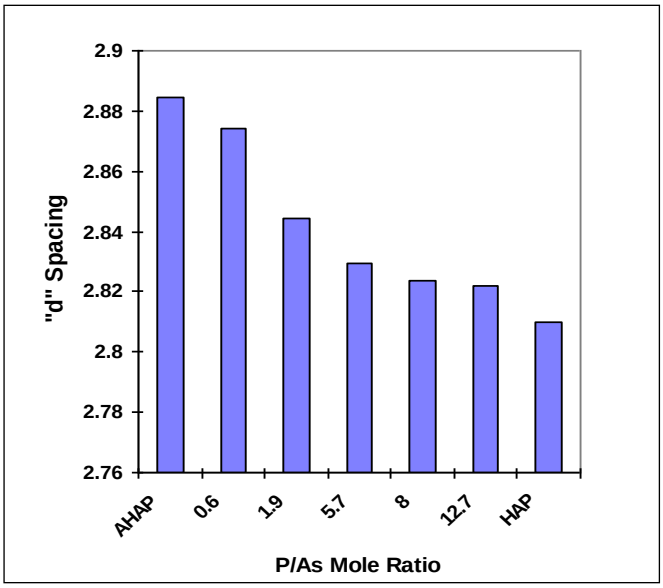


Figure 46. Variation in the XRD major peak "d" value as a function of P/As mole ratio in APHAP (precipitated at 95°C)

Table 4. Arsenate hydroxyapatite solid solution composition

P/As Mole Ratio	$Ca_w(As_xP_yO_4)_z(OH)_2$				As in Final Solid, %
	w	x	y	z	
0.06±0.01	10	0.94	0.06	6	28.6±0.7
0.6±0.1	10	0.63	0.37	6	18.5±2.1
1.9±0.0	10	0.35	0.66	6	13.7±0.4
5.7±0.4	10	0.15	0.85	6	5.9±0.3
8.0±0.2	10	0.11	0.89	6	4.4±0.2
7.9±0.1	10	0.11	0.89	6	4.3±0.2
12.7±0.1	10	0.01	0.99	6	2.9±0.02
No As	10	0.00	1.00	6	0.1±0.7
Hydroxyapatite	10	0.00	1.00	6	0

All AHAP compounds formed by precipitation from solutions held at 95°C, pH of 10-12 with potassium hydroxide, 18-24 hrs. The compounds were recovered by filtration, then dried at 105°C for 1 hr. The compounds element content was digested then analyzed by ICP-AES.

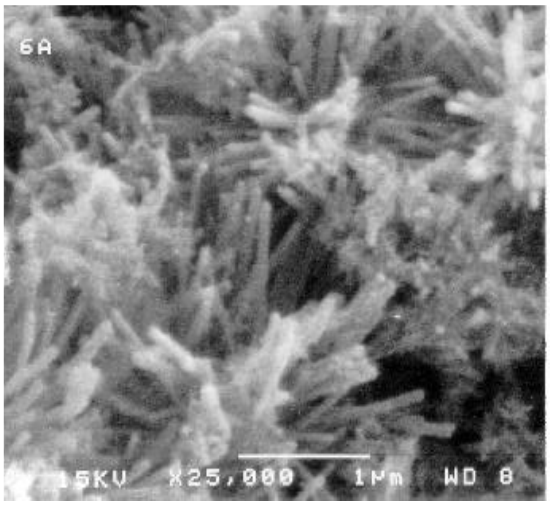


Figure 47. SEM photomicrograph for 95°C precipitated APHAP (P/As mole ratio=7)

Ambient temperature precipitated products (prepared by using the same procedures of the elevated temperature precipitation, except for the elevated temperature) have a mean particulate size of a few nanometers. When subjected to XRD the ambient temperature precipitated solids show a cluster of peaks over the two-theta range 30-36°. This peak range is where HAP and APHAP have their three major peaks. The major peaks formed in the ambient temperature products are boarder but agree with the major peaks present in the high temperature precipitated products (for the same P/As mole ratio in the initial solution). It is not possible to conclude (from the XRD data) that arsenate bearing apatites are formed via ambient temperature precipitation. However, it has been shown that the crystallinity is improved dramatically when the room temperature precipitated product was aged at an elevated temperature, i.e., ambient temperature precipitated solids (citrate leached) when aged in a slurry environment at 90-95°C quickly converted to crystalline solids. An example of this result is presented in Figure 48.

The demonstrations that APHAP compounds form when the precipitation is conducted at elevated temperatures or when the ambient temperature precipitated solids are aged at elevated temperature do not necessarily mean that the compounds form at ambient temperature. However, ambient temperature formation of APHAP was demonstrated by use of X-ray Photoelectron Spectroscopic (XPS) analyses. Ambient temperature samples were prepared by using the same high temperature precipitation procedure (for initial solution ratios of P/As = 0.7 and 7), except for the temperature of precipitation. The samples were citrate leached to remove calcium compounds (such as calcium hydroxide) other than the apatite-like compounds. These products were subjected to XPS. XPS analyses provide a measure of atomic binding energies. The binding energy spectra would be different if the room temperature precipitated solid contained different bonding associations than the high temperature precipitated solid. The binding energy spectra were the same for both the room temperature and high temperature products. This result was obtained for both the P/As = 0.7 ratio and the P/As = 7 ratio precipitated products. The important conclusion is, therefore, that the same phosphate/arsenate compounds form during room temperature and during high temperature precipitation. The major difference is the particle size and particle size distribution.

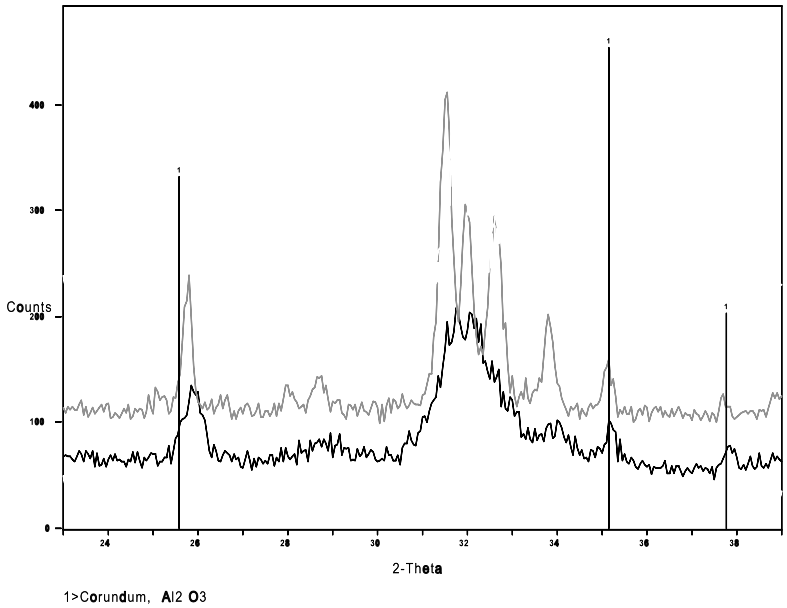


Figure 48. Ambient temperature APHAP (P/As=7) aged in solution at 90-95° C for 5 days

The bottom curve is the pattern for ambient temperature precipitated APHAP. The top grey curve is the pattern for the ambient temperature solids aged at 95° C for 5 days [Gale 1998].

The relative solubility of the various arsenate bearing compounds as a function of pH are presented in Figure 49. Figure 49a compares the solubility of $Ca_3(AsO_4)_2$ to HAP; Figure 49b compares the solubility of AHAP (Johnbaumite) to HAP; Figure 49c compares the solubility of APHAP (P/As=7) to HAP. The APHAP (P/As = 7) compound is less soluble as a function of pH (7-12) than calcium arsenate or Johnbaumite. A STABCAL 3-D visualization of the solubility of APHAP as a function of pH is presented in Figure 50.

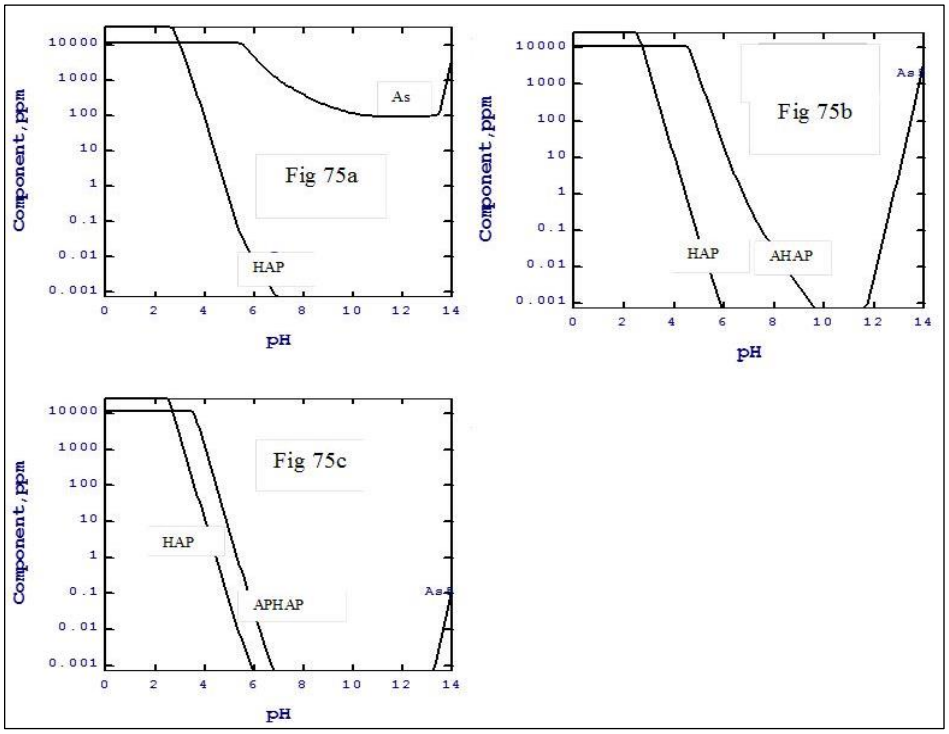


Figure 49. Comparison of relative solubilities of arsenate bearing compounds: (A) Calcium Arsenate [see CA] ($Ca_3(AsO_4)_2$ top left figure, HAP ($Ca_{10}(PO_4)_6(OH)_2$ bottom curve, (B) AHAP Johnbaumite ($Ca_{10}(AsO_4)_6(OH)_2$ top curve, HAP bottom curve, and (C) APHAP (P/As=7) top curve, HAP bottom curve. (Concentrations used for each calculation were based on stoichiometric addition of calcium for the formation of HAP ($Ca_5(PO_4)_3OH$) and each arsenate bearing compound).

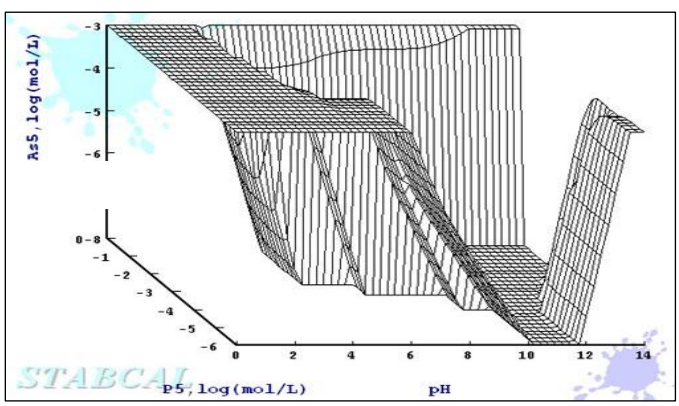


Figure 50. 3-D illustration of the solubility of APHAP (P/As=7) as a function of pH (Initial arsenic 0.01 mole/L). **[STABCAL 2010**).

Laboratory Studies-Arsenate can be effectively stripped from aqueous solutions by hydrated lime addition, but phosphate enhances the effectiveness of the precipitation, i.e., the effectiveness is enhanced by controlling the P/As mole ratio in the initial solution phase as shown in Table 5. Detailed results are presented elsewhere **(MWTP-82R 1998 and MWTP-82R1 1999; Twidwell et al. 2005; McCloskey et al. 2006).**

Table 5. Summary of experimental results for Arsenic removal by Hydrated Lime/Phosphate precipitation

System (initial arsenate concentration)	Arsenic after treatment, µg/L		
	P/As=0	P/As=5	P/As=7
Pure Synthetic Water (initial arsenic 1,000,000 µg/L)	58	<DL	-
Berkeley Pit Water (initial arsenic doped to 100,000 µg/L)	14	7-14	<DL
ASARCO Blowdown Water (initial arsenic >3,800,000 µg/L)	2776	19	24
*Ambient temperature precipitation using 2.2 times the stoichiometric requirement of calcium hydroxide based on the arsenic content in the AHAP and APHAP compounds. DL=1.4 µg/L			

Pilot Scale Treatment of Industrial Waters-Three industrial waters were evaluated by pilot-scale continuous water flow test work, e.g., ASARCO scrubber blowdown water (3.3 g/L As); ASARCO thickener overflow water (5.8 mg/L), and TRV Mineral Hill Mine groundwater (420 µg/L). The results are presented in Table 6.

Table 6. Mineral-like precipitation results for treatment of ASARCO Waters and Mineral Hill Mine Groundwater

Description			[As]	
Water	P/As Mole Ratio	Volume Treated, Liters (Gallons)	Inlet As (pH)	Effluent As, µg/L (pH)
Scrubber Blowdown	5.5	6300 (1665)	3.3 g/L (0.9-1.5)	7-9 (10.8-12.2)
Scrubber Blowdown	12	1530 (405)	3.3 g/L (0.9-1.5)	6-9 (10.8-12.2)
Thickener Overflow	10	4485 (1185)	5.8 mg/L (5.5-10.5)	6-15 (11.7-12.4)
Thickener Overflow	100	5390 (1425)	5.8 mg/L (5.5-10.5)	3-13 (11.7-12.4)
Mineral Hill Groundwater	10	4485 (1185)	420 µg/L (11.0-11.5)	6-7(12.5-12.7)
Mineral Hill Groundwater	100	14820 (3915)	420 µg/L (11.0-11.5)	4-7(12.5-12.7)

*Flowrate: 13.8 to 19-liters/minute (1 to 5 gallons/minute)

Long-Term Stability in Air Saturated Waters-To determine the response to long term aging, a series of ambient temperature laboratory scale samples were exposed to air-sparging for up to four years. Solids were formed from three water sources, i.e., arsenic doped deionized water, Berkeley Pitlake water, and ASARCO blow-down water. Solid/water slurries were prepared by ambient temperature precipitation in one liter HDPE bottles and were continuously sparged with air. Solutions were aged at ambient temperature and were monitored for pH as a function of time. Evaporated water was periodically replaced with pH adjusted water. Bottles were withdrawn from the test series at specific times, i.e., at 0, 3-months, 6-months and 18-months and in a few cases 4-years, filtered through a 0.2 µm HDPE filtering disk, preserved with high purity nitric acid to a pH<2, then analyzed for arsenic, calcium and phosphorus. Experimental results for the aqueous phase arsenic concentrations are summarized in Tables 5 through 6 and visualization of the aging process is presented in Figures 51 and 52 (synthetic water at 1 g/l As), 53 and 54 (ASARCO industrial process blowdown water at 3.8±0.9 g/L), and 55 and 56 (BERKELEY Pitlake water augmented with arsenic to 100 mg/L). Detailed individual analytical results are presented elsewhere **[MWTP-121 1999]** including concentration values for all associated elements, e.g., calcium, iron, copper, zinc and sulfate.

Arsenate (Phosphate Not Present)-The precipitated solids formed from the arsenic doped water (without phosphate present) showed considerable arsenic release back into the solutions phase (solution pH ranged from 10-11.5) in the air sparged samples (Table I). However, less than fifteen percent of the arsenic (for doped water) and eighteen percent of the arsenic (for ASARCO water) were recovered in the solutions even after 18 months of slurry/air aging (Tables 5 and 6). This suggests that the arsenate phase formed is likely something other than simple calcium arsenate; perhaps Johnbaumite forms or perhaps the arsenate is present as adsorbed species on the associated solids. XRD patterns of these solids showed the presence of calcium carbonate and an x-ray amorphous phase even after eighteen months of aging, i.e., not all the arsenate containing solids were converted to calcium carbonate.

Phosphate/Arsenate-The solids containing P/As mole ratios of seven or greater were all reasonably stable for the eighteen-month period investigated for both the doped water and the ASARCO water. The Berkeley Pitlake (Table 5) aging results showed excellent stability for solids produced with and without the presence of phosphate. The Berkeley Pitlake water contained a high iron concentration (1g/L) and the deportment of the arsenic is unknown, i.e., whether APHAP or other arsenic bearing solids were formed. The aging characteristics of the three systems are presented in Figures 50 to 55.

Several precipitated slurry samples (formed from arsenate doped deionized water) were aged at ambient temperature in the absence of air to determine if the solid particulate would grow in crystallite size. The sample preparation procedure used was the same as previously described. Because there was excess hydrated lime in the aged samples the samples were subjected to a citrate leach to remove the more soluble products (such as hydrated lime); then the samples were evaluated by XRD. Samples were evaluated at four and eight years. The precipitated solids formed in the absence of phosphate were all soluble in the citrate leach solutions at both four and eight years, i.e., no solids were recovered. The precipitated solids formed from the phosphate/arsenate solutions did yield material that was not solubilized by the citrate leach. These solids showed little to no evidence of crystal growth during the aging period. XRD patterns for the four and eight year aged samples are presented in Figure 10 (P/As = 7).

Table 7. Summary of experimental results for long-term air-sparged ambient temperature precipitated products: Arsenate doped water (no phosphate present)

Sample Description		Concentration, μg/L
Nominal P/As mole ratio in the initial solution	Months aged	Arsenic
Starting Water, μg/L		1,000,000
0	0	57.7
	1	42110
	3	78100
	6	85090±170
	18	121,300±4,200
	4 yrs	122,700±47,000
	4 yrs (no air exposure)	5(DL=1.4)
	8 yrs (no air exposure, pH 12.1)	15.5(DL= 0.5)
5	0	6.6
	1	<IDL
	3	34.3
	6	9.8±9.8
	18	498±98
	4 yrs (no air exposure)	<1.4 (DL=1.4)
	8 yrs (no air exposure, pH 12.4)	<1 (DL=0.5)
5 Duplicate	0	14.5±7.9
	6	1.0±2.1
7	0	-
	1	<IDL
	3	4.9
	6	3.4±1.0
	18	52±37 (DL=1.4)
	4 yrs (no air exposure)	<1.4 (DL=1.4)
	8 yrs (no air exposure, pH 12.3)	0.8 (DL=0.5)
20	24	20 (DL=1.4)
	4 yrs	<20 (DL=20)

*Reported sample values are averages based on one to three analyses.
Precipitation was conducted using 2.2 times the stoichiometric requirement of calcium hydroxide based on the arsenic content in the AHAP and APHAP compounds.

Table 8. Summary of experimental results for long-term air-sparged ambient temperature precipitated products: ASARCO blowdown water

Sample Description		Concentration, μg/L
Nominal P/As mole ratio in the initial solution	Months aged	Arsenic
Starting Water, μg/L		3.8±0.9 g/L
0	0	2776
	3	218,400±4,800
	6	601,000±58,900
	8 yrs (no air exposure, pH 10.9)	1,200
5	0	27.6
	3	13.8±6.2
	6	10.6±0.8 (DL=1.4)
	8 yrs (no air exposure, pH 12.3)	8.4 (DL=0.5)
7	0	23.9
	3	10.2±10.6
	6	28.9±0.6
	18	70±51 (DL=1.4)
	8 yrs (no air exposure, pH 12.3)	1.7 (DL=0.5)
10	18	23±20 (DL=1.4)

*Reported sample values are averages based on one to three analyses.

Precipitation was conducted using 2.2 times the stoichiometric requirement of calcium hydroxide based on the arsenic content in the AHAP and APHAP compounds. Nominal composition of initial ASARCO blowdown water (mg/L): 3800 As, 400 Cd, 5 Cu, 30 Fe, 10 P, 10 Pb, 140 Zn, 3000 S

Table 9. Summary of experimental results for long-term air-sparged ambient temperature precipitated products: Berkeley Pitlake water

Sample Description		Concentration, μg/L
Nominal P/As mole ratio in the initial solution	Months aged	Arsenic
Starting Water, μg/L		100,000
0	0	14.2
	1	21.9
	6	35.5±3.8
	18	15±9
	8 yrs (no air exposure, pH 12.3)	15.9 (DL=0.5)
5	0	14.6
	3	19.7
	6	17.9±1.5
	4 yrs (no air exposure)	14.5±7.9 (DL=1.4)
	8 yrs (no air exposure, pH 12.3)	1.9 (DL=0.5)
7	0	<1.4
	3	7.3
	6	7.5±2.4
	18	35±27
	8 yrs (no air exposure, pH 12.3)	1.7 (DL=0.5)
10	18	20±15 (DL=1.4)

*Reported sample values are averages based on one to three analyses.

Precipitation was conducted using 2.2 times the stoichiometric requirement of calcium hydroxide based on the arsenic content in the AHAP and APHAP compounds. Nominal composition of initial water (mg/L): 1 augmented to 100 As, 260 Al, 2 Cd, 170 Cu, 1000 Fe,, 5 Cu, 500 Zn, 2500 S

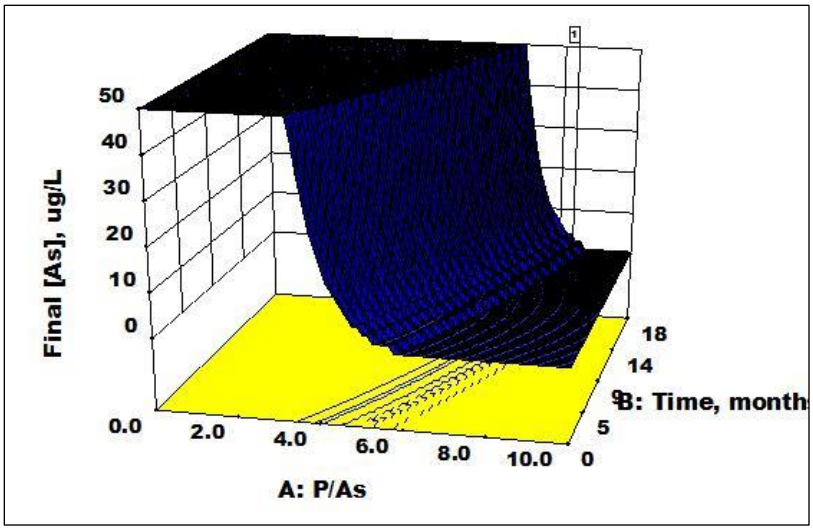


Figure 51. 3-D visualization of the influence of P/As mole ratio and ambient aging time for Synthetic water

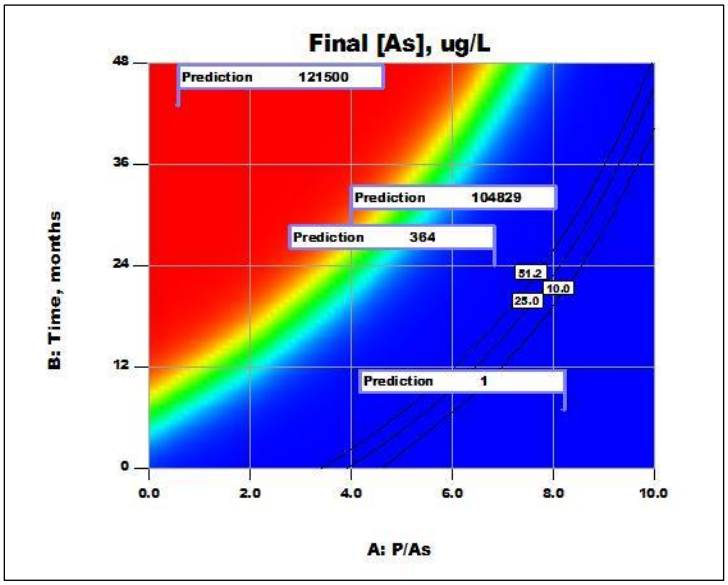


Figure 52. Contour visualization of the influence of P/As mole ratio and ambient aging time for Synthetic water

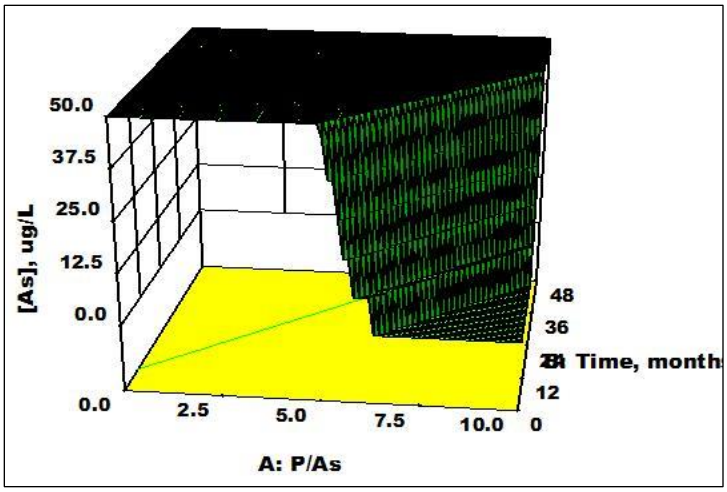


Figure 53. 3-D visualization of the influence of P/As mole ratio and ambient aging time for ASARCO water

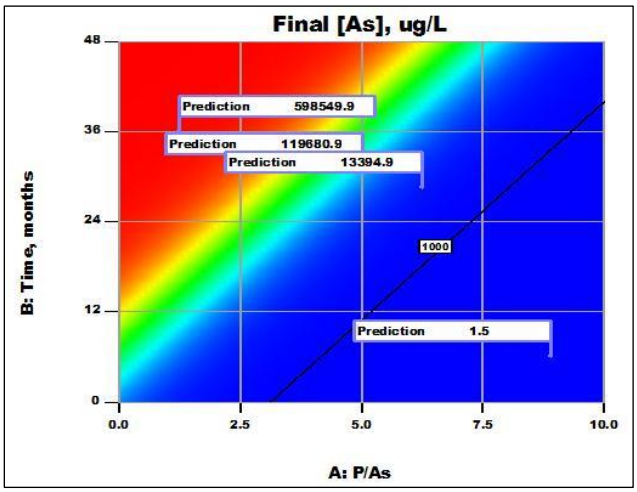


Figure 54. Contour visualization of the influence of P/As mole ratio and ambient aging time for ASARCO water

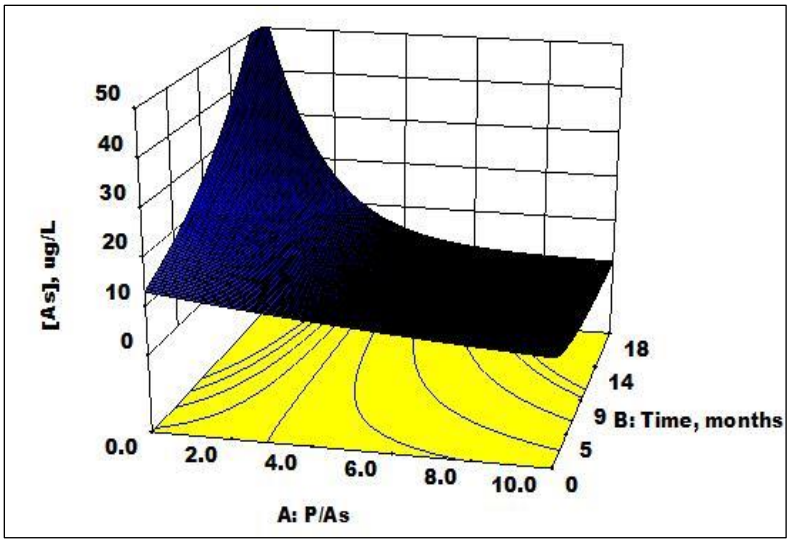


Figure 55. 3-D visualization of the influence of P/As mole ratio and ambient aging time for Berkeley Pitlake water.

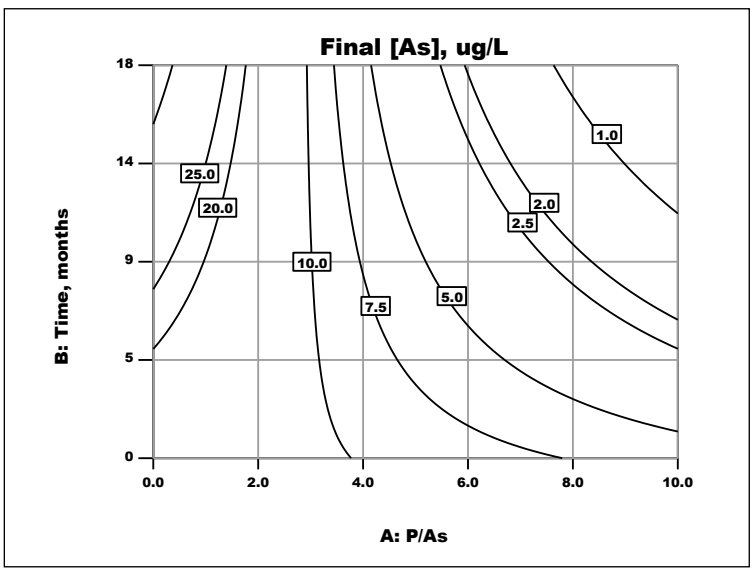


Figure 56. 3-D visualization of the influence of P/As mole ratio and ambient aging time for Berkeley Pitlake water

Summary

- Arsenate can be effectively stripped from aqueous solutions by hydrated lime addition, but phosphate enhances the effectiveness of the precipitation, i.e., the effectiveness is enhanced by controlling the P/As mole ratio in the initial solution phase (results shown previously as Table 7).
- The long-term stability of the ambient temperature precipitated P/As bearing compounds has been assessed, i.e., compound stability was tested by sparging air into aqueous/compound slurries for up to four years. The pH, solution arsenic, phosphorus, and calcium concentrations were monitored as a function of aging time. The six- and eighteen-month data show that the arsenic (no phosphate present) bearing solids slurries are not stable to air exposure. The solids containing P/As mole ratios of seven or greater are all reasonably stable up to at least eighteen months (Table 10).

Table 10. Summary of experimental results for long-term air-sparged ambient temperature precipitated products

System (initial arsenic concentration)	Arsenic in solution after aging for 6-months, µg/L	Arsenic in solution after aging for 18-months, µg/L
Pure (initial arsenic 1,000,000 µg/L)	3.4±1.0	52±37
Berkeley Pit Water (initial arsenic 100,000 µg/L)	7.5±2.4	35±27
ASARCO Water (initial arsenic >3,800,000 µg/L)	28.9±0.6	70±51

Nominal P/As mole ratio in the starting solution=7. Precipitation was conducted at ambient temperature. Aging was conducted in air-sparged vessels. Arsenic detection limit=1.4 µg/L for 6-month data; 0.5 µg/L for 18-month data.

ARSENATE REMOVAL as FERROUS ARSENATE

Twidwell and MSE-Technology Applications have conducted studies on arsenic removal using the formation of ferrous arsenate, Symplesite [$Fe_3AsO_4)_2$], precipitation for industrial water cleanup [Twidwell 2015].

Ferrous/Ferric Two-Stage Treatment: Industrial Example

The use of Fe(II) reagents for the removal of As(V) was recognized early by **Khoe et al. (1991)** and others **(Stefanakis 1988).** We, at Montana Tech, developed and demonstrated the ferrous arsenate process and MSE-Technology Applications have applied that technology to cleaning up contaminated ground waters at an industrial site in California. There is an operating plant using this procedure (Figures 57). The plant has been operating since 2002 and has achieved the lowering of arsenate concentrations from ~100 mg/L to <15 µg/L without a single violation of their NPEDS permit since the facility start up. The final solid products are disposed of in a regulated hazardous waste repository. The treatment sequence is a two-stage process, e.g., the first stage is the precipitation of ferrous arsenate by controlling the Eh/pH conditions as shown in Figure 58. The ferrous arsenate formed is separated from the slurry and disposed of in a hazardous waste facility; the separated solution is further treated by addition of ferric sulfate to form ferrihydrite (a non-hazardous product).

Figure 57. Photograph of a Sherwin Williams operating plant using ferrous sulfate reagent for arsenic removal from ground water
(designed and constructed by MSE-Technology Applications, Butte, MT)

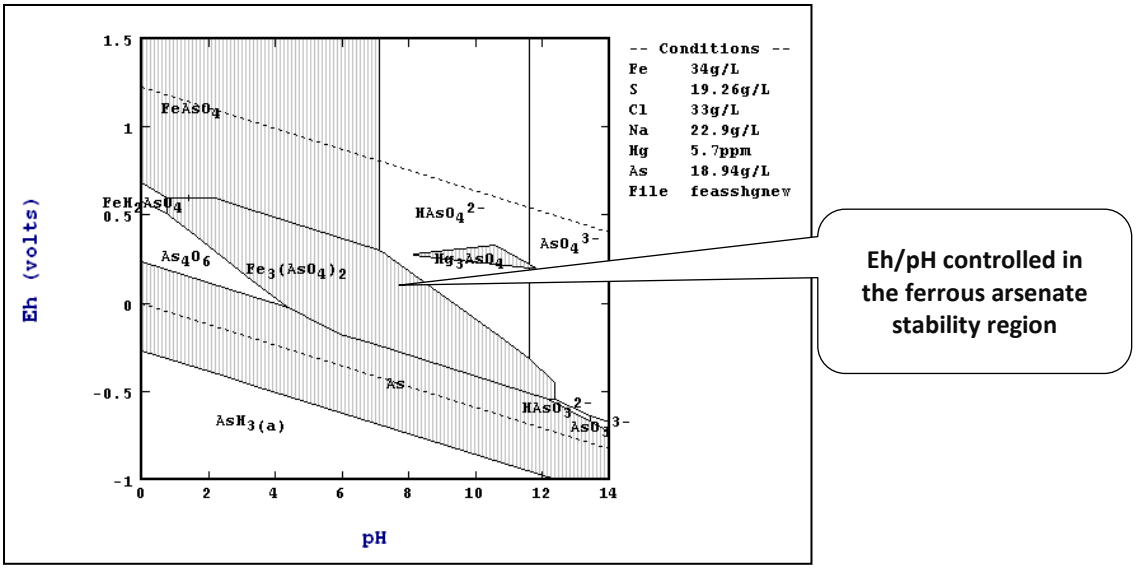


Figure 58. Potential/pH Diagram for the formation of ferrous arsenate.

McCloskey and Hiebert [MWTP-305 2008] have led a team to demonstrate the ferrous arsenate treatment process on a pilot scale at an abandoned mine site, Suzie Mine, Rimini, Montana. The pilot operation treated ten gallons of acid mine drainage solution per minute continuously for four months. The average arsenic concentration in the effluent was 248 ± 195 µg/L (initial arsenic was 23,300 µg/L).

Khoe, Huang and Robins [1991] have reported that arsenates form a **ferrous arsenate**. The free energy of formation of this compound is -421.5 kcal/mole and shows a minimum solubility (at pH 7.5) of 10^{-6} moles/liter (less than the World Health Organization, WHO, guideline value for drinking water). They suggest that ferrous arsenate would be environmentally stable if stored in sub-surface anoxic conditions (where ferrous iron would not be oxidized) at pH 7. It is interesting to note that Huang and Vane (1989) have achieved complete removal of arsenate from solutions by using activated carbon soaked in ferrous salt solutions. They postulate that ferrous arsenate surface complex species form**. Johnston and Singer [2007]** have reported a higher solubility for ferrous arsenate, i.e., a Ksp=$1x10^{-33.25}$. Our data support the value reported by Khoe.

Ferrous/Ferric Tw Stage Treatment for Concentrated Arsenic Solutions (smelter scrubber blowdown waters)

Additional studies are summarized here. These studies were conducted to determine if concentrated arsenic solutions (39.4 g/L As(V), 41 g/L S and 31.5 g/L As(V) containing 28.3 g/L Cl(-1)) could be treated by precipitating ferrous arsenate to remove the bulk of the arsenic followed by a polishing treatment with final arsenic removal by co-precipitation with ferrihydrite. We simultaneously evaluated the influence of amount of ferrous added, type of reagent, ferrous chloride or ferrous sulfate, time, and pH in the stage one treatment **(Twidwell 2015; Twidwell and McCloskey 2009, 2010)**. Ferrous Arsenate can be effectively precipitated if the solution potential (Eh) and pH are chosen within the regions noted on Figures 58 and 59.

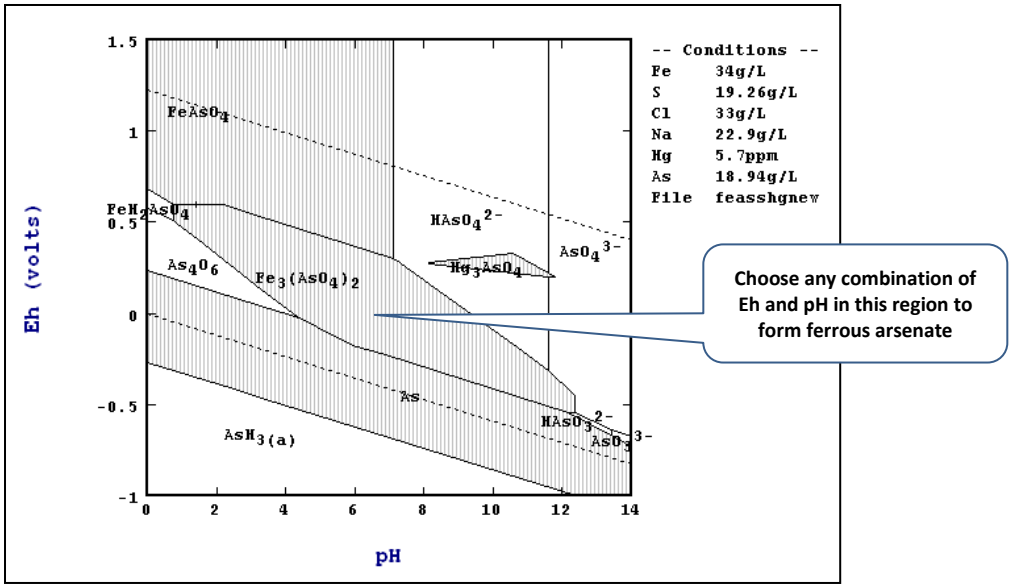


Figure 59. An illustration of the distribution of arsenic species (at 500 µg/L) as a function of solution potential and pH (Eh/pH) where ferrous sulfate is added at 1.6 times the stoichiometric requirement for the amount of arsenic present to form ferrous arsenate.
(Shaded regions denote the presence of arsenic bearing solids)

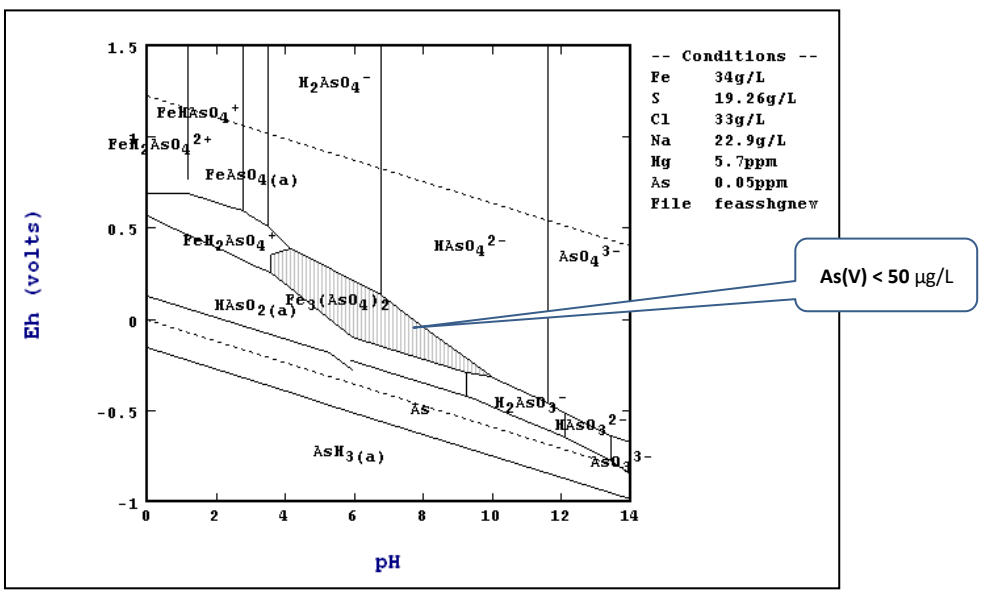


Figure 60. An illustration of the distribution of arsenic species (at 50 µg/L) as a function of solution potential and pH (Eh/pH) where ferrous sulfate is added at 1.6 times the stoichiometric requirement for the amount of initial arsenic present.
(The diagram illustrates the regions of stability when the arsenic concentration is reduced to 50 µg/L. Shaded regions denote the presence of the ferrous arsenate solid).

The bulk of the arsenic can be readily lowered in the first stage treatment to less than 500 mg/L by choosing combinations of pH, ferrous loading, and time conditions. Figure 61 is presented to illustrate that statement. Constraints can be placed on the studied variables and optimization can be investigated for those constraints. An example is presented in Figure 62. The example answers the question: What are the best conditions to achieve the minimum arsenic concentration for the condition ranges-ferrous

loading ratio 0.2 to 1.0 (based on the stoichiometric requirement for the formation of ferrous arsenate); pH 6 to 9; and time 20 to 60 minutes? The results are a ferrous loading ratio of 0.8, at a pH of 7.2, for a time of 60 minutes achieves a final arsenic concentration of 340 mg/L.

An attractive feature of this treatment scenario is that a wide range of processing conditions can be used to obtain appropriate arsenic removal. This means that process upsets can be handled without major changes in the effectiveness of arsenic removal.

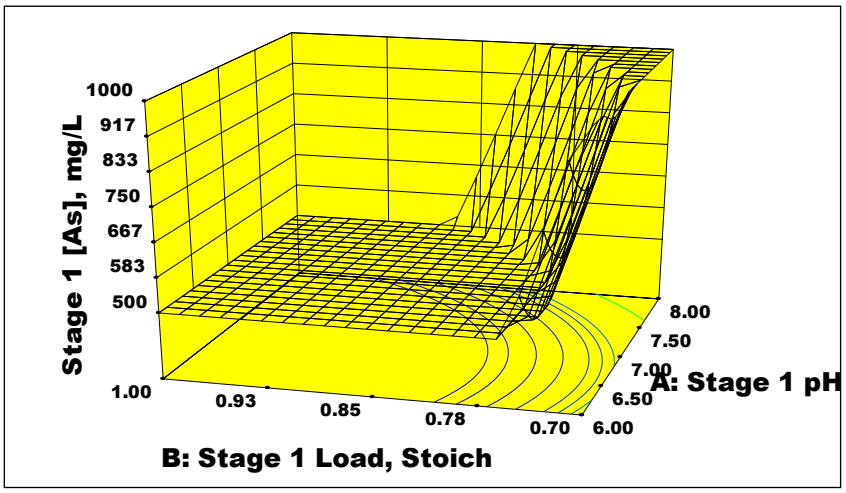


Figure 61. 3-Dimensional plot illustration of the final arsenic concentration achieved in Design Study One Stage 1 as a function of Stage 1 pH and stoichiometric requirement of ferrous to form ferrous arsenate for the initial input arsenic concentration of 12.1 g/L at 20 minutes. (A wide range of loading and pH combinations can be chosen to lower the arsenic concentration to < 1 g/L. For example, any combination of ferrous loading and pH in the flat portion of the diagram should be appropriate).

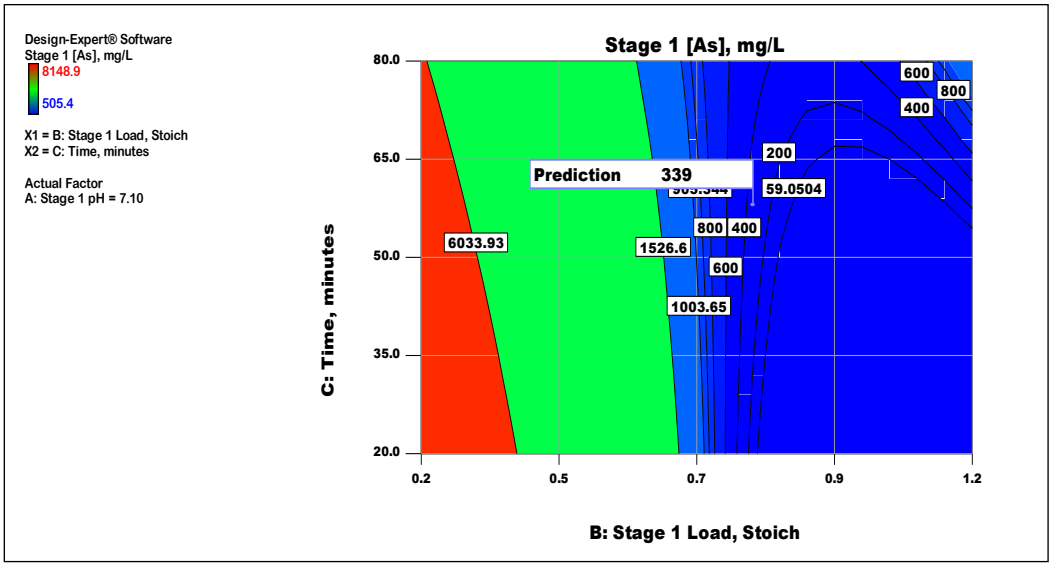


Figure 62. Best conditions to achieve the minimum arsenic concentration in stage 1 (This is an example to answer the question "what are the best conditions to achieve the minimum arsenic concentration for the variable ranges-loading ratio 0.2 to 1.0; pH 6 to 9; and time 20 to 60 minutes?" The projected values for the variables needed to achieve a minimum final arsenic

concentration of 340 mg/L are: a loading ratio of 0.8, at a pH of 7.1, for a time of 60 minutes).

MINERAL-LIKE ARSENIC COMPOUNDS

Twidwell and his graduate students conducted investigations for forming arsenate substitution in mineral compounds, i.e., arsenate incorporation into known environmentally stable mineral forms. This work was initially funded by the U.S. Bureau of Mines Waste Treatment Generic Center and later by the EPA MWTP.

Lead Arsenates/Phosphate Compounds

Comba [1987]; Comba et al. 1988; Twidwell et al. 1994] reported their results for the determination of the thermodynamic properties of lead chloro-arsenates and lead chloro-phosphate-arsenates and their long-term stability. Mimetite, $Pb_5(AsO_4)_3Cl$, readily forms when aqueous lead species are added to a solution containing arsenate and chloride. Comba investigated the solubility of this system and confirmed the free energy of formation at -625±2 kcal/mole. An example of Comba's solubility data is presented in Figure 63. The thermodynamic evaluation of the stability of mimetite to conversion by carbon dioxide in air to lead carbonate species predicts that the stability should be independent of storage time. It was confirmed that the compound is thermodynamically stable against forming lead carbonates when exposed to carbon dioxide in air, Figures 64 and 65. Long-term stability test work was conducted to experimentally validate this conclusion, see Figure 66. The conditions for the long-term tests were as follows: the mimetite solids were formed by treating a solution at a pH of 5.5 that contained 2.2 g/L As (stoichiometric addition of lead and two times the required stoichiometric amount of chloride was added) and then the solution/solid mixture was continuously sparged with air for a period of nine months. The results showed arsenic was not released above the projects analytical detection limit of 0.3 µg/L at pH levels above five.

Arsenate substituted lead chlorophosphate, i.e., polymorphite, was also formed by Comba and its solubility was determined. The relative solubilities for mimetite and arsenate-pyromorphite are compared in Figure 67. Note that the solubility of the arsenate-pyromorphite (phosphatian mimetite) is approximately 20 times lower than mimetite in the neutral pH range.

The advantages of removing arsenic as mimetite [$Pb_5(AsO_4)_3Cl$] or phosphatian mimetite [$Pb_5(As,PO_4)_3Cl$] are that the precipitation can be effectively performed at neutral pH and the solids formed are easily separated by conventional solid/liquid mineral processing equipment. The filterability is rapid and effective because the precipitated solids are small microspheres as shown in Figure 68. The disadvantages are that if an excess of reagent lead is used then subsequent treatment is required to lower the lead to acceptable levels.

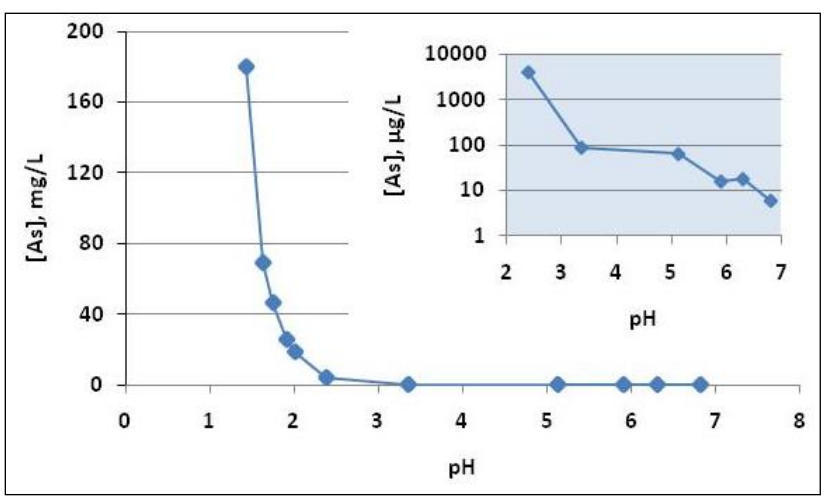


Figure 63. Experimental solubility of laboratory prepared Mimetite, $Pb_5(AsO_4)_3Cl$

(Comba 1987)

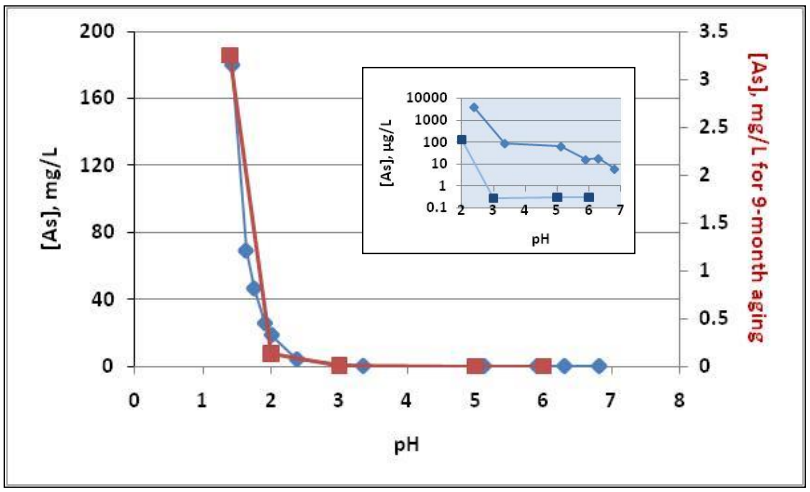


Figure 64. Laboratory Mimetite Arsenic solubility as a function of pH for solids formed at ambient temperature and aged for 9-months in air sparged aging reactors.

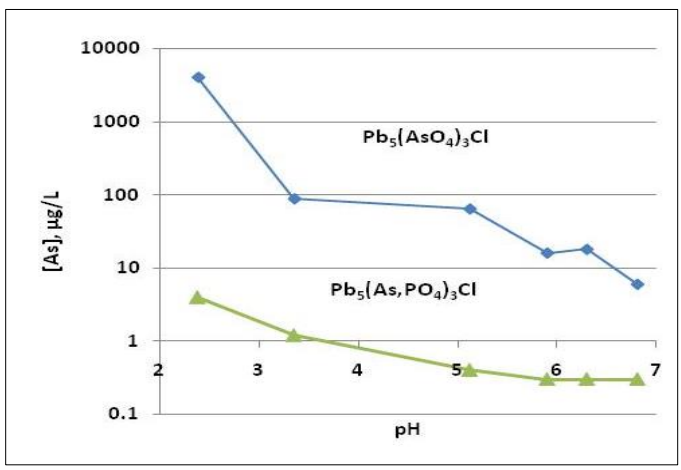


Figure 65. Laboratory Mimetite and Phosphatian Mimetite Arsenic Solubility as a function of pH. (The solubility of arsenate pyromorphite is approximately 20 times lower than Mimetite in the neutral pH range).

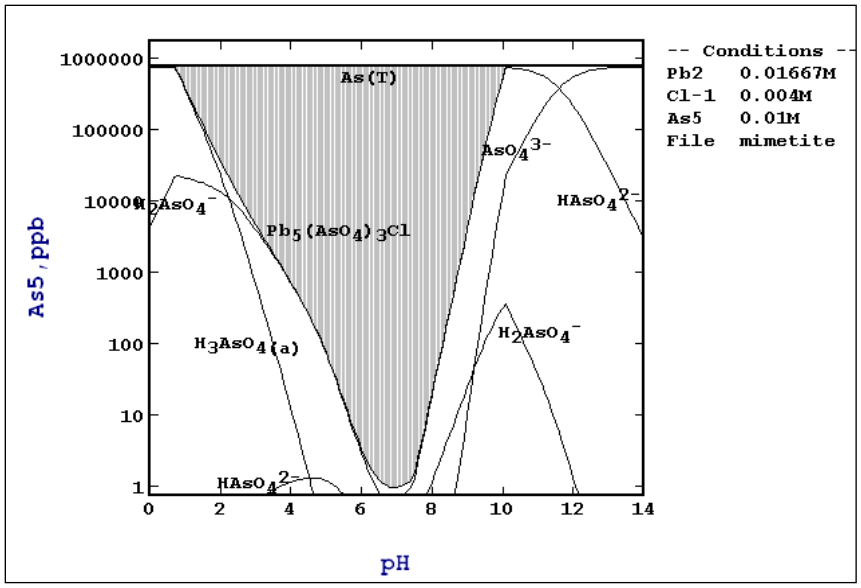


Figure 66. Modeled arsenic speciation for Mimetite precipitation as a function of pH. STABCAL [2009].

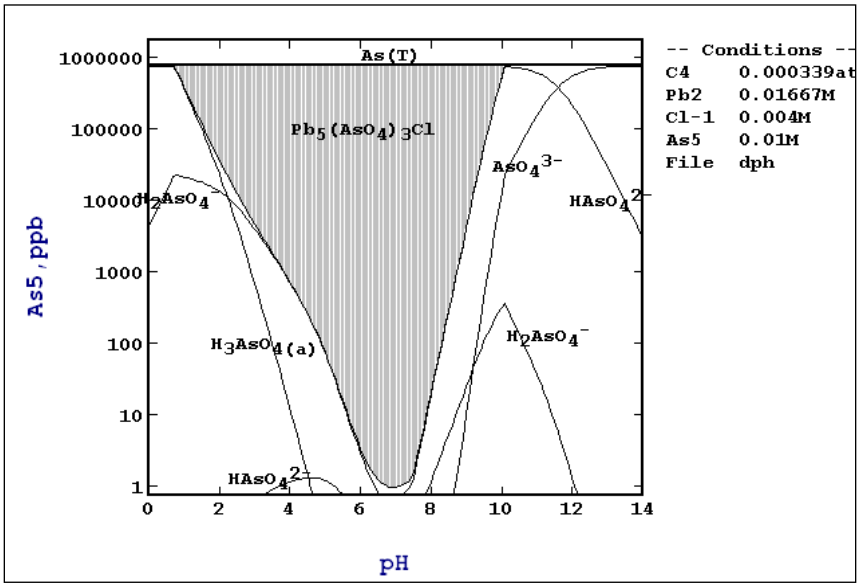


Figure 67. Modeled arsenic speciation for Mimetite stability in the presence of carbon dioxide (concentration as in air) as a function of pH. STABCAL [2009]. (Note the thermodynamic solubility of Mimetite is unaffected by the presence of carbon dioxide and, therefore, should be stable for long-term outdoor storage)

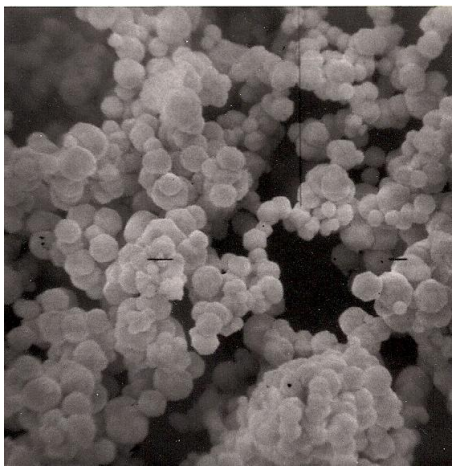


Figure 68. Photomicrograph for laboratory formed Mimetite. (Scale is 2000x)

Compound Formation and Stabilization of Copper Smelter Flue Dusts

Our first arsenic study was conducted in 1977-78 by **Mehta [1978]** who investigated the stabilization of Anaconda and other copper smelter flue dusts using lime/dust, ferric compounds/dust and copper smelting slag/dust mixtures by thermal roasting to fixate the arsenic. A portion of Mehta's results are summarized in Figures 69-72 and Table 6. The experimental design parameters were wt.% flue-dust/(lime or slag), time, and temperature. The measured responses were amount of arsenic retained in the roasted solids and the arsenic content of the solids. Table 11 is presented to illustrate one of many possible comparisons for stabilizing smelter flue dust using lime or copper smelting slag. Lime roasting results in higher retention and arsenic content in the roasted product at 25% lime/75% flue dust than did the 25% slag/75% flue dust. However, recycling the slag/flue dust product to the smelting furnace may be more desirable so that the composition of the smelting furnace slag would not be impacted by the lime content.

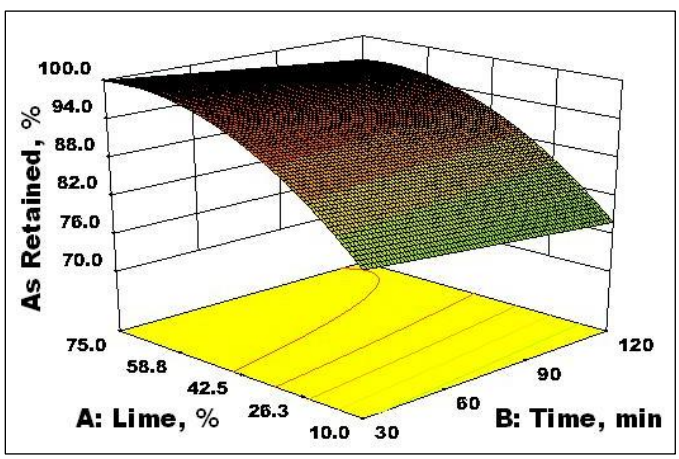


Figure 69. 3-D illustration of the influence of amount of lime and time on the retention of arsenic in the roasted flue dust/lime solids (Initial flue dust contained 18% arsenic, 8.2 % copper, 12.75 iron, 5.9% zinc. The retention was independent of roast temperature between 200 and 400°C).

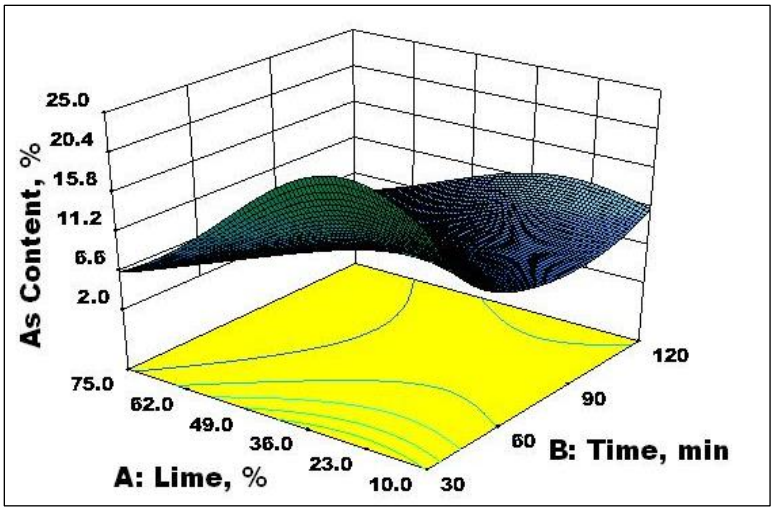


Figure 70. 3-D illustration of the influence of amount of lime and time on the concentration of arsenic in the roasted flue dust/lime solids (Initial flue dust contained 18% arsenic, 8.2 % copper, 12.75 iron, 5.9% zinc. The arsenic content was independent of roast temperature between 200 and 400$^{o)}$C.

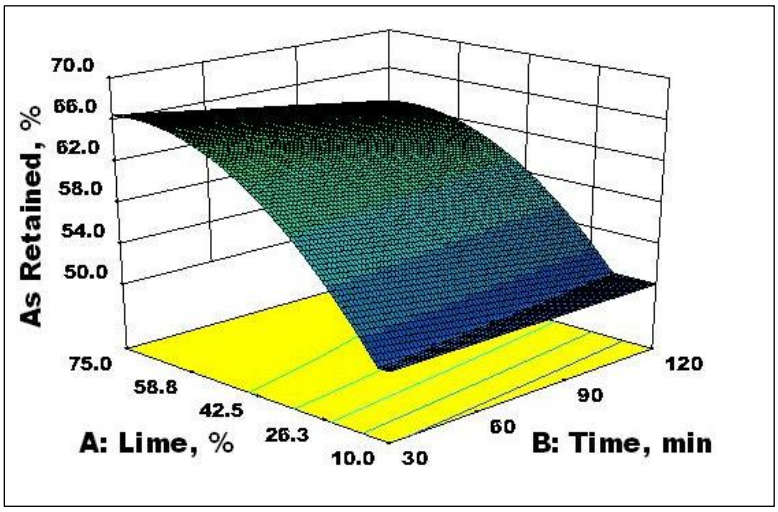


Figure 71. 3-D illustration of the influence of amount of lime and time on the retention of arsenic in the roasted dust/slag solids (Initial flue dust contained 18% arsenic, 8.2 % copper, 12.75 iron, 5.9% zinc. The retention was independent of roast temperatures between 200 and 400°C).

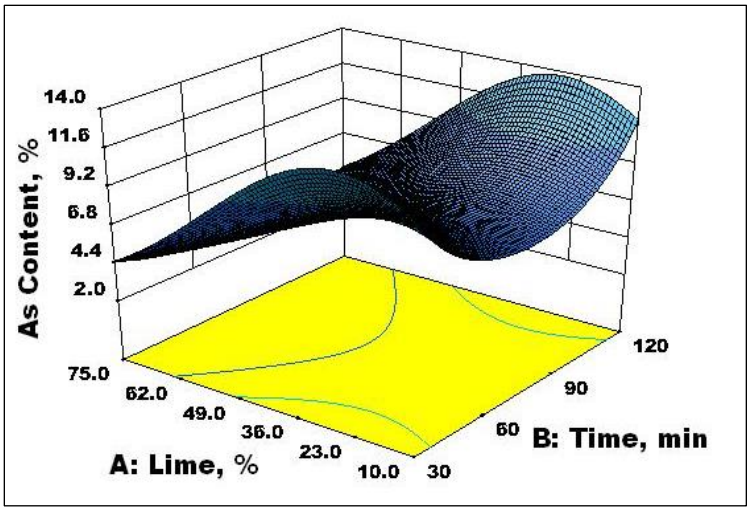


Figure 72. 3-D illustration of the influence of amount of lime and time on the concentration of arsenic in the roasted dust/slag solids (Initial flue dust contained 18% arsenic, 8.2 % copper, 12.7% iron, 5.9% zinc. The arsenic content was independent of roast temperatures between 200 and 400°C).

Table 11. Comparison between Flue Dust/Lime and Flue Dust/Slag retention of Arsenic in roasted products

Factor	Level	Low Level	High Level
Flue Dust, %	24.9	10	75
Time, min	30	30	120
Temp, C	200	200	400
Additive	Slag or Lime, %		
Result, %	Lime	Slag	
As Retained, %	90.3±2.1	53.3±2.9	
As Content, %	24.2±4.5	13.7±2.6	

(The STATEASE Design Expert software can be used to investigate the effect of changing the input parameters on the retention and content values).

The ARCO company closed their Anaconda copper smelter in Anaconda Montana in 1982 and disposed of over 400,000 tons of arsenic contaminated flue dust by encapsulating it in lime/cement mixtures (without roasting) and placing it into a permanent "C" class repository near the former smelter site **(Dames and Moore 1991).**

Twidwell and Chatwin [1989] conducted a treatability study at the Whitmoyer superfund site for stabilization of calcium and iron arsenate contaminated soils and demonstrated that cement encapsulation was not appropriate unless the cement/soil mixtures were roasted prior to disposal. The roast/cement stabilization was chosen as the alternative for clean-up.

Compound Formation and Encapsulation

Copper smelter flue dust can contain up to thirty percent arsenic primarily present as arsenic oxide. **Mehta [1978]** investigated several encapsulating materials for containing untreated flue dust, e.g., clays, cements and concretes. He found significant arsenic release from these matrices when exposed to water for short periods. He then investigated the fixation of arsenic using hydrated lime and ferric hydroxide to form calcium and ferric arsenates. The arsenates were then encapsulated in clays and cements. The

products were leached tested (L/S=100 wt ratio) as a function of time up to seven years **[Twidwell 1983, Twidwell and Mehta 1985]**. Initially the arsenate/clay mixtures showed only limited release of arsenic but showed appreciable release during the seven-year leach period. A secondary approach was to form non-volatile arsenates by roasting at 400°C, then dissolving the products in molten copper smelting slags at normal slag tapping temperature (1250°C). The slags were doped with arsenic up to approximately twelve percent. The results for leach testing as a function of pH and particle size for approximately five years are presented in Table 12. Samples of arsenic doped slag was encapsulation in concrete and leached at pH seven for seven years. The results showed less than ten parts per billion for the copper smelter slag, Table 13.

Table 12. Influence of pH on Arsenic extraction from Arsenic doped slag (5 yrs)

As, % in Slag	Arsenic Extracted, mg/L					
	pH 5			pH 7		
	¼ inch	-8/+10 mesh	-60/+100	¼ inch	-8/+10	-60/+100
Copper Reverberatory Slag						
11.8	<1	1	10	<1	1	<1
12.0	1	5	10	<1	<1	<1
Lead Blast Furnace						
13.6	8	-	19	4	6	8

(Liquid/Solid weight ratio=100, pH maintained at the above levels for over 2300 hrs and then allowed to seek its natural level)

Table 13. Influence of long-term leaching on Arsenic extraction from Arsenic doped slag

As in Mixture, %	Aggregate Size	Extraction, µg/L (%) after 7 years
1	¼-inch	<DL (<0.002)
3	¼-inch	<DL (<0.001)
10	¼-inch	3 (<0.001)
10	¼-inch	6 (<0.001)
2	-8/+10 mesh	<DL (<0.001)
2	-8/+10 mesh	<DL (<0.001)
5	-8/+10 mesh	<DL (<0.001)
1	-60/+100 mesh	7 (<0.007)
2	-60/+100 mesh	<DL (<0.001)

(Concrete mixture contained 20% slag)

Dissolution of Stabilized Flue Dust and Smelter By-Products in Copper Reverberatory Slag

The encapsulation work was continued by **Downey (1982), Blaskovich (1982),** and **Roset (1998)**. They investigated the possibility of encapsulating arsenic in copper smelter slag by forming calcium arsenate or ferric arsenate and subsequently dissolving the material in molten Reverberatory or Electric Furnace slag during the smelting process, i.e., raising the arsenic content in the molten slag by addition of calcium or iron arsenate to the high temperature matte/slag smelting operation. The goal for these studies was to evaluate the recycle of roasted flue dust to the smelting reactors to recover additional copper and to increase the content of arsenic in the slag phase. The final solidified slag would then be the long-term repository for arsenic and the recovery of additional copper would help offset the cost of smelter by-product wastes. Downey investigated the recycle of flue dust to a matte/slag reactor, Roset studied the recycle of lime-roasted flue dust to a matte/slag reactor, and Blaskovich studied the recycle of lime roast/lead blast furnace smelter speiss to a matte/slag reactor.

The concept of the Downey study was to add lime to the flue dust to form a relatively non-volatile arsenic compound (calcium arsenate) and to recover copper from recycled flue dust**.** The initial arsenic

concentration in the flue dust was 3.2%, the copper content was17.5%. Most smelters stabilize and discard their flue dust and thereby lose the metal values.

Two-level factorial experimental design conditions were followed to investigate the influence of several variables: time, temperature, matte grade, dust/lime weight ratio, and oxygen pressure. The results are briefly discussed here and are illustrated in Figures 73-76.

- Appreciable copper can be recovered by recycling flue dust, but the dust must be pretreated to form arsenate compounds and for agglomeration so that the dust doesn't blow out of the reactor.
- It is known that recycling the flue dust results in appreciable volatilization of the arsenic. However, if the dust is pretreated to form non-volatile calcium or iron arsenate, pelletized, and then fed into the reactor the arsenic behaves differently. This study has shown that the behavior of arsenic is a complex function of initial matte grade and the dust/lime weight ratio as shown in Figure 61.
- The final conclusion of this and the Downey and Blaskovich studies is that recycling lime stabilized flue dust or speiss to an operating reverberatory, electric, or flash furnace will result in recovery of the copper from the flue dust but the arsenic content of the slag will not be increased and therefore the slag will not offer a way to dispose of the systems arsenic. The reason for the inability to increase the arsenic content in the slag is that copper smelting slag contains sufficient ferrous species to reduce the arsenate to volatile arsenic oxide (As_2O_3).
- Additional test work has shown that dust/lime roasted products can be added to the molten slag after exiting the smelting reactor to raise the arsenic content of the slag. However, adoption of this approach would require two additional unit operations to the smelting circuit, i.e., a lime/dust preroast and the addition of this material to ladles of tapped slag. However, most smelting operations water granulate their slag as it exits the smelting furnace and tapping into ladles is unlikely. Also, the copper content in the flue dust would not be recovered.

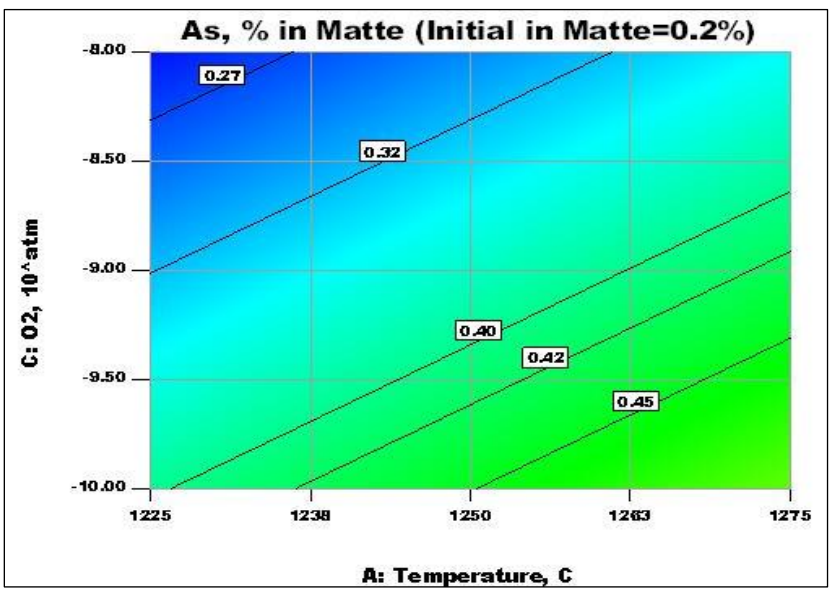


Figure 73. Illustration of the arsenic content in the matte phase as a function of oxygen partial pressure and temperature. Constants: initial copper in the matte = 50%, dust/lime weight ratio=9, time=10 hrs. (The desire would be to distribute as little arsenic as possible to the matte phase, and to do this lower temperature and higher oxygen partial pressures are preferred. These conditions also cause the largest amount of copper to distribute from the flue dust to the matte phase)

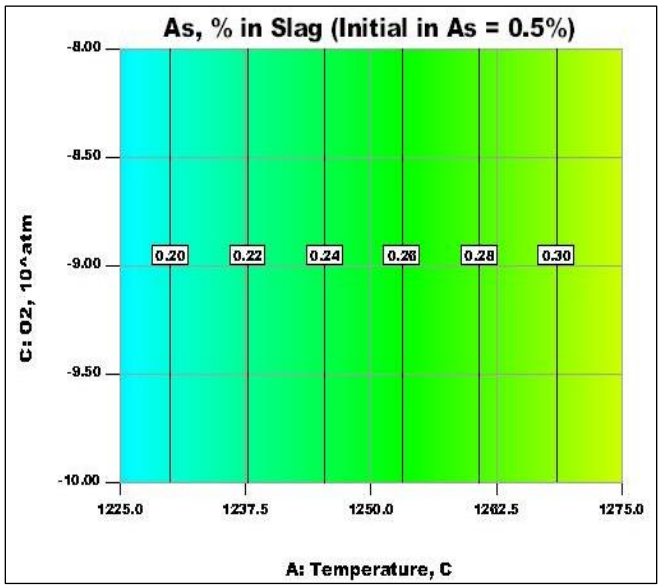


Figure 74. Illustration of the arsenic content in the slag phase as a function of oxygen partial pressure and temperature. Constants: initial copper in the matte=50%, dust/lime weight ratio=9, time=10 hrs

The desire would be to distribute as much arsenic as possible to the slag phase. However, all temperatures and oxygen pressures show a decrease in arsenic content compared to the initial arsenic in the input slag. The reason for this is discussed in the referenced paper.

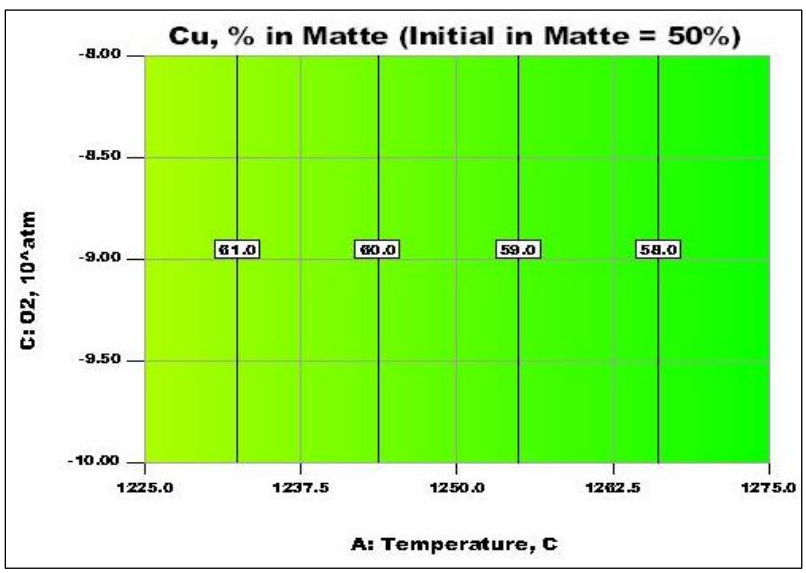


Figure 75. Illustration of the copper content in the matte phase as a function of oxygen partial pressure and temperature. Constants: initial copper in the matte = 50%, dust/lime weight ratio=9, time=10 hrs. (As noted in Figure 73 lower temperatures show the presence of less arsenic in the matte phase and this figure illustrates a major increase in the matte grade at all temperatures but especially at lower temperatures).

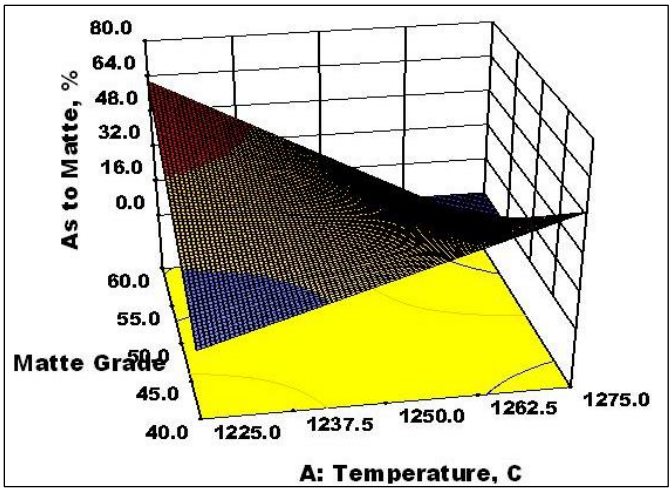


Figure 76. Illustration of the distribution of arsenic to the matte phase as a function of initial matte grade and temperature. Constants: dust/lime weight ratio=9, time=10 hrs. (As noted in the figure the distribution of arsenic to the matte phase is a complex function of the two variables).

ELECTROCHEMICIAL REDUCTION of ARSENATE and SELENATE

The reduction of dissolved oxyanions of arsenic and selenium from mine wastewater utilizing elemental iron cementation technology has been studied on a laboratory scale at Montana Tech and on a pilot scale at MSE-Technology Applications as a water treatment process potentially capable of removing dissolved arsenic and selenium to <10 µg/L and <50 µg/L, respectively. Laboratory and pilot scale studies using elemental iron have demonstrated effective removal of dissolved arsenic and selenium. Enhanced oxyanion reduction rates have been demonstrated when galvanically coupled iron/copper and iron/nickel are utilized. The laboratory and pilot scale results are presented and discussed below.

Plessas (1992) began our reductive cementation investigations for removing arsenic and selenium from wastewaters. She conducted experiments using shredded iron scrap in columns. Additional studies have been performed by **Dahlgren (2000), Hadden (2002), McCloskey et al. (2008, 2010), Park et al. (2006)** and the results are summarized in the EPA MWTP reports: **MWTP-106 1999; MWTP-191 2001; MWTP-213 2004.**

The Concept

Many solution species can be effectively removed from mine water by electrochemical reduction of aqueous species to solid elemental species on the surface of a metal (referred to as cementation). Aqueous solution species can be reduced to the solid elemental state on an iron surface, e.g., arsenic (referenced above), antimony **(McCloskey 2003)**, copper **(Davenport et al., 2002), mercury (Rockandel and Twidwell 1993, 1994]**, selenium (referenced above), can be reduced to the solid elemental state on an iron surface. Presently, the industrial use of cementation has been limited to copper and mercury recovery **[Twidwell and Thompson 2001].** The basis for the technology is that elemental iron controls the solution potential for the reduction of selenium or arsenic species to their elemental (or compound) form on the surface of iron. An example is presented in Figure 77 for selenium.

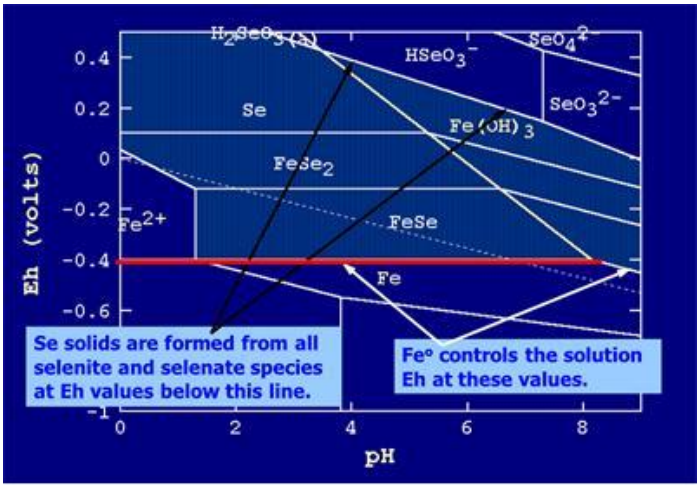


Figure 77. Eh/pH diagram illustrating the conditions to reduce selenium aqueous species to either elemental selenium or selenium compound solids on an iron surface.

Experimental Results for the Iron/Selenium and Iron/Arsenic Test Work

Dahlgren [2000] demonstrated experimental conditions to successfully lower selenium and arsenic concentrations by cementation using elemental iron as the reductant. The treatment system used in the following studies consisted of contacting the water to be treatment in an agitated reactor containing 100 g/L of elemental iron (-20 mesh). Laboratory test work was conducted in a batch reactor. In later pilot scale test work the design was such that the iron was retained in an agitation reactor. The effectiveness of the treatment system for removing of selenium is illustrated in Figures 78-85 and for arsenic in Figures 86-88.

Electrochemical Characterization of Iron and Galvanically Coupled Surfaces

Selenate/Selenite Reduction

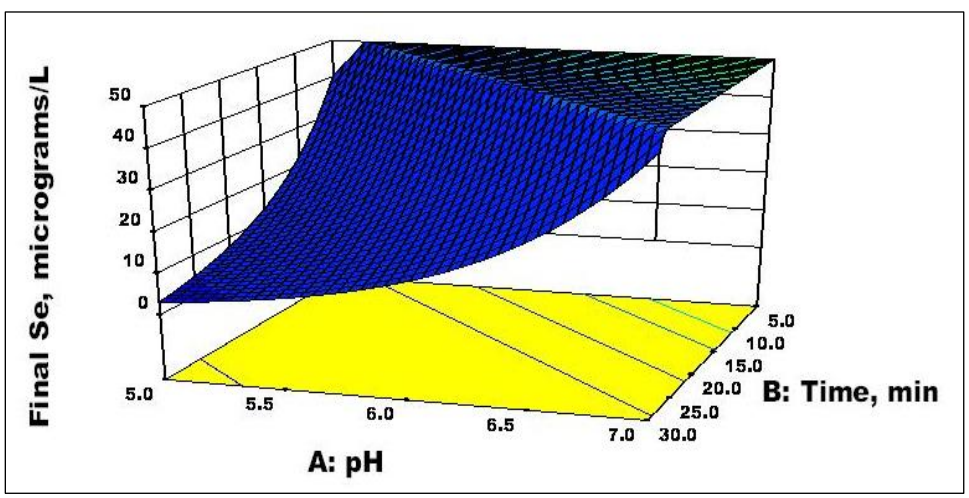


Figure 78. 3-D illustration of the influence of pH and time on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [Se] = 2 mg/L. (Also, see the contour plot in the next figure).

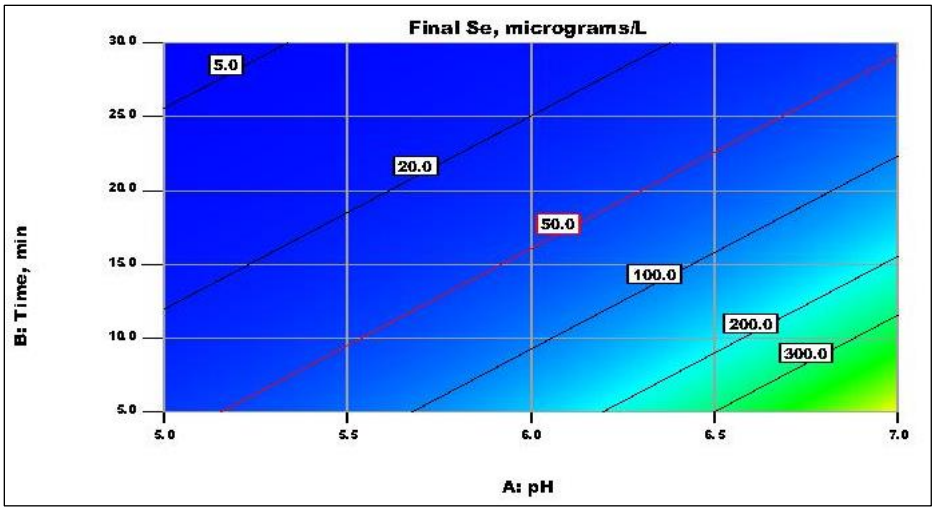


Figure 79. Contour illustration of the influence of pH and time on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [Se] = 2 mg/L (Combinations of pH and time above the 50 µg/L contour will achieve project goal concentration).

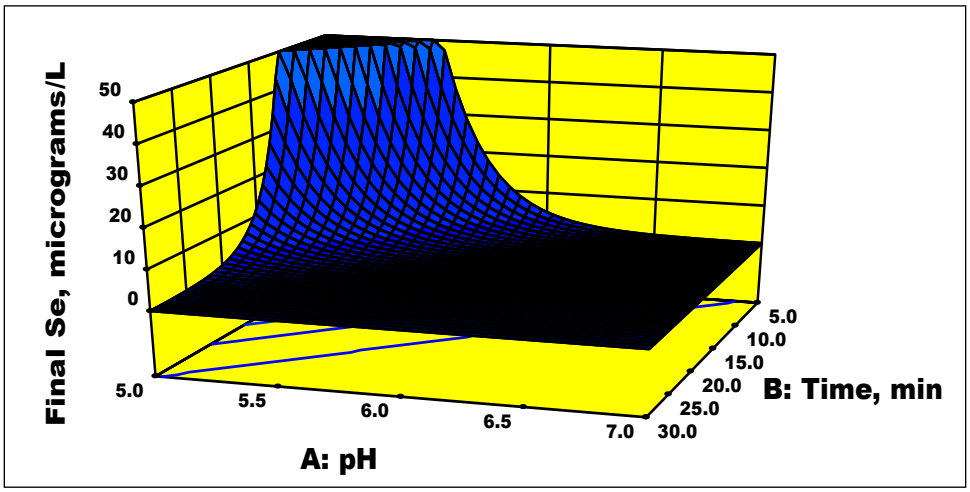


Figure 80. 3-D illustration of the Influence of pH and time on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [Se] = 10 mg/L (Also, see the contour plot in the following figure).

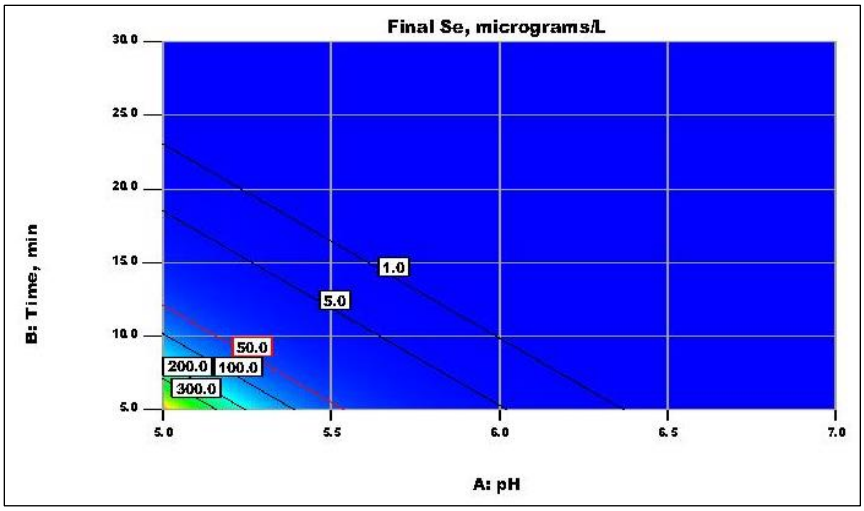


Figure 81. Contour illustration of the Influence of pH and time on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [Se] = 10 mg/L

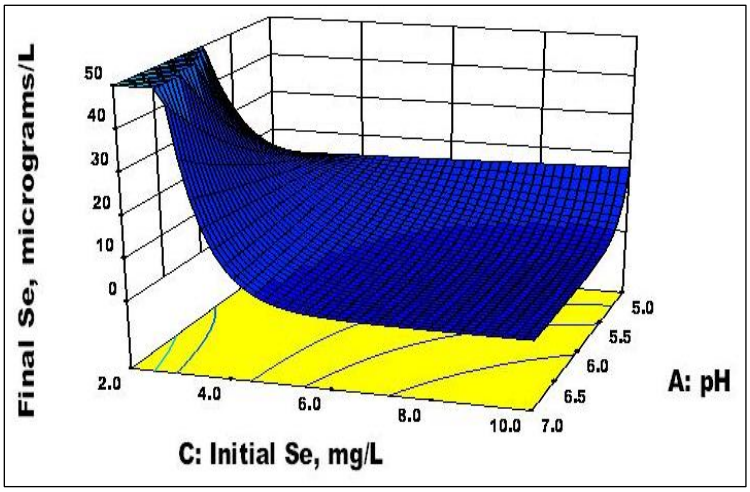


Figure 82. Illustration of the Influence of pH and initial selenium concentration on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh iron, ambient temperature, 15-minute reacting time.

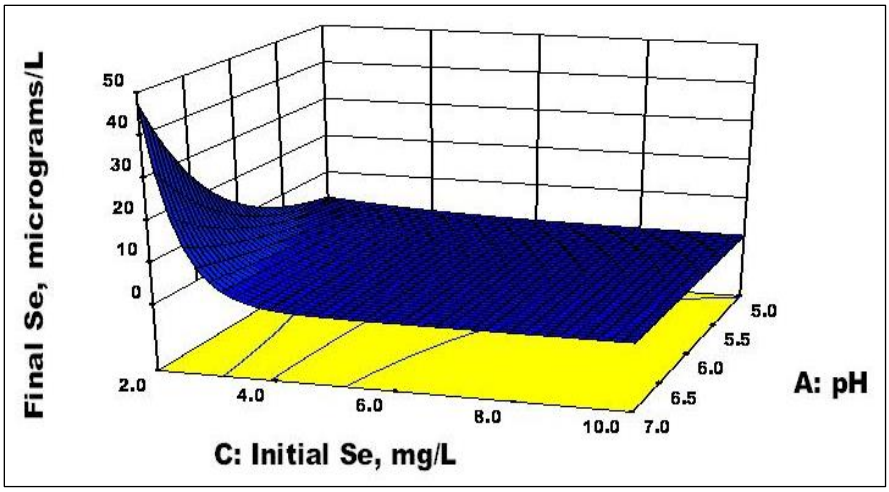


Figure 83. Illustration of the Influence of pH and initial selenium on the removal of selenium in an agitated reactor containing 100 g/L elemental iron, <20 mesh iron, ambient temperature, 30-minute reacting time

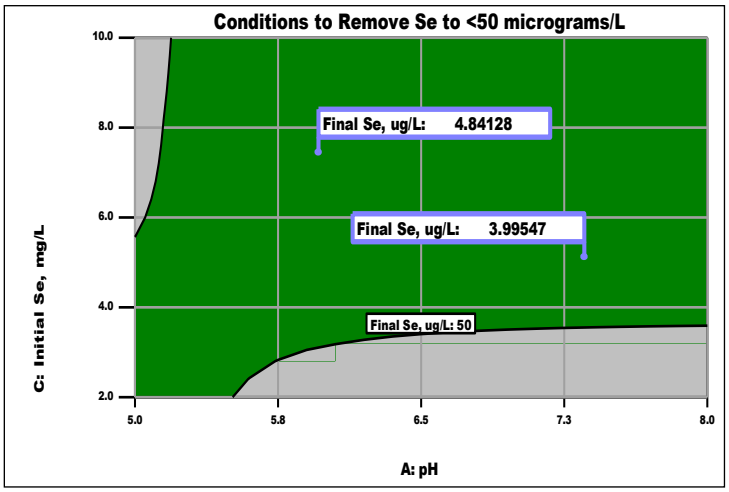


Figure 84. Overlay illustration of the influence of pH and initial selenium the removal of selenium to <50 µg/L in an agitated reactor containing 100 g/L elemental iron,<20 mesh iron, ambient temperature, 10-minute reacting time. (Combinations of initial selenium concentration and pH selected in the dark region will allow the final selenium to be <50 µg/L. Note the example flags presented in the dark region).

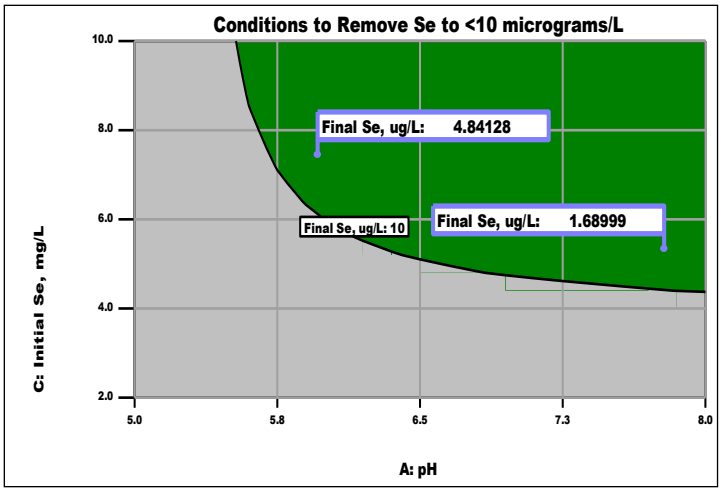


Figure 85. Overlay illustration of the Influence of pH and initial selenium on the removal of selenium to <10 µg/L in an agitated reactor containing 100 g/L elemental iron, <20 mesh iron, ambient temperature, 30-minute reacting time. (Combinations of initial selenium concentration and pH selected in the dark region will allow the final selenium to be <10 µg/L. Note the example flags presented in the dark region).

Demonstration of Selenium Removal by Electrochemical Reduction

The Dahlgren laboratory study was followed by an EPA MWTP sponsored demonstration study at the Kennecott Garfield Smelting facility **(MWTP-191 2001**. Final Report-Selenium treatment/removal alternatives demonstration project , Activity III, Project 20, EPA/600/R-01/077. Pilot Scale Demonstration).

Three projects were selected for field demonstration during this project: Ferrihydrite Precipitation/Selenium Adsorption (considered the baseline technology); Catalyzed Cementation (developed by **Twidwell, McCloskey, Dahlgren, and Hadden MWTP-191 2001)**; and Biological Selenium Reduction (BSeRTM). The report results were *"All three of the processes were able to achieve the target level for selenium in effluent samples under optimized condition".* The selenium target level was 50 µg/L. Test results are summarized in Table 14.

The conclusions for the demonstration are paraphrased and quoted here:

> The baseline FH/Se adsorption *"can be optimized to achieve the desired level of selenium removal; however, reagent usage is excessive and cost prohibitive. Although this technology is considered the BDAT by EPA, it would not be feasible to utilize this technology to treat Garfield Wetlands-Kessler Springs water*". Also, *"filter-cake samples did not pass TCLP for selenium".*
>
> *"The catalyzed cementation technology has also produced promising, albeit, erratic results. Additional testing of this process is necessary. " The recent work of* ***Dahlgren (2001)*** *and the continuation work by* ***Dr. Twidwell (2001****) has shown that iron packed columns are very effective for selenium removal".*
>
> BSeRTM was not tested in the field, however it was studied in laboratory bench scale conditions*. "More research is necessary to gain a better understanding of what is occurring in the immobilization of the enzymes and the linking of electron donors within the various immobilization techniques. If the enzyme matrix can be demonstrated to be stable for 6 to 9 months, the process may be an economical treatment alterative".*

Table 14. Summary of results comparing the different selenium removal technologies

Table ES-1. Demonstration results summary.

Ferrihydrite Adsorption Results

Treatment Condition	Mean Selenium Effluent Concentration ±Standard Deviation (n = sample size)	Minimum Selenium Concentration
Low iron (~1400 mg/L iron)	304 µg/L ±69 (n = 27)	115 µg/L
Medium iron (~3000 mg/L iron)	201 µg/L ±103 (n = 13)	42 µg/L (at midpoint of process)
High iron (~4800 mg/L iron)	90 µg/L ±28 (n = 5)	35 µg/L (at midpoint of process)
Ferrous/ferric (~1200 mg/L ferrous/1200 mg/L ferric iron)	563 µg/L ±280 (n = 5)	409 µg/L
Recycle Sludge (~2340 to 13,290 mg/L iron)	387 µg/L ±58 (n = 12)	77 µg/L

Catalyzed Cementation Results

Treatment Condition	Mean Selenium Effluent Concentration (µg/L) ±Standard Deviation (n = sample size)	Minimum Selenium Effluent Concentration (µg/L)
Catalyzed Cementation	834 µg/L ±204 (n = 42)	193 µg/L
Catalyzed Cementation with Increased Oxidation/Decreased pH in the reactor tank	35 µg/L (n = 2)	26 µg/L
Additional Testing of Catalyzed Cementation at MSE	3 µg/L[1] ±4.4 (n = 5)	<1 µg/L

BSeR™ Process Results

Residence Time	Mean Selenium Effluent Concentration (µg/L)[2] ± Standard Deviation (n - sample size)	Minimum Selenium Effluent Concentration (µg/L)
12 hrs (Series 1)	8.8 µg/L ±10.2 (n = 17)	< 2 µg/L
11 hr (Series 2)	4.9 µg/L ±4.9 (n = 16)	< 2 µg/L
8 hr (Series 3)	< 2 µg/L ±2.6 (n = 12)	< 2 µg/L
5.5 hr (Series 2)	< 2 µgL ±2.1 (n = 26)	< 2 µg/L

Arsenate Reduction

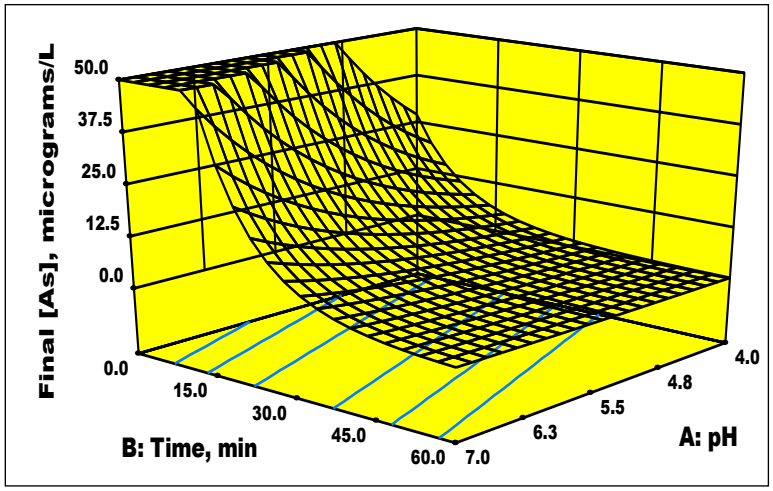


Figure 86. 3-D illustration of the influence of pH and time on the removal of arsenic in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [As] = 2 mg/L. (Also, see the following contour plot).

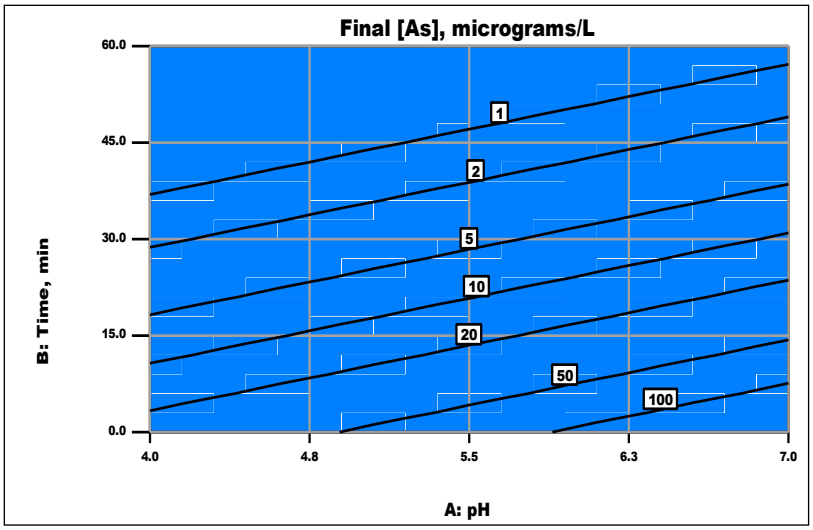


Figure 87. Contour illustration of the influence of pH and time on the removal of arsenic in an agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [As] = 2 mg/L. (Combinations of pH and time above the 10 µg/L contour will achieve project goal concentration).

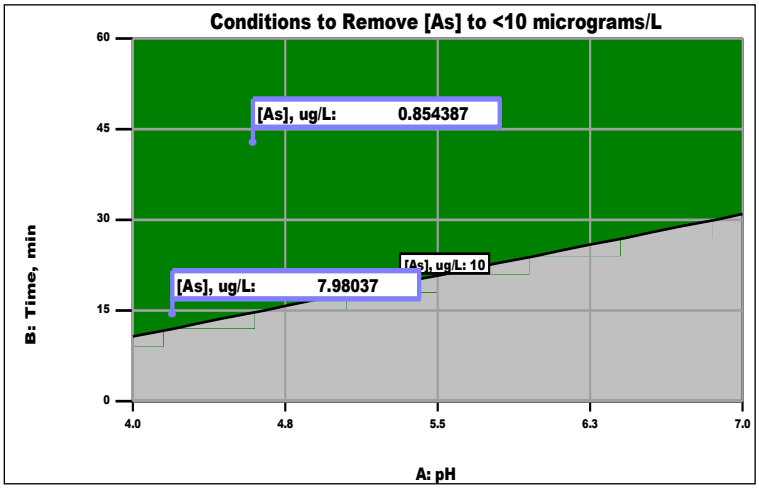


Figure 88. Overlay illustration of the influence of pH and time on the removal of arsenic to <10 µg/L in an agitated reactor containing 100 g/L elemental iron, <20 mesh iron, ambient temperature, 10-minute reacting time. (Combinations of reaction time and pH selected in the dark region will allow the final arsenic to be <10 µg/L. Note the example flags presented in the dark region).

Iron and Galvanic Couples for Selenium/Arsenic Removal

The work of **Dahlgren (2000)** and **Hadden (2002)** shows that the rate of reduction of arsenic (arsenate, arsenite) and selenium (selenate, selenite) can be increased dramatically by using galvanically coupled substrates (instead of pure iron). Galvanically coupled substrates provide greatly enhanced active metal dissolution rates. The enhanced metal dissolution rates (called anodic dissolution) are accompanied by the production of electrons in the substrate (iron). The available electrons in the substrate metal (iron) must be discharged at cathodic sites on the more noble metal surface. The consumption of electrons is characterized as reduction reactions, i.e., reduction of aqueous species in the solution phase to the elemental state on the more noble cathodic surface. Therefore, if the metal dissolution rate is enhanced

increased) then the reduction rate of oxyanions (arsenic and selenium) will also be increased. A cartoon illustration of this technique is presented in Figure 89.

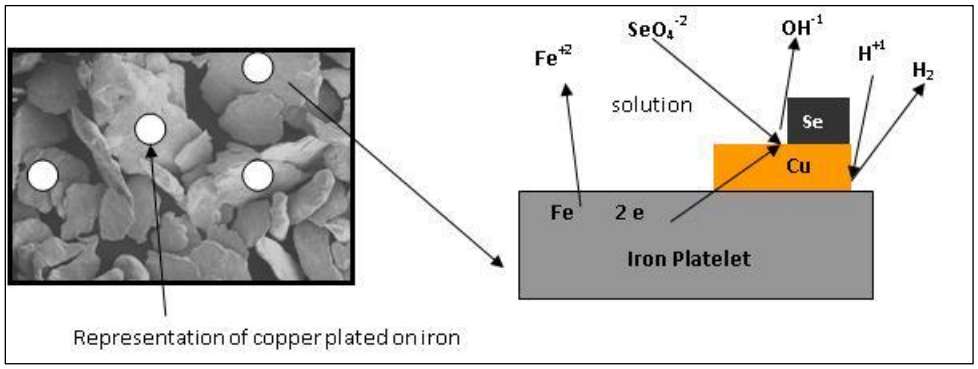


Figure 89. Illustration of the anodic dissolution of iron and the reduction of selenate to selenium on a copper cathodic surface.

Two major experimental studies were conducted by Hadden, i.e., electrochemical characterization of iron and metal coupled surfaces using electrochemical potentiostat measurements (Figure 90) and application of iron and galvanic couples for selenium/arsenic removal from synthetic and real solutions using a kettle reaction system (Figure 91). The conclusions drawn from each of the major studies are briefly presented below.

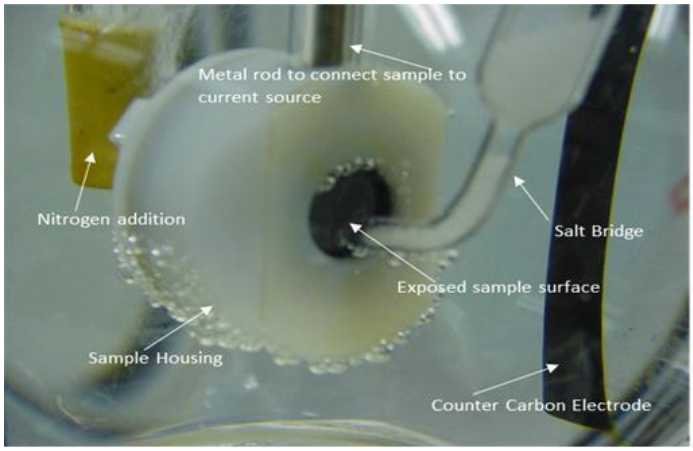


Figure 90. Interior parts for the potentiostat measurement system

Electrochemical Characteristics of Iron and Galvanically Coupled Surfaces

Selenate-The **conclusions** drawn from the electrochemical studies include:

- The selenate reduction reaction proceeds rapidly on an iron substrate.
- The selenate reduction reaction rate is enhanced by using galvanically coupling. Coupling of iron with copper approximately doubles the selenate reduction rate (for equal surface areas of iron and copper in the presence of 2 mg/L Se at pH 7). Coupling of iron with nickel increases the selenate reduction rate by a factor of approximately 25 (for equal surface areas of iron and nickel in the presence of 2 mg/L Se at pH 7). Also, see Table 15.

Arsenate-The **conclusions** drawn from the electrochemical studies include:

- The arsenate reduction reaction proceeds rapidly on an iron substrate.
- The hydrogen ion reduction reaction rate is increased by using galvanically coupling. Coupling of iron with copper increases the hydrogen ion reduction rate by a factor of 18 times (for equal surface areas of iron and copper at pH ~7).

- The effect of the presence of arsenate in the Fe/Cu/As system is to decrease the rate of the hydrogen ion reduction reaction. This effect is opposite to the effect of the presence of arsenate in the Fe/As system, e.g., the presence of arsenate in the Fe/As system increased the overall rate. The reasons for the noted effect are presently unknown.

Table 15. Predicted rate of deposition of Selenium on Iron, Iron/Copper and Iron/Nickel substrates

System	$i_{o,\ selenate}$, amp/cm^2	Se deposited, mg/min	Time to remove 2 mg/L Se, min
Fe/Se	0.25E-06	0.15	13
Fe/Cu/Se	0.51E-06	0.31	6
Fe/Ni/Se	6.24E-06	3.73	0.5

The iron/metal galvanic couples contained equal surface areas (one centimeter diameter disks) exposure to the solution phase.

Application of Iron and Galvanic Couples for Selenium/Arsenic Removal

Kettle Reactor Test Work

Studies were conducted in kettle reactors (Figure 91) to further explore the cementation process on a laboratory scale. The tests were conducted to evaluate the variables: initial arsenic or selenium concentration, pH and the amount of copper used to form the galvanic coupled iron reductant. The results achieved in the kettle tests are illustrated in Figures 91-93.

Figure 91. Photograph of the kettle reactor experimental set-up

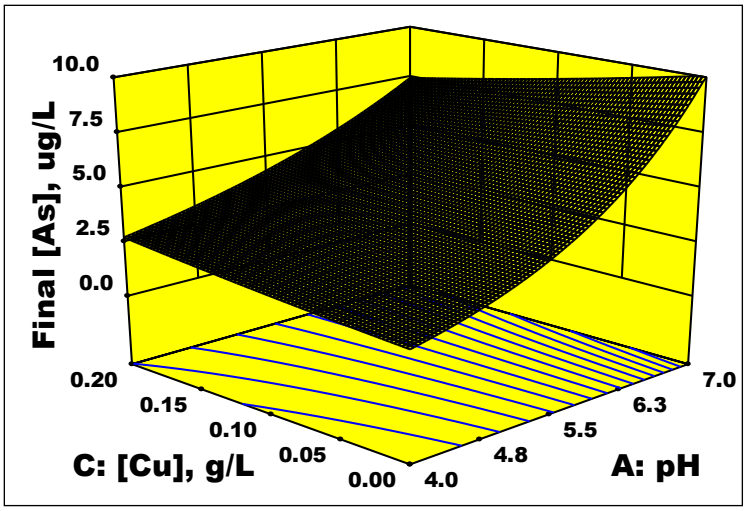


Figure 92. 3-D visualization of the influence of copper addition and pH on the removal of arsenic by elemental iron. Conditions: agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [As] = 2 mg/L, Time= 30 minutes.

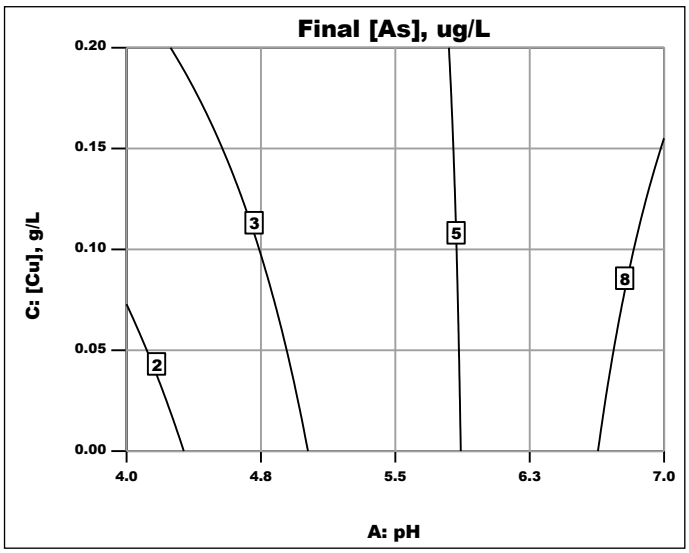


Figure 93. Contour visualization of the influence of copper addition and pH on the removal of arsenic by elemental iron. Conditions: agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [As] = 2 mg/L, Time = 30 minutes.

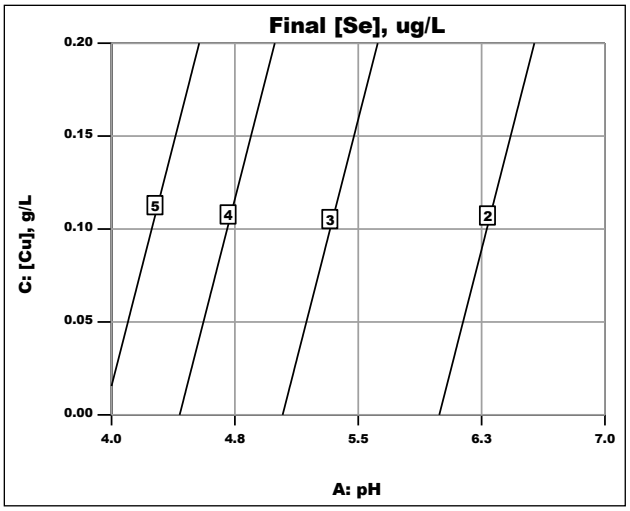


Figure 94. Contour visualization of the influence of copper addition and pH on the removal of selenium by elemental iron. Conditions: agitated reactor containing 100 g/L elemental iron, <20 mesh, ambient temperature, Initial [Se] = 2 mg/L, Time= 30 minutes.

Treatment of Industrial Waters

Several industrial waters were treated by Dahlgren [2000] in kettle reactor tests. The results are presented in Table 16.

Table 16. Elemental Iron treatment of Industrial waters for removing Arsenic and Selenium

Industrial Water Source	Contaminant Levels		Required Treatment Level, µg/L		Study Results, µg/L
	Se	As	As	Se	
Kennecott Effluent Drainage	1.7 mg/L	12 µg/L	50	50	Required final concentrations achieved: As <1 in 5 min; Se 5 in30 minutes
Hecla Heap Leach Discharge	55 µg/L	< D.L.	50	6	Required final Se not achieved: 20 in 30 minutes
Phelps Dodge Lined Storm Pond	1.30 mg/L	1.32 mg/L	50	130	Required final concentrations achieved: As 10 in 30min; Se 200 in 30 minutes
Phelps Dodge Combined Process	1.43 mg/L	14.4 mg/L	50	130	Required As not achieved, Se achieved : As 10mg/L in 30min; Se 120 in 30 minutes
San Joaquin Valley Agricultural Drainage	76 µg/L	11 µg/L	50		Required final concentration of Se achieved: <1 in30 minutes

Treatment conditions: 100 g iron, -20 mesh, ambient temperature.

Potential Advantages of the Metallic Reduction Technology

EPA has selected ferrihydrite (ferric oxyhydroxide) precipitation as the preferred Best Demonstrated Available Technology (BDAT) for removing arsenic and selenium oxyanions by adsorption from wastewater solutions. The problem with applying this technology to the removal of arsenic from wastewater is that it is only effective for those situations where the arsenic is present in its highest oxidation state, i.e., arsenate, AsO_4^{-3}. However, many waste waters contain an appreciable concentration of arsenite, i.e., AsO_3^{-3}. Those solutions that contain arsenite must be subjected to oxidation prior to performing the BDAT adsorption unit operation. The oxidation of arsenite to arsenate is difficult and expensive. The proposed alternative technology is effective regardless of the valence state of the dissolved arsenic specie.

A problem also exists with applying ferrihydrite technology to the removal of selenium from mine water, groundwater and wastewater. The problem is that these waters generally have the selenium present in the highest oxidation state, selenate, SeO_4^{-2}. Selenate is not effectively adsorbed by ferrihydrite; selenite, SeO_3^{-2}, is effectively adsorbed. Therefore, for effective removal of selenium from solutions the selenate must be reduced prior to ferrihydrite adsorption. The reduction of selenate to selenite is difficult using normal chemical reductant reagents. The proposed alternative technology possesses a much stronger driving force for reduction that does normal chemical reductants, and the galvanic coupled particulate surfaces drives the reduction of selenate or selenite to elemental selenium (therefore, subsequent adsorption on a ferrihydrite surface is unnecessary). The problem with using FH as an adsorbent for arsenic and selenium species is illustrated in Figure 95, i.e., the adsorbent is not very effective for arsenite or selenate.

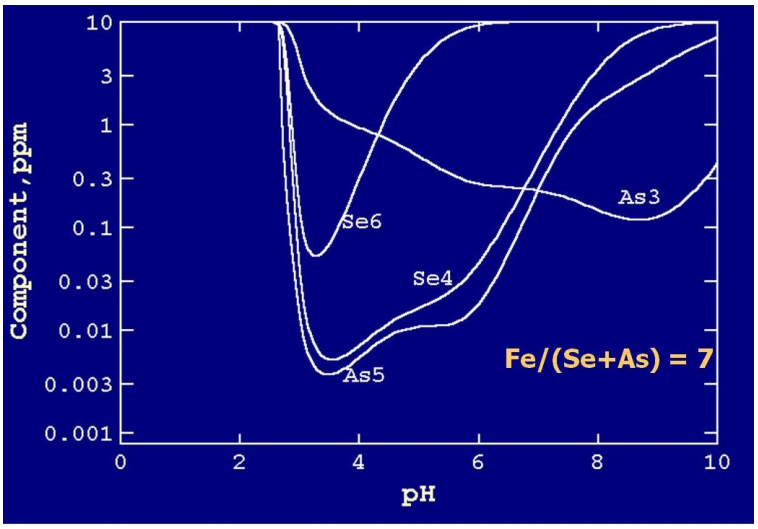


Figure 95. An illustration of the influence of pH and speciation of arsenic and selenium on the final specie concentrations.

The use of iron or galvanic couples as the reductant substrate appears to hold promise for future applications for removal of arsenic (iron alone appears to be appropriate) and selenium (both iron alone, iron/copper or iron/nickel couples are appropriate). The advantages of the proposed technology include: the process is independent of the impurity species valence state; it is not influenced by the presence of sulfate and other anions; heavy metals more noble than iron are coextracted; and, mininal solid waste products are produced.

FERRIHYDRITE/METALS AND ALUMINUM MODIFIED FERRIHYDRITE/METALS

Leonhard (2000)] and **Twidwell and Leonhard (2008)** continued the AMF/FH adsorption and aging studies for solutions containing dissolved metals. This study was conducted for the MWTP center [**MWTP-262 2005; MWTP-293 2008].**

Adsorption Studies

The basis for these studies was the desire to evaluate the concurrent removal of a suite of metals, e.g., cadmium, copper, nickel, and zinc by FH and AMF adsorbents. Two-level full-factorial Design of Experiments (DOE) studies were conducted to determine the adsorption characteristics of FH and AMF as a function of four variables, e.g. Fe/M or [Al+Fe]/M mole ratio (3.8 to 7.5), Al/Fe mole ratio (0 to 1), initial total M concentration (13 to 126 mg/L), and pH (4 to 9). The measured responses included the final concentration of cadmium, copper, nickel, and zinc, and in, most cases, aluminum and iron.

The DOE-1 study required a minimum of sixteen tests; each test required a different combination of the four variables. A full replication of the sixteen tests was performed to generate information concerning experimental and analytical reproducibility. The DOE-1 study was followed by a second study (DOE 2) to investigate the possible interactions between individual metals, i.e., to gain information concerning the possible competition of each metal for available adsorption sites. Five variables were investigated, e.g., initial concentration of each metal (four different metals each at two concentrations levels) and pH.

The project goal was to lower the individual metals to concentrations less than the levels required by the Record of Decision for cleanup of the Berkeley Pitlake **(EPA-ROD 1994).** The individual goal concentrations for each metal, in µg/L, were Cd 1, Cu 30, Ni 100, Zn 338.: The suite of metals used in this study were (mg/L): Low level-Cd 2.5, Cu 2.9, Ni 4.4, Zn 3.3; High level-Cd 26.3, Cu 27.1, Ni 42.8, Zn 33.0.

Summary of Adsorption Results

AMF and FH heavy metal adsorption characteristics were similar for each metal and for the combination of the suite of metals (DOE-1). In general, the most important variables controlling the metals removal was the initial concentration of the metals and pH, i.e., for the variable ranges studied metals removal were independent of type of adsorbent and Fe/M or [Al+Fe]/M mole ratio. Figure 96 depicts a 3-D illustration of the influence of initial total metals concentration and pH on the percentage of metals transported to the precipitated solids. The results were independent of the other two variables, Al/Fe and loading ratio [Al+Fe]/M, for the studied design space, e.g., Al/Fe of 0 to 1; loading ratio from 3.8 to 7.5. All tests were performed at ambient temperature. For specific initial total metals concentration, a range of pH levels can be specified where the project goal levels for copper, nickel, and zinc can be attained (Figure 97). However, the cadmium goal level of less than one microgram per liter was more difficult to attain and more stringent conditions were required, e.g., higher adsorbent/metals loading levels and higher pH levels were required.

There is no apparent advantage for using AMF as the adsorbent compared to FH when considering the variable ranges investigated in the present study, both are equally effective adsorbents.

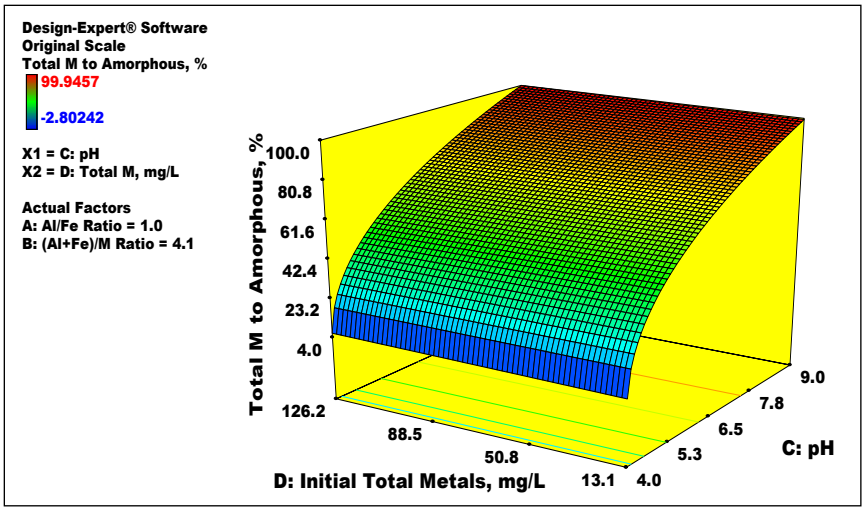


Figure 96. 3-D illustration of the influence of initial total metals concentration and pH on the percentage of metals transported to the precipitated solids (The results were independent of the other two variables, Al/Fe ratio and loading ratio [Al+Fe]/M, for the studied design space, e.g., Al/Fe of 0 to 1; loading ratio from 3.8 to 7.5. All tests were performed at ambient temperature).

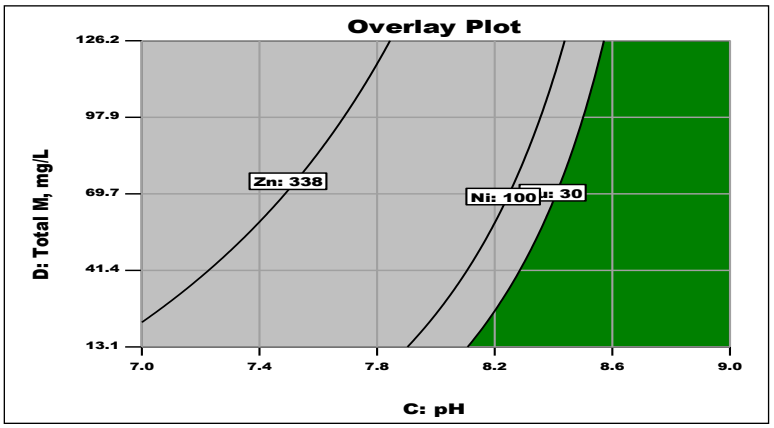


Figure 97. Influence of initial total metals concentration and pH on the final concentration of metals.

Project goal levels can be achieved (except for cadmium) for any combination of pH and initial total metals concentration selected in dark area. The study design space is independent of type of adsorbent (FH or AMF) and loading ratio within the design space. Goal concentrations for zinc and nickel can be achieved by any combination of initial total metals concentration and pH selected to the right of the respective contours.

Long-Term Aging Studies

Studies were also conducted to evaluate the long-term storage stability of the metal laden solids. Stability test work was conducted at ambient temperature and at an elevated temperature (70°C) to enhance the rate of conversion to more thermodynamically stable crystalline products. The aging characteristics of FH, AMF, M-loaded FH, and M-loaded AMF were studied by conducting full two-level full-factorial Design of Experiments (DOE) matrices at each sample time. All test work was performed using EPA QA/QC protocols.

Summary of Long-Term Aging Results

Experimental design studies were conducted at ambient (20-25°C) and 70°C temperatures to determine the aging characteristics of FH and AMF and metal-loaded FH and AMF solids as a function of three

variables, Al/Fe mole ratio, initial total M concentration, and pH. The emphasis of the aging studies was placed on the 70°C temperature, to accelerate the rate of conversion of amorphous to crystalline solids. The objective of the elevated temperature study was to identify whether initially adsorbed metals would be released back into the solution phase (desorbed) as a function of long-term aging.

Ambient Temperature Aging

The pH range used in industrial applications to treat their dissolved metal containing wastewater is 7.0-8.5. Therefore, it is interesting to observe the influence of aging time at a fixed pH, e.g., at pH 8.0 (Figure 35). The project goal concentrations for all the metals (except cadmium) were met for initial total metals concentrations up to approximately 65 mg/L, and the final total metals concentrations remained at goal levels as a function of aging time. The influence of pH and aging time, at initial total metals concentration of 8 and 40, is presented in Figures 98 and 99.

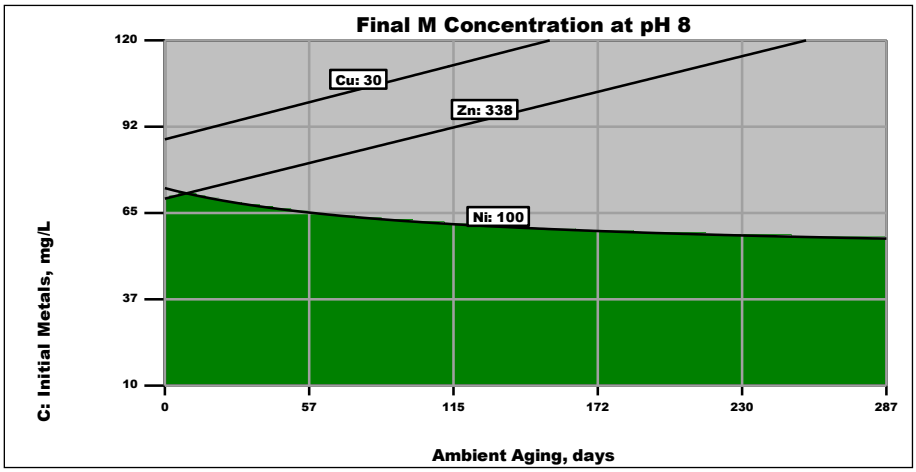


Figure 98. Overlay plot illustrating the influence of initial total metals concentration at pH 8 on attainment of the project goal concentration as a function of aging time at 25°C for all metals except cadmium

The criteria set for the above plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing initial metals concentrations in the dark region. Note that Cu and Zn goal concentrations are attained for initial metals below each contour line. The aging characteristics are independent of type of adsorbent (FH or AMF).

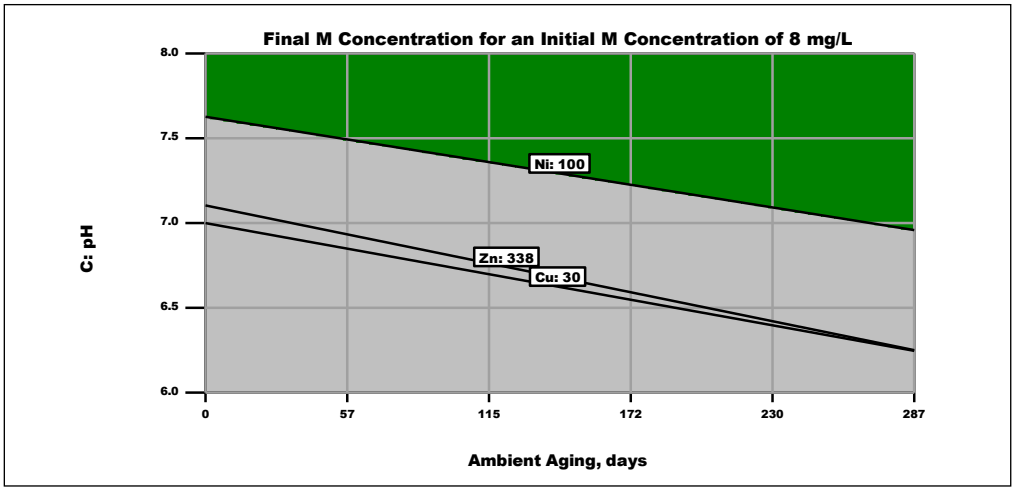


Figure 99. Overlay plot illustrating the influence of pH on attainment of the project goal

concentrations as a function of aging time at 25°C for all metals except cadmium (initial total metals 8 mg/L)

The criteria set for the above plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing pH values in the dark region. Note that Cu and Zn goal concentrations are attained at pH values above each contour. Note that each of the metals are transported from the solution (at a constant pH) to the solids as aging continues. The aging characteristics are independent of type of adsorbent (FH or AMF). The results are a function of the initial total metals concentration. This plot is for an initial total metal's concentration of 8 mg/L. The following Figure 100 is for the same conditions except the initial total metal's concentration is for 40 mg/L.

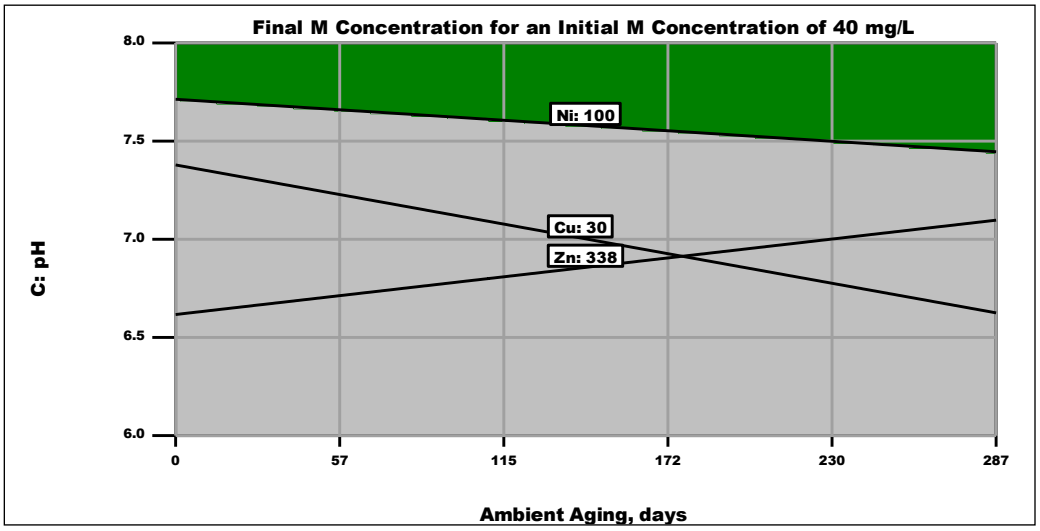


Figure 100. Overlay plot illustrating the influence of pH on attainment of the project goal concentrations as a function of aging time at 25°C for all metals except cadmium (initial total metals 40 mg/L)

The criteria set for the above plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing pH values in the dark region. Note that Cu and Zn goal concentrations are attained at pH values above each contour. Note that each of the metals are transported from the solution (at a constant pH) to the solids as aging continues. The aging characteristics are independent of type of adsorbent (FH or AMF). The results are a function of the initial total metals concentration. This plot is for an initial total metal's concentration of 40 mg/L.

Elevated Temperature Aging

Figures 101 is presented to illustrate that the conditions to achieve the project goal metal concentrations are not very different from the conditions required at ambient temperature (compare Figure 101 and Figure 99. Therefore, the conclusion is that the metal adsorbed by the solids will be successfully retained in the precipitated solids. In fact, the aging data illustrates that the metals in the solution phase decreases with aging time regardless of the aging temperature.

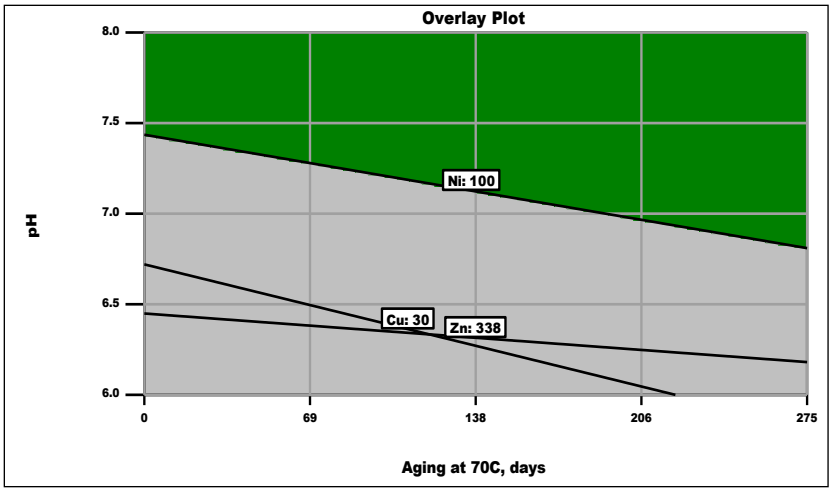


Figure 101. Overlay plot illustrating the influence of pH on attainment of the project goal concentrations as a function of aging time at 70°C for all metals (Cu, Ni, Zn) except cadmium

The criteria set for the plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing pH values in the dark region. Note that Cu and Zn goal concentrations are attained at pH values above each contour. Note that each metal is transported from the solution (at a constant pH) to the solids as aging continues. The aging characteristics are independent of type of adsorbent (FH or AMF) and loading ratio within the design space.

Comparison of Aging at Ambient and 70°C Temperatures

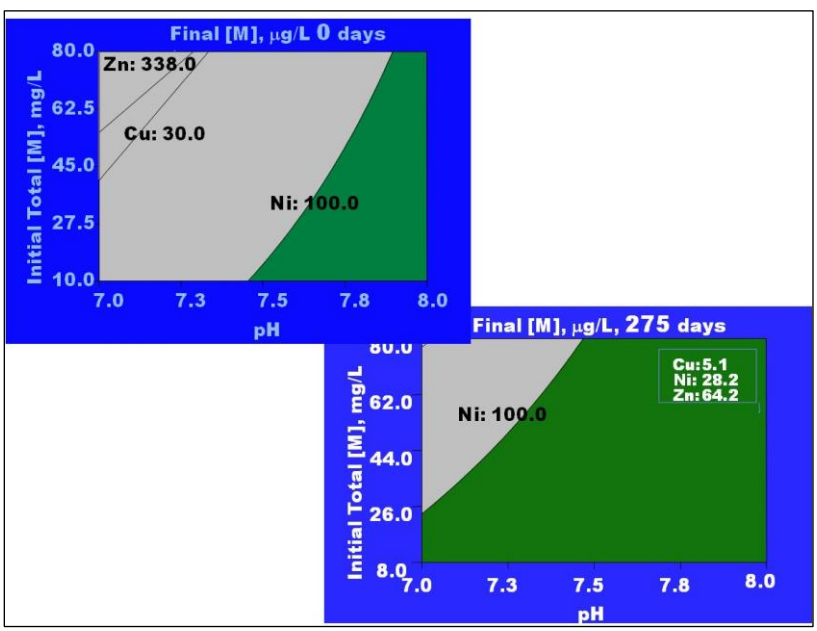


Figure 101. Overlay plots illustrating the influence of pH in near neutral conditions on attainment of the project goal concentrations as a function of aging time (0 days and 287 days) at 70°C for all metals except Cd

The criteria set for the plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing pH values in the dark region. Note that Cu and Zn goal concentrations are attained (except for cadmium) at pH values below each contour before aging was

initiated. Note that nickel and copper are transported from the solution (at a constant pH) to the solids as aging continues. The aging characteristics are independent of type of adsorbent (FH or AMF) and loading ratio within the design space.

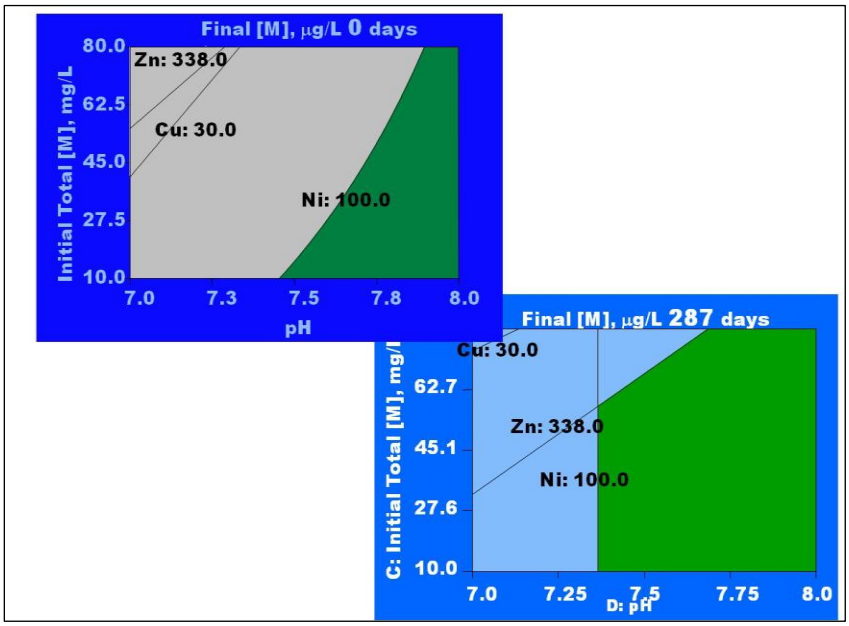


Figure 102. Overlay plots illustrating the influence of pH in near neutral conditions on attainment of the project goal concentrations as a function of aging time (0 days and 287 days) at 25°C for all metals except for cadmium

The criteria set for the plot was the project goal concentrations: 30 µg/L Cu, 100 µg/L Ni, and 338 µg/L Zn. These concentrations are all attained by choosing pH values in the dark region. Note that Cu, and Zn goal concentrations are attained at pH values below each contour before aging was initiated. Note that Cu, Ni and Zn are transported from the solution (at a constant pH) to the solids as aging continues. The aging characteristics are independent of type of adsorbent (FH or AMF) and loading ratio within the design space.

The influence of aging time on the final concentration of each metal is presented in Figures 103-107. Two contour plots are presented for each metal, one at a low initial total metals and another at a high initial total metals.

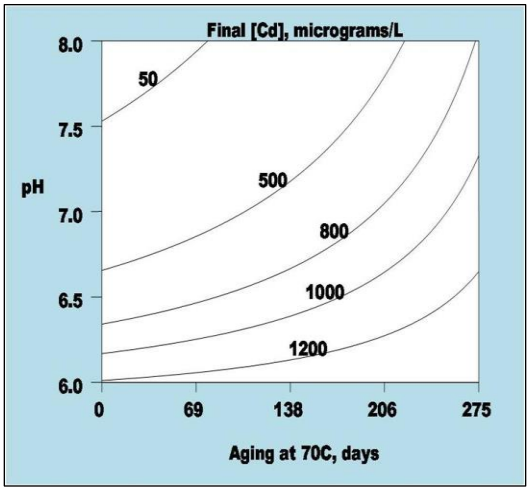


Figure 103. Influence of aging time and pH on the final

concentration of cadmium in the solution phase. Initial total metals concentration was 8-mg/L

The design space was independent of the other two variables, Al/Fe and loading ratio [Al+Fe]/M, e.g., Al/Fe of 0 to 1; loading ratio from 3.8 to 7.5. Note that cadmium solubility decreases as time of exposure is increased at a constant pH.

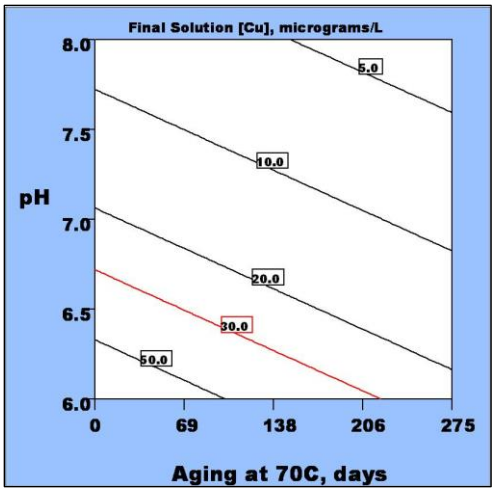


Figure 104. Influence of aging time and pH on the final concentration of copper in the solution phase. Initial total metals concentration was 8-mg/L

The design space was independent of the other two variables, Al/Fe and loading ratio [Al+Fe]/M, e.g., Al/Fe of 0 to 1; loading ratio from 3.8 to 7.5. Note that copper solubility decreases as time of exposure is increased at a constant pH.

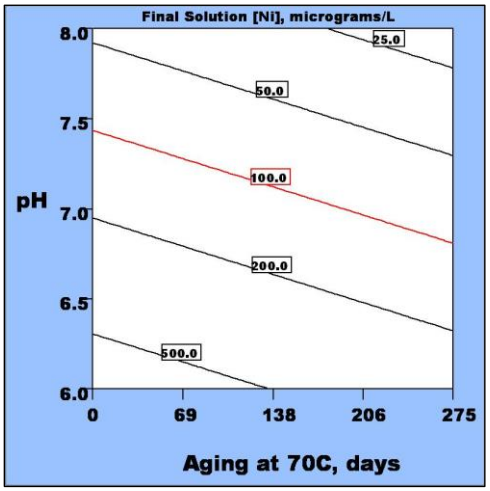


Figure 105. Influence of aging time and pH on the final concentration of nickel in the solution phase. Initial total metals concentration was 8 mg/L

The design space was independent of the other two variables, Al/Fe and loading ratio [Al+Fe]/M, e.g., Al/Fe of 0 to 1; loading ratio from 3.8 to 7.5. Note that nickel solubility decreases as time of exposure is increased at a constant pH. The final nickel concentration is a function of initial total metals concentration, see next figure.

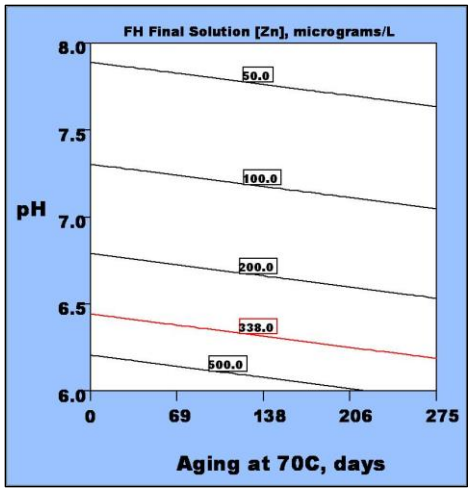


Figure 106. Influence of aging time and pH on the final concentration of zinc in the solution phase using the AMF adsorbent at an Al/Fe mole ratio of one

Initial total metals concentration was 8 mg/L. The **d**esign space was dependent of the type of adsorbent but was independent of the loading ratio,

LIME TREATMENT OF BERKELEY PIT WATER: LONG-TERM STABILITY

Huang et al. at Montana Tech began to investigate the characteristics of removal of arsenic and metals from Berkeley Pitlake water **(Shi 1992; Liu 1994)**. Huang's two-stage lime treatment technique is now the basis of the Record of Decision promulgated in 1994 **[EPA-RD 1994]** for the treatment of Berkeley Pitlake water (pictures of Berkeley pit, Figure 107). ARCO has constructed and implemented a treatment plant being used. The treatment is a two-stage high-density pH controlled system, Figures 108. The MWTP program **(MWTP-56 1991)** supported a study of the long-term stability of the solids formed by the Huang treatment recipe applied to Berkeley Pitlake water and a local mine drainage water (Crystal Mine, not discussed here). The initial Berkeley Pitlake water composition is presented in Table 17. This project was initiated 1991 and has continued to the present time. Columns were filled with lime-treated water and sludge, Figure 109. These columns have been sampled, initially monthly, then after the first year **(Gensler 1995)** and after the tenth year **(Powell 2005)**. The results are summarized in Table 3. The precipitated sludge continues to show long-term stability after ten years of storage. The mode of removal of the arsenic and metals was determined to be by a combination of hydroxide precipitation and metal adsorption.

Figure 107. Photographs of the Berkeley Pit prior to flooding (1979) and partially filled with water in 2008.

Figure 108. Berkeley Pitlake water treatment plant 2009

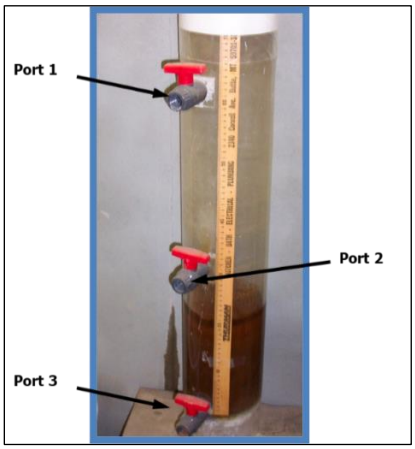


Figure 109. Column for long-term aging (one of five) lime precipitated Berkeley Pitlake water

Table 17. Long-Term stability of lime precipitated Berkeley Pitlake water

Element	DL input/1 yr/10 yr, µg/L	$BPit_{initial}$, µg/L; 200 ft level		µg/L				
				After Treatment	1 yr		10 yrs	
					Port 2	Port 3	Port 2	Port 3
As	0.1/0.1/1	1,030		0.1	BDL	BDL	BDL	BDL
Al	139/71/41	240		446	BDL	153	BDL	99

Cd	9/10/0.1	1,650		BDL	BDL	BDL	6	1.2
Cu	24/17/2	16,400		BDL	18	20	52	287
Fe	32/21/14	1,123,000 (Fe^{+2})		BDL	BDL	BDL	22 (Fe^{+3})	229 (Fe^{+3})
Ni	62/28/14	980		BDL	BDL	BDL	26	15
Zn		579,000		49	542	109	473	1690
SO_4^{2-}		8,480 mg/L						
pH/Eh		2.78/-130mv		10.1/400	7.5	10.6/200	7.4	10.2/200

Initial preparation of the aging columns occurred in November 1994

Element	TCLP Requirement µg/L	MCL or (SMCL) µg/L	NPDES Ore Mining 1 day/30 days µg/L
As	5000	10	1000, 500
Al		(50 to 200)	
Cd	1000	5	5
Cu		1300	300, 150
Fe		300	
Ni			
Zn		5000	1500, 750
SO_4^{2-}		250,000	250,000

SULFATE REMOVAL from MINE WASTE WATERS

A corollary MWTP study to the Berkeley Pitlake study was initiated to evaluate the removal of sulfate from waste waters or waters that were previously treated by lime precipitation **(MWTP-240 2005; Twidwell and Young).** Additionally, two studies evaluated and characterized the Berkeley Pitlake surface waters, and the results are reported by Young (**Young et al. 2007; Young et al. 2008).**

The Sulfate Problem

Mine waters and process effluent waters often contain elevated concentrations of sulfate, i.e., concentrations well above the proposed Secondary Drinking Water Standard (250 mg/L sulfate).

Two technologies are presently utilized industrially for removing sulfate from wastewater, e.g., bioreduction of sulfate to sulfide and exclusion by membrane filtration. These technologies have several disadvantages including; they are relatively expensive processes to operate, require specialized equipment, require long residence time reactors (bioreduction), high pressure (membrane processes like reverse osmosis and nanofiltration), and have difficult to deal with solid/liquid separations and membrane fouling problems. It is desirable to have a simple, relatively inexpensive inorganic removal process. This desire was the basis for this study.

Compound Precipitation

The concept for the study program was to evaluate compound precipitation techniques to sequester the sulfate in a solid phase product. The precipitation of two relatively insoluble metal sulfates have been studied and are extensively reported in the technical literature, i.e., the precipitation of barium sulfate and strontium sulfate. However, barium is an EPA "characteristic" hazardous metal and strontium is very expensive. There are metal hydroxysulfates that are very insoluble that do not contain hazardous or expensive constituents. Specific examples of this are Alunite [$KAl_3(OH)_6(SO_4)_2$] and Ettringite

[$Ca_6Al_2(SO_4)_3(OH)_{12}$:$26H_2O$]. These compounds were investigated in this study and Ettringite was chosen for detailed study.

Potential Benefits of the Compound Precipitation Technology

- Effective sulfate removal is possible over a wide range of experimental conditions. This is important because restrictive operational controls will not be required, e.g., solution pH, initial aluminum/calcium reagent addition variations and fluctuations in initial sulfate concentration need not be controlled within tight limits.
- The technology can be conducted in readily available conventionally used mineral processing/extractive metallurgy precipitation and solid/liquid separation equipment. Therefore, the compound precipitation technology should be cost competitive and can be applied at a lower cost than other removal technologies.
- The technology does not add toxic elements to the water and therefore the process does not create hazardous waste that must be disposed of at a premium cost. The sulfate is collected into a concentrated solid form that can be disposed of in a non-hazardous repository site or the product has the potential of being utilized as a chemical or metallurgical feedstock.

Conclusions for the Sulfate Removal Technology Studies

It was demonstrated in this project that sulfate can be effectively removed to <250 mg/L from solutions by compound precipitation in reasonable residence times. The compound form investigated in this study was **Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}$:$26H_2O$**. The results of this study demonstrated that sulfate removal is a function of the amount of aluminum added as sodium aluminate ($Na_2Al_2O_4$), amount of calcium added as hydrated lime, time and interactive combinations of initial sulfate concentration/hydrated lime and initial sulfate/time. Two figures are presented to illustrate that the project goal can be attained using reasonable reagent additions. Figure 110 is presented as a 3-D illustration of the effect of reagent additions for an initial sulfate concentration of 1 g/L, exposure time was 60 minutes. The initial concentration of sulfate was chosen because it was envisioned that a pretreatment stage would be used, i.e., the removal of the bulk amount of sulfate by precipitation of gypsum. Figure 111 illustrates the same information in a contour format. Note that many combinations of sodium aluminate and hydrated lime can be selected to achieve the project goal sulfate concentration of 250 mg/L The flat portion of the 3-D illustration denotes conditions where the final sulfate concentration is higher than 250 mg/L. The reason for this occurrence is illustrated in the STABCAL distribution diagram shown as Figure 50, i.e., when the hydrated lime content is high then the pH level is high enough that Ettringite becomes unstable. The STATEASE statistical design software can be used to investigate the influence of reagent conditions for other initial sulfate concentrations.

Other aluminum reagent sources were investigated, such as aluminum hydroxide or alumina (which had to be initially dissolved in a strong acidic solution). It is important to know that the formation of Ettringite must occur from the solution phase and does not readily occur in a reasonable reaction time by the additions of an aluminum containing solid phase like aluminum hydroxide. The source of aluminum must be sodium aluminate which is readily soluble at pH levels of four to six. Therefore, the proper preparation procedure must be to initially dissolve sodium aluminate, then to add the hydrated lime to control the amount of calcium required for Ettringite formation and for raising the pH to the level of 10 to 13. The disadvantage is that sodium aluminate is a relatively expensive reagent, and its addition should be minimized.

Industrial Waters

Four industrial waters containing different levels of sulfate were treated by compound precipitation, i.e., Kessler Springs Water (Kennecott Copper Corporation), ASARCO Smelter Pond Water, Berkeley Pitlake Well F (well water in the vicinity of the Berkeley Pit), and Travona Mine (mine water in the vicinity of the

Berkeley Pit). The experimental results are presented in Table 18. Note that the sulfate concentration was reduced below the goal limit for all the treated waters. Also, the formation of Ettringite results in appreciable metals removal as illustrated for Berkeley Pitlake water in Table 19

Ettringite precipitation has also been studied for possible heavy metals impoundment in cement solidification/stabilization processes. An extensive literature review on this subject has been performed by **Klemn [1998]** for the Portland Cement Association. The emphasis of the present study was, of course, placed on sulfate removal technology development, however the potential for the removal of heavy metals along with sulfate would make the technology even more attractive. Therefore, an experimental study was conducted during our MWTP study to investigate heavy metal co-removal with sulfate. The experimental results are summarized in Table 20. Note that indeed heavy metals are effectively removed along with the sulfate.

Proposed Treatment

The proposed treatment sequence is envisioned to a two-stage process, e.g., the water is initially treated with lime to produce a gypsum product. This will lower the sulfate content to approximately one gram per liter. This stage would be necessary to keep the process cost as low as possible by minimizing the amount of sodium aluminate required. After lime treatment the solid gypsum would be removed and the water (after pH adjustment to 5-7) would be subjected to stage two treatment using sodium aluminate and additional hydrated lime.

Disposal of Ettringite

Ettringite is relatively insoluble when stored at elevated pH levels. However, it is susceptible to conversion to calcium carbonate in the presence of carbon dioxide. Therefore, the precipitated product would have to be stored dry, incorporated in cement or, perhaps, marketed. **Havlica [2002]** claims that Ettringite may be a marketable product, "Massive ettringite utilization may be in civil engineering in the production of composites, chemical admixtures prevent salt damage to concrete, non-explosive demolition agent, water resistant hydraulic binder, solidifying fly ash, water proofing and sound absorbing materials, inorganic foaming materials, antibacterial and anti-mold agent."

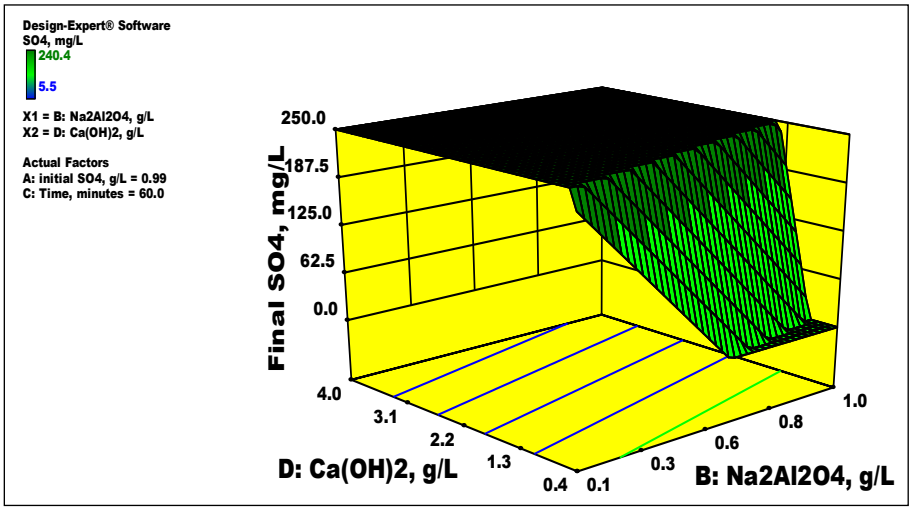


Figure 110. 3-D illustration of the influence of reagent addition on the final sulfate concentration. Initial sulfate=1 g/L, reaction time = 60 minutes.

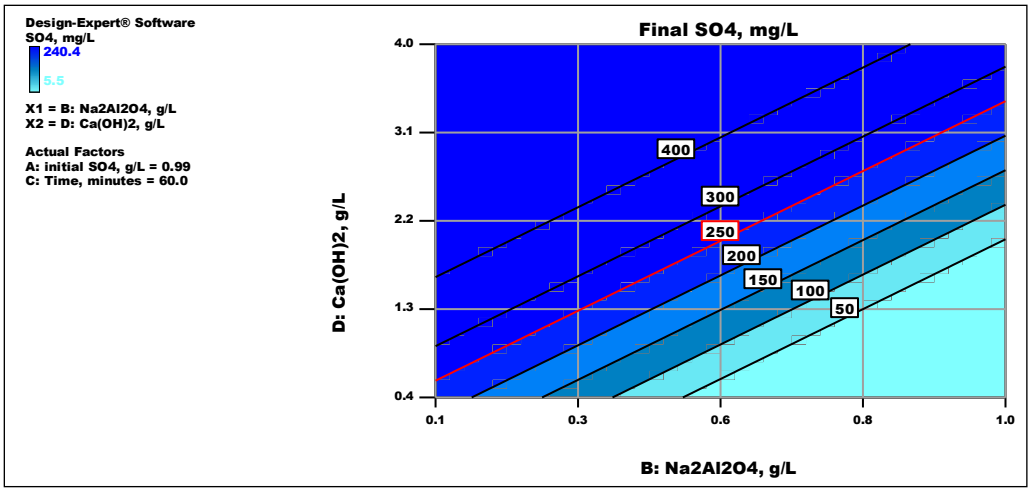


Figure 111. Contour illustration of the influence of reagent addition on the final sulfate concentration. Initial sulfate=1 g/L, time=60 minutes.

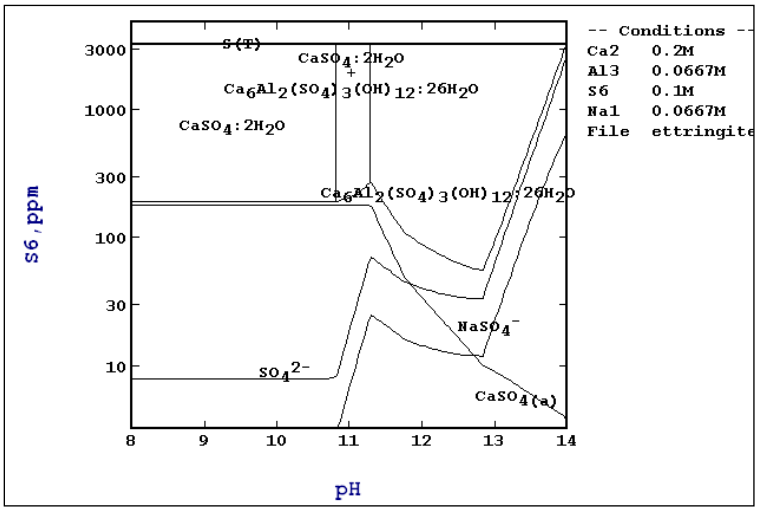


Figure 112. STABCAL illustration of the influence of pH on the solubility of Gypsum and Ettringite solubility

The solubility of Ettringite controls the solution sulfur concentration over the pH range of approximately 10 to 13. The addition of hydrated lime would have to be limited to prevent redissolution of the Ettringite.

Table 18. Reagent concentrations selected for the treatment of various mine waters

Water Source	$Na_2Al_2O_4$	$Ca(OH)_2$
Kesseler Springs, Salt Lake City, UT	1.2x	1.8x
ASARCO Pond Water, Helena, MT	1.3x	1.5x
Well F, Butte MT	0.6x, 0.8x	1.5x, 1.2x
Travona Mine Water, Butte, MT	0.6x, 0.8x	0.8x, 1.2x

(x represents the stoichiometric fraction of aluminum and calcium added to the system based on the sulfate in $Ca_6Al_2(SO_4)_3(OH)_{12}$)

Table 19. Exploratory test results for the treatment of Mine Waters

Water	$SO_{4\,(initial)}$, mg/L	Measured $SO_{4\,(final)}$, mg/L
Kesseler Springs	933	227(1 hr), 65 (2 hrs)
ASARCO Pond	853	207 (3 hrs)
Well F	700, 852	44 (1 hr), 152 (1 hr)
Travona	328, 392	192 (1hr), 116 (1 hr)

Table 20. Experimental results for the treatment of Mixed Metal/Sulfate water by Ettringite precipitation

Field Id	Metal Concentration, mg/L				
	Cd	Cu	Ni	Zn	SO_4
BERK7-40803-Head	1.94	0.977	0.978	1.96	1839.2
BERK7-40803-30 minutes	<0.004	<0.001	<0.013	0.551	446.2
BERK7-40803-60 minutes	0.011	<0.001	<0.013	0.198	238.5
BERK7-40803-240 minutes	0.011	0.007	<0.013	0.349	63.0

(Conditions: Berkeley Pitlake Water, Butte, MT, $Na_2Al_2O_4$ =1.35x, $Ca(OH)_2$ =0.96x)

CHARACTERIZATION of SLUDGE in the BOTTOM of the BERKELEY PITLAKE

Introduction and Methods (Twidwell, et al. 2006; MWTP-133, 1999)

The general features of the historical formation and chemical characteristics of the Berkeley Pitlake have been presented by **Gammons and Duaime (2006)** and will not be repeated here. The main objective of the present study was to characterize the chemistry and mineralogy of solids and pore fluids in the uppermost meter of the pit lake sediment, and to form hypotheses as to the chemical or biological reactions that may or may not be occurring in this unique benthic environment. One of the key questions that we set out to answer was whether sulfate reduction was occurring in the pit lake sediment. If so, this would have important implications to possible in-situ bioremediation of the acidic and metal-laden waters in the overlying water column. Details not given in the present summary regarding the sampling program, the methods used for chemical and mineralogical characterization of the sediment and sediment pore waters, as well as the complete tables of analytical results, are available **(Twidwell et al. 2000; MWTP-133, 1999).** Surface water characterization has been reported by Young and others **(Young et al. 2007; Young et al. 2008)**.

Two sediment surface solid samples for preliminary characterization were retrieved on Nov. 1997 at 182 m (600 ft) and 213 m (700 ft) depths (location unspecified). A more detailed sampling including three core samples (Core 1, 2, 3) and one deep water sample (BPD-1) was conducted at a site near the maximum depth of the Berkeley Pitlake in April and May 1998. Sampling was conducted using a NISKEN vertical sampler for collecting deep water samples and a Benthos sediment core sampling device for the core and pore water samples. The location of the core-sampling site was Latitude 46° 01' 03.50", Longitude 112° 30' 41.00" at an approximate surface water/sediment depth of 220 m.

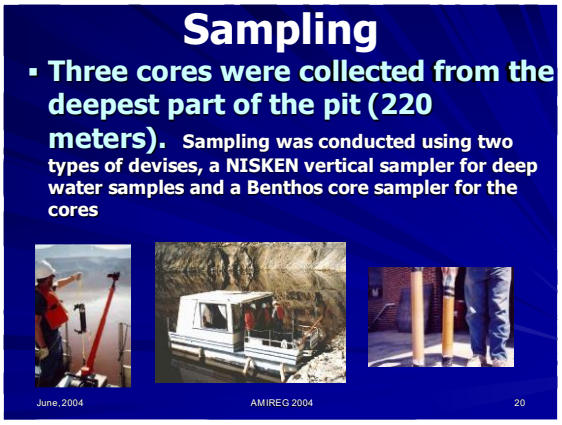


Figure 113. Pictures of core collection

Study Results

This presentation documents the chemical composition of solids and coexisting pore waters in the upper meter of sediment collected at the bottom of the Berkeley pit lake. Overall, the chemistry of the pore waters had a similar pH and metal content as the overlying lake waters. The pit lake sediments are not sulfidic but do show a general trend of lower redox potential with depth. Although the observed mineralogy of the sediment did not change in an obvious way with depth, thermodynamic calculations suggest that Schwertmannite may be dissolving near the top of the sediment pile, and then re-precipitating as K-jarosite deeper in the pile. Further work is needed to confirm whether these changes are indeed occurring, and whether they are mediated by bacteria or are the result of essentially abiotic processes.

Unconsolidated sediment at the bottom of the Berkeley pit lake is a mixture of detrital silicate minerals derived from sloughing of the pit walls and secondary minerals precipitated out of the water column. The latter include gypsum and K-rich jarosite. The pore waters have a similar pH to the overlying lake waters (pH 3.1 to 3.4), and have similarly high concentrations of dissolved heavy metals, including Al, Cd, Cu, Mn, Ni, and Zn. Sediment cores show that the top meter of the sediment column is moderately oxidized (jarosite-stable). Petrography, chemical analysis and geochemical modelling all suggest a transformation of poorly crystalline ferric compounds such as Schwertmannite and/or ferrihydrite near the sediment surface to jarosite with depth in the core. No evidence of bacterial sulphate reduction was found in this study, despite the presence of 0.3 to 0.4 wt% organic carbon in the pit lake sediment.

THALLIUM

Literature Review (MWTP-143 2001)

Thallium is more toxic to humans than mercury, cadmium, lead, copper or zinc. Its chemical behavior resembles the heavy metal lead and the alkali metals (potassium, rubidium, and cesium). Thallium occurs almost exclusively in natural waters as monovalent thallium (Tl+1). The solubility of thallous compounds (e.g., thallous hydroxide) is relatively high so that Tl+1 is readily transported through aqueous routes into the environment. The major sources of thallium are the base metal sulfides and precious metal bearing sulfides. Therefore, it has been shown to be a contaminant constituent in waters emanating from heavy metal deposits, e.g., sulfide-bearing deposits.

The Mine Waste Technology Program commissioned Montana Tech (L.G. Twidwell) to review the literature to determine if thallium is an important constituent in mine wastewaters and whether there are appropriate documented technologies to remove it from mine waste and related waters. A comprehensive review of the literature was performed **(MWTP-143 2001; MWTP-204 2003)** and the results showed that:

- thallium is a constituent of concern in waters emanating from sulfide bearing deposits; and
- only two industrial removal technologies exist for recovering thallium from process solutions:

(1) oxidative precipitation of thallic (valence for thallium is +3) hydroxide; and

(2) reductive cementation of thallium using elemental zinc as the precipitant.

Thallium exits in wastewater solutions in the +1 valence state; to be effectively removed via precipitation of Tl(OH)3 requires that Th(+3) be formed by very strong oxidation, see Figure 114. However, note that at a thallium concentration of 50 µg/L no solid can exist (Figure 115), which is well above the human health standard for thallium of 1.7 µg/L. Therefore, Tl(OH)3 solubility is much greater than the desired solubility concentration pH values and therefore, the formation of the hydroxide is not appropriate.

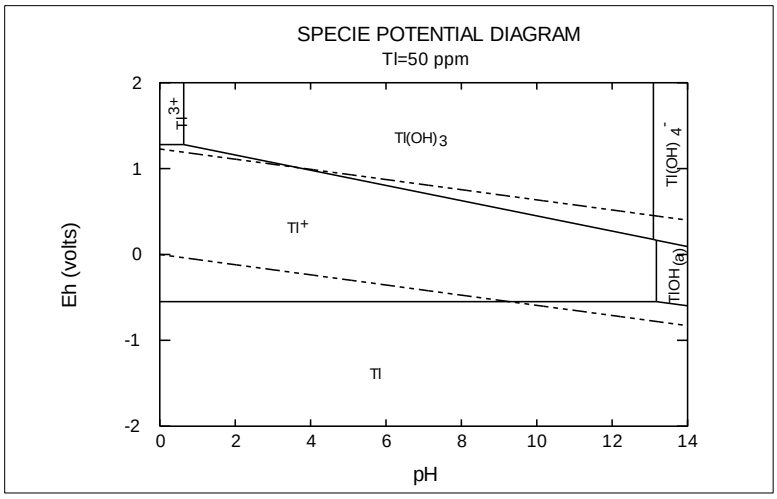


Figure 114. Eh/pH diagram for the Tl/H_2O system (50 mg/L) at 25o C

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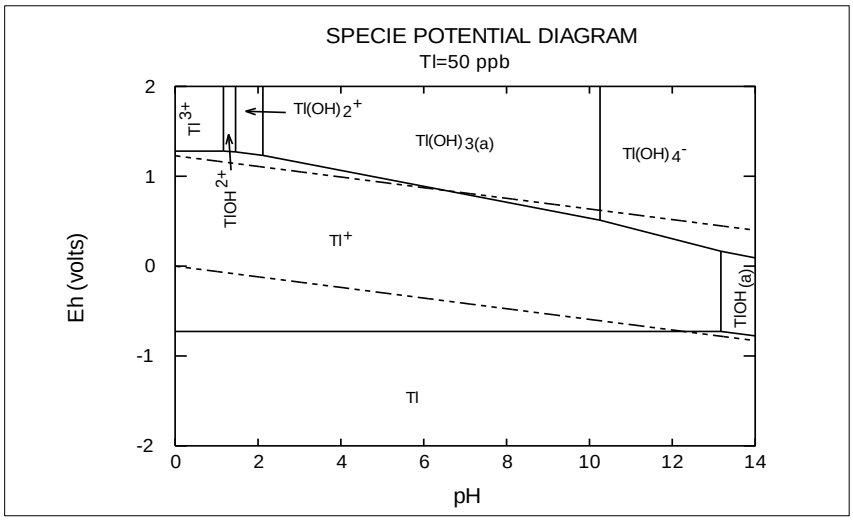

Figure 115. Eh/pH diagram for the Tl/H_2O system (50 μg//L) at 25°C

The thallium literature review was conducted as a necessary precursor study as part of the MSE Technology Applications, Inc., report, Mine Waste Pilot Program, Activity I, Volume VIII, Issues Identification and Technology Prioritization Report: **Thallium (MWTP-143)** to determine whether a pilot scale demonstration of thallium removal should be performed by the Mine Waste Technology Program (MWTP). The result of the literature review was that there is no known technology that is presently available capable of removing thallium to the desired environmental levels. The conclusion is that further test work and development were required before pilot-scale demonstrations were performed (Table 21).

Table 21. Summary of technologies recommended for further evaluation.

Technology	Description	Precautions	Product
Manganese Dioxide Adsorption	Manganese dioxide adsorption of heavy metals has been extensively investigated. Conditions for thallium (+1) removal from solution can be specified. The presence of other	Most of the experimental test work has been directed toward adsorption of thallium from the solution phase; very little information is available as to the	Thallium-loaded manganese dioxide or, if the thallium can be effectively stripped from the manganese dioxide, elemental thallium.

Technology	Description	Precautions	Product
	aqueous species in the solution to be treated will likely influence the removal of thallium, i.e., the order of adsorption (at pH 4) has been shown to be. Pb+2>Cu+2>Tl+1>>Cr+3.	extraction of thallium from the adsorbent and the possibility of reuse of the manganese dioxide in order to minimize adsorbent cost. Also, only laboratory studies have been performed. The technology has not advanced to pilot- or full-scale utilization.	
Ferrihydrite	Predicted order of adsorption effectiveness for thallium ferrihydrite at pH 6 is: thallium(+1)>thallium(+3)> lead(+2)>copper(+2)>> zinc(+2)>cadmium+2. Surface adsorption modeling suggest that ferrihydrite adsorption may be effective at pH levels greater than approximately 6.	This technology has not been experimentally demonstrated to be very effective for adsorption of thallium. Successful application to a variety of mine waters needs to be demonstrated.	Ferrihydrite (ferric oxyhydroxide) sludge. This sludge should be considered a hazardous material. The sludge would have to be treated for proper disposal (probably as a hazardous waste).
Metal Reduction	This process is based on industrial practice for treating process solutions, i.e., the process is zinc electrochemical reduction of thallium ions (zinc cementation of thallium). Other cementing reagents may be effective, e.g., iron or aluminum scrap or powders.	The product from this treatment cannot be disposed in tailings ponds. The extent of thallium removal is unknown, i.e., it is unknown whether thallium concentrations in solution can be lowered to the ppb range.	The product from this treatment is elemental zinc containing deposited elemental thallium. The thallium concentration can be built up to relatively high levels, i.e., several percent. The product should be marketable as a source of thallium.

Experimental Studies

Two studies were conducted in response to the need to develop appropriate thallium removal technologies before a pilot-scale demonstration project. The question was whether technologies could be developed that may be appropriate for removing thallium to levels of a few micrograms per liter.

The two technologies experimentally investigated for removing thallium from wastewater were , **thallium adsorption onto manganese dioxide** and **thallium removal by precipitation of thallium sulfide** under controlled pH and solution potential conditions (reductive precipitation).

Thallium Adsorption on Manganese Dioxide

The objectives of the thallium adsorption on manganese dioxide technology were:

- Perform exploratory test work to optimize removing of thallium from synthetic water by adsorption on manganese dioxide and exploratory test work to optimize the recovery of thallium from the manganese dioxide solids (so that the solids can be recycled repeatedly); and
- Demonstrate the application of the thallium adsorption technology on "real" thallium bearing wastewaters.

Experimental Studies

Extensive investigations were conducted and the conclusion was that not all the objectives were achieved. The results presented in the referenced report demonstrated that thallium can be effectively loaded onto manganese dioxide. However, stripping the thallium from the loaded manganese dioxide was found to be very difficult and an appropriate stripping technique was not found. Therefore, it would be necessary to further investigate stripping alternatives or to apply the present loading technology to a once through system, i.e., the product from the adsorption process would be disposed and the original manganese dioxide would be lost in the disposal process. Using manganese dioxide ore was also investigate and its use would be relatively inexpensive but loading thallium on this product was not nearly as effective as loading it on electrolytic manganese dioxide. Whether the economics would allow using a once through system has yet to be determined.

With respect to the second objective, experimental test work was conducted in an exploratory cursory manner only because of the difficulty experienced during the thallium stripping from the manganese dioxide. Several loading experiments were conducted on ASARCO smelter wastewater treatment discharge water. The optimum conditions developed in the synthetic solution test work were used on the ASARCO water. Thallium was lowered from approximately 300 μg/L to <1.7 μg/L. Therefore, the process was deemed possible but with the caveat that the manganese dioxide would be lost.

Reductive Precipitation Technology

The original work plan was written to investigate cementation (a process whereby thallium ions are electrochemically exchanged for iron ions at an iron particulate surface) as a potential technology for removing thallium from wastewater. However, the final direction taken during the research was to use metallic iron to establish a desirable reducing environment for the precipitation of thallium sulfide (referred to here as reductive precipitation). The study focused on achieving the following three objectives:

- Conduct a laboratory study to delineate the important experimental variables that must be controlled for removing thallium from wastewater by reductive precipitation to <1.7 μg//L.
- Characterize the thallium bearing solids formed.
- Apply the optimized conditions to an industrial wastewater.

Experimental Studies

Preliminary experiments were performed using iron cementation in a stirred reactor. The results showed poor thallium recovery so a different approach was formulated based on the concept of reductive precipitation, i.e., iron was used to control the solution potential at a level that would promote the vi precipitation of thallium sulfide. The Eh/pH diagram in Figure 116 illustrates this concept. The shaded area on the figure illustrates the solution potential/pH conditions required to promote thallium sulfide precipitation, i.e., iron lowers the potential of the solution to levels that are favorable for the precipitation of thallium sulfide. The iron/solution phase boundary is darkened to denote the solution potential achievable with elemental iron present. Note that the achievable potentials pass through the thallium.

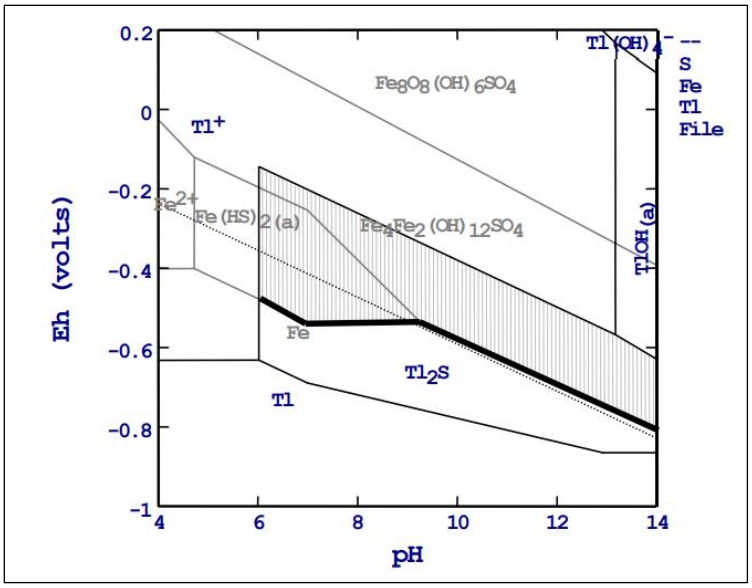

Figure 116. Illustration of the concept for reductive precipitation using iron to control the solution potential at a level that would promote the precipitation of thallium sulfide

The concept for removing thallium from an aqueous environment by controlled potential sulfide precipitation was confirmed. Experiments using the same experimental setup and experimental procedure were conducted on solutions that did not contain iron (thallium sulfide precipitation without solution potential control), on solutions that contained iron but did not contain any sulfide (direct cementation), and on solutions that contained iron and sulfide (controlled potential sulfide precipitation). The results are compared in Table 22.

Table 22. A Comparison of results obtained for removing Thallium by Sulfide Precipitation, Cementation, and Controlled Potential Sulfide Precipitation (Source **MWTP-204**)

Precipitation of Sulfide		Cementation of Thallium		Controlled Potential Sulfide Precipitation	
Sulfide, mg/L	**Final Tl, µg/L**	**Sulfide, mg/L**	**Final Tl, µg/L**	**Sulfide, mg/L**	**Final Tl, µg/L**
pH 5	Head, 880	pH 5	Head, 800	pH 5	Head, 980
5.7	590	0	570	5.7	21
57	290	---	---	57	2
pH 8	Head, 850	pH 7	Head, 980	pH 8	Head, 800
5.7	700	0	640	5.7	8
57	530	---	---	57	1
Note: pH levels are nominal values					

The controlled potential reductive precipitation concept is a valid technology for removing thallium from wastewater. The test work performed during this study validates the concept, but experimental conditions have not been optimized. It is likely that the experimental variables will have to be optimized for each real water system, as is true in applying any new technology. The technology was applied to ASARCO solutions and the results are reported in Table 23. Note that the final thallium concentration achieved the desired EPA value of <1.7 µg//L.

Table 23. Comparison of Results obtained for Removing Thallium by Controlled Reduction Precipitation from Synthetic and Real Waters
(Source: **MWTP-204**)

Water	Sulfide Addition, mg/L	Thallium, μg/L
Synthetic	5.7	69
	11.4	10
	22.8	<1
	45.6	<1
ASARCO	5.7	5
	11.4	1
	22.8	2

Detection limit: 1 μg/L.
Constants: 1,200 rpm; 100 g/L –20 mesh iron powder; ambient temperature; and 1.8 L/min N_2, pH~5.

APPENDIX A. Master Science Theses by the Twidwell Research Team (M.Sc. student thesis studies for the treatment of arsenic, selenium, or thallium solutions and sludges are highlighted in the following table)

Author	Year	Master of Science Thesis Title
Dufrense, R.	1974	*Leach of Copper Reverberatory Slag*
Knoepke, J.	1974	*Treatment of copper dross flue dust for the extraction of Arsenic*
Mehta, A.	1976	*Fixation of Arsenic in copper smelter flue dust*
Hwang, J.	1975	*Lime Roast and Leach of Sulfuric Acid Treated Copper Reverberatory Slag*
Mansanti, J.	1978	*The Precipitation of Iron as a Jarosite from Iron, Copper, and Zinc Containing Solutions*
Flynn, H.	1980	*Treatment of Lead Smelter Speiss*
Blaskovich, S.	1982	*Elemental Distribution of Lime-Roasted Lead Smelter Speiss in a Copper Matte-Slag System*
Roset, G.	1982	*The Influence of Experimental Variables on the Elemental Distribution of Lime-Roasted Smelter Dusts in a Copper Matte-Slag System*
Downey, J.	1982	*Elemental Distribution of Lime-Roasted Smelter Dusts in a Copper Matte-Slag System*
Anderson, C.	1982	*A Survey of Roasting Techniques to Volatilize Arsenic and Antimony from Copper Smelter*
Laney, D.	1984	*The Application of Solvent Extraction to Complex Metal Bearing Solutions*
Newhouse, J.	1984	*Segregation Process Applied to Copper Smelter Flue Dust*
Peterson, M.	1985	*Treatment of Lead Smelter Speiss*
Dahnke, D.	1985	*Removal of Iron from Process Solutions*
Arratia, J.	1985	*Optimization of Copper Recovery from Smelter Flue Dust*
Downey, J.	1986	*Separation and Recovery of Chromium and Nickel from Mixed Metal Solutions*
Fitzpatrick, G.	1986	*The Influence of Additive Compounds on Copper Segregation*
Nordwick, S.	1987	*Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide*
Arthur, B.	1987	*Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation*
Rapkoch, J.	1988	*The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide*
Abbas, M.H.	1987	*Formation and stability studies of some iron-arsenic and copper-arsenic compounds (Hsin Huang was thesis advisor)*
Comba, P.	1987	*Removal of Arsenic from Process and Wastewater Solutions*
Quinn, J.	1988	*Conversion of Chromium Phosphate to Chromic Acid by Fusion Process*
Neira, M.	1990	*Recovery of Elemental Arsenic from Copper Smelter Flue Dust by Volatilization*
Flynn, D.	1990	*Treatment of Electromachining Waste for Selective Nickel/Cobalt Separation*

Author	Year	Master of Science Thesis Title
Leary, R.	1990	*Treatment of Stainless Steel Pickling Liquors*
Honoras, C.	1992	*Recovery of Copper and Zinc from Copper Reverberatory Slags*
McGrath, S.	1992	*The Rate of Precipitation of Chromium Phosphate*
Shuey, S.	1992	*Selective Separation of Nickel and Cobalt from Electro-machining Sludges*
Dover, L.	1992	*Treatment of Chromium Contaminated Soils*
Tang, X.	1992	*Recovery of Copper from Copper Smelter Flue Dust*
Plessas, K.	1992	*Recovery of Arsenic from Process Wastewaters*
Shi, Y.	1992	*Treatment of acid mine drainage at the Berkely Pit, Butte, Montana by Chemical Precipitation (Hsin Huang was thesis advisor)*
Pande, P.	1993	*Lead Blast Furnace and Dezinced Slag Stability*
Krishnan, S.	1994	*Arsenic Removal by Soil Washing*
Weldon, T.	1994	*Slag Chemistry Refining of Molten Stainless Steel*
Gensler, C.	1994	*Stability of Lime-Initiated Hydroxide Precipitation Sludge*
Liu, C.	1994	*Bench scale chemical Treatability Study of Berkeley Pit Water in Mine Waste, Pilot Program (Hsin Huang was thesis advisor)*
Miranda, P.	1996	*Removal of Arsenic from Wastewaters as Stable Iron Mineral Compounds*
Wilson, S.	1998	*Removal of Arsenic from ASARCO Blow-Down Water and Long-Term Stability of the Product Solids*
Saran, J.	1997	*Removal of Arsenic from Berkeley Pit Wastewater and Long-Term Stability of the Product Solids*
Gale, M.	1998	*Removal of Arsenic from Wastewaters by Iron/Phosphate Precipitation*
Dahlgren, E.	2000	Dahlgren, E. *Parameters Affecting the Cementation of Selenium from Wastewaters*
Williams-Beam	2001	*Technologies for the Recovery of Thallium from Wastewaters*
Orser, T.	2001	*Removal of Arsenic from Wastewaters as Stable Calcium Mineral Compounds*
Hadden, G.	2002	*Rate of Removal of Oxyanions of Arsenic and Selenium from Mine Wastewater using Galvanically Enhanced Cementation*
Sunberg, J.	2003	*Removal of Heavy Metals from Wastewater by Reductive Precipitation*
Hohn, J.		Hohn, J., *Arsenic Removal by Modified Ferrihydrite Adsorption*
Leonhard, J.	2006	Heavy Metals *Removal by Modified Ferrihydrite Adsorption*
Glasgow, M.	2007	*Modified Ferrihydrite/Arsenic: Effect of Anions*

Appendix B. Treatment of Electroplating and Electromachining Hydroxide Sludges (1984 to 2001; see Part 2 Report)

Researcher	Reference	Publication
Laney, D.	M.Sc. Thesis (1984) *The Application of Solvent Extraction to Complex Metal Bearing Solutions*	
Twidwell, L.G., A. Mehta, G. Hughes	*Metal Value Recovery from Metal Hydroxide Sludge*	EPA-60019-84-022, Sept. 1984, pp. 129-133.
Dahnke, D.	M.Sc. Thesis (1985) *Removal of Iron from Process Solutions*	
Dahnke, D. R., L. G. Twidwell, B. W. Arthur and S. M. Nordwick	*Selective Recovery of Metal Values from Electroplating Sludge by the Phosphate Process*	Proceedings of SUR/FIN-86, 73rd AESF Annual Technical Conference, Philadelphia, PA, June 23-26, 1986, Session C-3, 20 p.
Downey, J.	M.Sc. Thesis (1986) *Separation and Recovery of Chromium and Nickel from Mixed Metal Solutions*	

Researcher	Reference	Publication
Twidwell, L.G., D.R. Dahnke, W.L. Huestis, J. P. Quinn, P.G. Comba	*Pilot Scale Results of Metal Value Recovery from Mixed Metal Hydroxide Sludge*	Proceeding's 8th AESF/EPA Conference on Pollution Control for the Metal Finishing Industry, San Diego, CA, February 9-11, 1987.
Nordwick, S.	M.Sc. Thesis (1987) *Conversion of Precipitated Ferric Phosphate to Ferric Hydroxide,*	
Arthur, B.	M.Sc. Thesis (1987) *Treatment of Iron, Chromium, and Nickel Aqueous Chloride Acidic Solutions by Phosphate Precipitation*	
Twidwell, L.G., D.R. Dahnke	*Metal Recovery from Electroplating Waste*	Proceedings of the First International Conference on Hydrometallurgy, (ICHM '88), Edited by Z. Yulian, X. Jiazhong, Beijing, China, October 1988, International Acad. Publishers, pp. 394-388.
Rapkoch, J.	M.Sc. Thesis (1988) *The Effects on Metal Phosphate Precipitation from Complex Solutions by Substituting Sodium Hydroxide, the Titrant, with Ammonium Hydroxide*	
Quinn, J.	M.Sc. Thesis (1980) *Conversion of Chromium Phosphate to Chromic Acid by Fusion Process*	
Twidwell, L.G., D.R. Dahnke, S.F. McGrath	*Detoxification of and Metal Value Recovery from Metal Finishing Sludge Materials*	Innovative Hazardous Waste Treatment Technology Series, Volume 2, Physical Chemical Processes, Editor H. M. Freeman, Technomic Publishing Company, 1990, pp. 56-62.
Flynn, D.	M.Sc. Thesis (1990) *Treatment of Electro-machining Waste for Selective Nickel/Cobalt Separation*	
Flynn, D.R., L.G. Twidwell	*Selective Recovery of Nickel and Cobalt from Electromachining Process Solutions*	Copper, Nickel, Cobalt Metallurgy, AIME Symposium, New Orleans, LA, February 1991.
Dahnke, D.R., D. Flynn, S.A. Shuey, L.G. Twidwell	*Selective Recovery of Metal Values from Electrochemical Machining Sludge: Recovery of Cobalt*	Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium, EPA/600/R-92/028, Cincinnati, OH, April 14-16, 1992, pp. 96-100.
McGrath, S.	M.Sc. Thesis (1992) *The Rate of Precipitation of Chromium Phosphate*	
Shuey, S.	M.Sc. Thesis (1992). *Selective Separation of Nickel and Cobalt from Electro-machining Sludges*	

Researcher	Reference	Publication
Twidwell, L.G., S.A. Shuey, D.R. Flynn, D.R. Dahnke	*Selective Recovery of Nickel and Cobalt from Electro-machining Sludge Materials*	J. Haz. Waste and Haz. Mat., Vol. 10, No. 4, 1993, pp 297-311.

APPENDIX C. List of Presentations and Publications by the Twidwell Research Group (treatment of metal hydroxide solutions and sludges are highlighted in the following information)

LARRY G. TWIDWELL

[Contact Information: 1300 W. Park Street, Butte, Montana; 406 560 2263, ltwidwell@mtech.edu, enviromet1@gmail.com; Engineering Classroom Building (ELC-216); Metallurgical and Materials Engineering Building, Montana Technological University]

Brief Bio

Larry G. Twidwell, D.Sc. is Emeritus Professor in the Department of Metallurgical and Materials Engineering at Montana Tech. He has forty-five years of experience in teaching and directing research in Metallurgical Engineering at Montana Tech. Twidwell and his graduate students and coworkers have conducted research emphasizing extractive metallurgy and the application of extractive metallurgical engineering to the treatment of metallurgical wastes, process waters and by-products. Four books, fifty-eight theses, one hundred twenty-seven publications and one hundred ten national and international presentations have resulted from their research efforts. Twidwell has received several outstanding teacher/researcher awards during his tenure at Montana Tech, e.g., TMS-EPD Distinguished Lecturer Award, 2011; TMS-EPD Best Technology Paper Award, 2006; AIME Frank Aplan Award, 2004; Montana Tech Lifetime Distinguished Researcher Award, 2002; AIME Mineral Industry National Education Award, 2001; Montana Academy of Sciences Mershon Award as Outstanding Montana Researcher, 1989; Outstanding Scholar Award, Montana Tech, 1985; and Outstanding Educator Awards, Montana Tech, 1970, 1971, 1973, 1974.

Technical Presentations (Arsenic, Selenium, Thallium presentations are highlighted)

1. Montana Society of Engineers, Feb. 1974, *Recovery of Metals from Reverberatory Slags*, Butte, Mt. (Presenter: **L.G. Twidwell**).
2. Society of Exploration Geophysicists, Dec. 1975, *Self-Paced Tutorial Instruction.* (Presenter: **L.G. Twidwell**).
3. American Society for Engineering Education, June 1978, *Self-Paced Instruction on Extractive Metallurgy,* Vancouver, WA. (Presenter: **L.G. Twidwell**).
4. American Institute of Chemical Engineers, Nov. 1978, *Fixation of Arsenic in Copper Smelter Flue Dust by Lime Roasting* (co-authors: A. Mehta, J. Burckle), Atlanta, GA. (Presenter: **L.G. Twidwell**).
5. INDO-U.S. Workshop on Mineral Processing and Chemical Metallurgy, *AMAX Segregation Process: The Distribution of Impurities, Recovery of Metal Values and Disposal of Arsenic from Smelter Flue Dusts,* Proceedings INDO-U.S. Workshop on Mineral Processing and Chemical Metallurgy, Dec. 14-17, 1981, Udaipur, India, pp. 184-85. (Presenter: **L.G. Twidwell**)
6. American Institute of Mining, Metallurgical Engineers, Feb. 1984, *Segregation Applied to Copper Concentrate: Distribution of Impurities,* 113th Annual Meeting, Los Angeles, CA (Presenter: **L.G. Twidwell**, Co-author: K. Beuerman).
7. Tenth Annual Research Symposium Land Disposal, Incineration and Treatment of Hazardous Waste, April 1984, *Recovery of Metals from Electroplating Sludge,* (Presenter: **L.G. Twidwell**, Co-authors: A. Mehta, G. Hughes), Cincinnati, OH.
8. California Environmental Health and Safety Annual Meeting, May 1984, *Recovery of Metal Values from Electroplating Wastes, Phase II,* (Presenter: **L.G. Twidwell**, Co-authors: A. Mehta, G. Hughes), Sacramento, CA.
9. American Institute of Mining, Metallurgical Engineers, March 1986, *Treatment of Speiss for Metal Value Recovery,* 115th Annual Meeting, (Presenter: **L.G. Twidwell**, Co-author: M. Peterson) New Orleans, LA.

10. Twelfth Annual Hazardous Waste Symposium, April 21-23, 1986, *Recovery of Metal Values from Metal Finishing Hydroxide Sludge: A Project Summary,* (Presenter: **L.G. Twidwell**, Co-authors D. Dahnke, B. Arthur, S. Nordwick) Cincinnati, OH.
11. SUR/FIN '86, American Electroplating and Surface Finishing Conference, June 1986, *Selective Recovery of Metal Values from Electroplating Hydroxide Sludge by the Phosphate Process,* ((Presenter: **L.G. Twidwell**, Co-authors: D. Dahnke, B. Arthur, S. Nordwick) Philadelphia, PA.
12. European Economic Commission Symposium, May 27-28, 1986, *Disposal of Arsenic Bearing Waste Material and Smelter By-Product,* (Presenter: **L.G. Twidwell**, Co-authors: M. Peterson, P. Comba) University of Maryland.
13. International Symposium on Solubility, August 1986, *Solubility Diagrams for Aqueous Metal Phosphate Systems,* (Presenter: **L.G. Twidwell**, Co-author: R. G. Robins, D. R. Dahnke) Newark, NJ.
14. International Symposium on Iron Control in Hydrometallurgy, CIM, October, 1986, *Selective Iron Removal from Process Solutions by Phosphate Precipitation,* (Presenter: **L.G. Twidwell**, Co-authors: D. Dahnke and R. Robins) Toronto, Canada.
15. 116th AIME Annual Meeting, February 23-26, 1987, *Removal of Arsenic from Process and Wastewater Solutions,* (Presenter: **L.G. Twidwell**, Co-authors: P. G. Comba, D. R. Dahnke) Denver, CO.
16. Pacific Northwest Metals and Minerals Conference, April 27-28, 1987, *Treatment of Electroplating Sludge Material for Metal Recovery,* (Presenter: **L.G. Twidwell**, Co-author: J. Quinn).
17. Pacific Northwest Metals and Minerals Conference, April 27-28, 1987, *Removal of Arsenic from Process and Wastewaters,* (Presenter: **L.G. Twidwell**, Co-author: P. G. Comba) Portland, OR.
18. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, May 1987, *Removal of Arsenic from Process and Wastewater Solutions,* (Presenter: **L.G. Twidwell**, Co-author: P. G. Comba) Socorro, NM.
19. 117th AIME Annual Meeting, January 25-28, 1988, *Removal of Arsenic from Process and Wastewater Solutions: Update,* (Presenter: **L.G. Twidwell,** Co-authors: P. G. Comba, D. R. Dahnke) Phoenix, AZ.
20. First International Conference on Hydrometallurgy, October 1988, *Metal Recovery from Electroplating Waste,* Beijing, China, (Presenter: **L.G. Twidwell**, Co-author D. R. Dahnke)
21. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1989, *Removal of Arsenic from Wastewaters,* (co-author T. Bowler) Reno, NV (Presenter: **L.G. Twidwell**)
22. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1989, *Recovery of Metal Values from Stainless Steel Pickling Liquors,* Reno, NV. (Presenter: **L.G. Twidwell**, Co-author: D. Donelon)
23. Sabbatical Presentations, Jan. - June 1990, *Removal and Stabilization of Arsenic Wastes*, Tohoku Engineering Faculty (Sendai, Japan), Government Institute for Research (Sendai, Japan), Akita University Engineering Faculty (Akita, Japan), Akita Zinc Smelter (Akita, Japan), Mitsubishi Copper Company (Naoshima, Japan), EZ Zinc (Hobart, Tasmania), Australian Nuclear Science and Technology Organization (Sydney, Australia), Mt. ISA Mining and Minerals (Mt. ISA, Australia). (Presenter: **L.G. Twidwell**).
24. Annual Meeting USBM Generic Center for Mineral Industry Waste Treatment, June 1990, *Survey Techniques to Treat Stainless Steel Pickling Liquors* (co-author R. Leary), Reno, NV. (Presenter: **L.G. Twidwell**).
25. 1990 Minerals and Hazardous Waste Symposium, October 1990, *Recovery of Chromium from Electroplating Solutions*, Butte, MT. (Presenter: **L.G. Twidwell**, Co-authors: S. F. McGrath, D. R. Dahnke, B. A. Arthur),
26. 1990 Mineral and Hazardous Waste Processing Symposium, October, 1990, *Removal of Arsenic from Process Solutions and Stabilization of Solids*, Butte, MT. (Presenter: **L.G. Twidwell**)
27. 119th Annual AIME Meeting, EPD CONGRESS 1991, Extractive Metallurgy of Copper, Nickel, Cobalt, Feb. 1991, *Selective Recovery of Nickel and Cobalt from Electromachining Process Solutions.* New Orleans, LA, (Presenter: **L.G. Twidwell,** Co-author D. R. Flynn),
28. 119th Annual AIME Meeting, EPD CONGRESS 1991, Extractive Metallurgy of Copper, Nickel, and Cobalt, Feb. 1991, *Solubility of Metal Phosphates*, (Presenter: **L.G. Twidwell**, Co-authors: R. G. Robins, D. R. Dahnke, S. F. McGrath, and G. H. Khoe)
29. Montana Academy of Science, Treating Contaminated Soils and Water, Bozeman, MT, March 27, 1992, *Treatment of Chromium Contaminated Soils,* (Presenter: **L.G. Twidwell,** Co-author: L. Dover).

30. Eighteenth Annual Risk Reduction Engineering Laboratory Research Symposium, EPA, Cincinnati, OH, April 14-16, 1992, *Recovery of Metal Values from Electrochemical Machining Sludge*, . (Presenter: **L.G. Twidwell**), Co-authors: D. R. Dahnke, D. Flynn, S. Shuey).
31. Spectrum 92, Boise, Idaho, August 1992, *Slag Chemistry and Metals Volatilization in the Plasma Arc Furnace Experiment*, (Presenter: **L.G. Twidwell**, Co-authors: C. G. Whitworth, T. W. Jenkins, G. F. Wyss).
32. Mine Waste Management & Remediation Conference, Butte, MT, July 7-9, 1992, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Materials.* . (Presenter: **L.G. Twidwell**).
33. Cooperative Research Center, Stabilization of Arsenic Waste, Sydney, Australia, July 20, 1992, *Recovery of Metal Values from Mineral Processing and Electro-finishing Waste.* (Presenter: **L.G. Twidwell**).
34. EPA Workshop on ARSENIC, Washington, DC, August 17-17, 1992, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Solids,* (Presenter: **L.G. Twidwell**, Co-authors: K. O. Plessas, T. P. Bowler).
35. EPA Workshop on MERCURY, Washington, DC, August 19-20, 1992, *Hydrometallurgical Process for Mercury Recovery from F106 Muds*, (Presenter: **L.G. Twidwell,** Co-author: M. A. Rockandel).
36. Mine Closure Short Course, Helena, MT, April 27-29, 1993, *Arsenic and Heavy Metal Mobility Considerations*, (Presenter: **L.G. Twidwell,** Co-author H.H. Huang).
37. Australian Water and Wastewater Association, Sydney, Australia, May 27, 1993, *Mine Waste Environmental Research Programs.* (Presenter: **L.G. Twidwell**).
38. Murdock University, Perth, Australia, June 1, 1993, *Removal of Arsenic from Wastewaters and Stabilization of Arsenic Bearing Waste Materials.* (Presenter: **L.G. Twidwell**).
39. Mine Waste Center Arsenic Seminar, November 4, 1994, *Removal of Arsenic from Mine Water*", Montana Tech, Butte, Mt. (Presenter: **L.G. Twidwell**).
40. Australian Nuclear Science and Technology Organization (ANSTO), February 9, 1994, *Decontamination of Radioactive Scrap Stainless Steel by Melt/Slag Refining.* (Presenter: **L.G. Twidwell**).
41. SME-AIME Annual Meeting, Albuquerque, NM, Feb. 15, 1994, *Recovery of Silver from Manganiferous Silver Ores by Segregation Roasting-Flotation*. (Presenter: T.J. Jordan, Coauthors: C. Flores, **L.G. Twidwell**).
42. Montana Academy of Sciences, Montana Tech, Butte, MT, April 15-16, 1994, *Treatment of Anaconda Smelter Site Soil for Arsenic Removal*, (Presenter, S. Krishnan, Co-author: **L.G. Twidwell**).
43. Montana Academy of Sciences, Montana Tech, Butte, MT, April 15-16, 1994, *Bioleaching of Arsenopyrite*, (Presenter D. Anderson, Co-author: **L.G. Twidwell**).
44. International Symposium on the Problems of Complex Ore Utilization, Saint Petersburg, Russia, May 10-14, 1994, *Part Seven Waste Disposal and Utilization-Removal of Arsenic from Wastewater and Stabilization of Arsenic Bearing Waste Solids: Summary of Experimental Results,* (Presenter, **L.G. Twidwell,** Co-authors: K. Plessas, P. Comba, D. Dahnke).
45. Am. Vacuum Society Conference on Liquid Metal Processing, Santa Fe, NM, Sept 11-14, 1994, *Decontamination of Metals by Melt Refining/Slagging,* (Presenter, S. Worcester, Co-authors: **L.G. Twidwell**, T. Weldon, D. Paolini, R. Mizia).
46. SPECTRUM 96, Seattle, WA, August 19-21, 1996, *Decontamination and Decarburization of Stainless Steel by Vacuum Induction Melting,* (Presenter, S. Worcester, Co-authors: **L.G. Twidwell**, D. Webber, R. Mizia), Seattle, WA.
47. Am. Vacuum Society Conference on Liquid Metal Processing and Casting, Santa Fe, NM, February 16-19, 1997, *Decontamination, Decarburization and Conversion of Carbon Steel to Stainless Steel by Vacuum Induction Melting Using Gaseous and Solid Oxygen Sources,* (Presenter, S. Worcester, Co-authors: **L.G. Twidwell**, D. Webber), Santa Fe, NM.
48. SME, 1998 Annual Meeting, Orlando, Florida, February 1998, *An Overview of Innovative Processes that Show Potential for Arsenic Removal and Long Term Stability,* (Presenter, P. Miranda, Co-authors: **L.G. Twidwel**l, J. McCloskey).
49. Hazardous Substance Research Center, 1998 Conference Snowbird, Utah, *Characterization of Berkeley Pit Deep Waters and Sediments*, (Presenter, **L.G. Twidwell**, Co-authors: C. Young, R. Berg).
50. ICMR'98 Akita, October 1998, Akita, Japan, The Recovery and Recycle of Mercury from Chlor-alkali Plant Wastewater Sludge, (Presenter, **L.G. Twidwell,** Co-author: M. Rockandel).
51. Montana Academy of Sciences, Montana Tech, Butte, MT, April 15-16, 1999, *Characterization of Berkeley Pit Deep Waters and Sediments*, (Presenter, **L.G. Twidwell**, Co-authors: C. Young, R. Berg).

52. EPA, 1998 Annual Meeting, Orlando, Florida, February 1998, *An Overview of Innovative Processes that Show Potential for Arsenic Removal,* (Presenter, J. McCloskey, Co-authors: **L.G. Twidwell**, P. Miranda, M. Gale).
53. EPA/DOE, August 1999, Alta, Utah, Eliminating Heavy Metal Contaminants from Water Resources, *Arsenic Removal and Long Term Stabilization for Solids*, (Presenter, J. McCloskey, Co-authors: **L.G. Twidwell**, P. Miranda, M. Gale, G. Vicevic).
54. TMS, 1999 Fall Meeting, REWAS'99, San Sabastian, Spain, September 5-9, 1999, *The Recovery and Recycle of Mercury from Chlor-Alkali Plant Wastewater Sludge*, (Presenter, **L.G. Twidwell,** Co-authors: J. Selby).
55. TMS, 1999 Fall Meeting, REWAS'99, San Sabastian, Spain, September 5-9, 1999, *Technologies and Potential Technologies for Removing Arsenic from Process and Wastewater*, (Presenter, **L.G. Twidwell**, Co-authors: J. McCloskey, P. Miranda, M. Gale).
56. TMS, 1999 Fall Meeting, REWAS'99, San Sabastian, Spain, September 5-9, 1999, *Technologies and Potential Technologies for Removing Selenium from Process and Wastewater*, (Presenter, **L.G. Twidwell**, Co-authors: J. McCloskey, P. Miranda, M. Gale).
57. EPA, August 2-4, 1999, *Arsenic Removal and Long-Term Stabilization for Solids*, Second Annual Western Environmental Technology Office, Snowbird Center, Alta, UT. (Presenter, J. McCloskey, Co-authors: P. Miranda, M. Gale, **L.G. Twidwell**).
58. SME, 2000 Annual Meeting, Minor Elements 2000, February, 2000, *Technologies and Potential Technologies for Removing Selenium from Process and Wastewater: Update,* San Antonio, TX (Presenter, **L.G. Twidwell**, Co-authors: J. McCloskey, P. Miranda, M. Gale).
59. MWTP, Short Course, April 2000, *Technologies for Removing Arsenic, Selenium and Thallium from Wastewater*, Mine Operations and Closure, Helena, MT (Presenter, **L.G. Twidwell**, Co-author: J. McCloskey).
60. University Concepcion, May 9-13, 2000, *The Removal of Arsenic from Hydrometallurgical Process and Effluent Streams*, International Conference on Clean Technology for the Mining Industry, Santiago, Chile (Presenter, T. Nishimura, Co-authors: R.G. Robins, **L.G. Twidwell**).
61. TMS, 2001 Annual Meeting, February 2001, Cyanide: Social, Industrial and Economic Aspects, *Cobalt/Nickel Separation by Cyanide Complexation*, Salt Lake City, UT (Presenter, **L.G. Twidwell,** Co-author: S.A. Shuey).
62. TMS, 2002 Annual Meeting, February 2002*, Utilization of Calculational Programs for Teaching Hydrometallurgy*, (Presenter, H.H. Huang, Co-authors: C. Young, **L.G. Twidwell**)
63. TMS, 2002 Fall Meeting, June 2002, *Technologies For Removing Thallium From Wastewater to Achieve Environmental Standards*, Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects, Lulea, Sweden, (Presenter, **L.G. Twidwel**l, Co-authors: C. Williams-Beam).
64. SME/CIM, Oct 2002, *Hazardous Constituent Removal from Wastewater*, Mineral Processing Plant Design, Control and Practice, Vancouver, BC, CN (Presenter, J. McCloskey, Co-authors: **L.G. Twidwell**, M. Gale)
65. Akita University, Dec 2002, Appropriate Technologies for Removing Arsenic, Selenium and Thallium from Wastewater and Effluents, Akita, Japan (Presenter, **L.G. Twidwell**)
66. Nogoya University, Jan 2003, Appropriate Technologies for Removing Arsenic and Selenium from Wastewater and Effluents, Nagoya, Japan (Presenter, **L.G. Twidwell**)
67. TMS, 2003 Annual Meeting, March 2003, *Utilization of Calculational Programs to Demonstrate the Hydrometallurgical Treatment of Mercury Waste*, San Diego, CA, (Presenter, H.H. Huang, Co-authors: **L.G. Twidwell,** C.A. Young)
68. MWTP Mine Closure, May 2003*, Modified Ferrihydrite for Enhanced Removal of Arsenic from Effluent and Mine Wastewater*, Polson, MT (Presenter, R.G. Robins, Co-author: **L.G. Twidwell**)
69. TMS/SME/CIM, August 2003, *Removal of Thallium from Wastewater*, Hydrometallurgy 2003, Vancouver, BC, Canada (Presenter, **L.G. Twidwell,** Co-author: C. Williams-Beam)
70. MJMP&EP, June 2004, *Deep Water Sediment/Pore Water Characterization from an Acidic Metal-Laden Pitlake*, 1st International Conference Advances in Mineral Resources Management and Environmental Geotechnology, Chania, Crete, Greece (Presenter, **L.G. Twidwell,** Co-authors: C. Young, R. Berg)
71. MJMP&EP, June 2004, *Removal of Selenium from Mine and Waste Waters*, 1st International Conference Advances in Mineral Resources Management and Environmental Geotechnology, Chania, Crete, Greece (Presenter, **L.G. Twidwell**, Co-authors: E. Dahlgren, S. McGrath).

72. TMS, February 2005, **Invited Keynote Lecture,** *The Removal of Arsenic from Aqueous Solution by Coprecipitation with Iron (III)*, Arsenic Metallurgy: Fundamentals and Applications, San Francisco, CA (Presenter, **L.G. Twidwell,** Co-authors: R.G. Robins, J.W. Hohn)
73. TMS, February 2005, *Arsenic Removal from Mine and Process Waters by Lime/Phosphate Precipitation,* Arsenic Metallurgy: Fundamentals and Applications, San Francisco, CA (Presenter, **L.G. Twidwell**, Co-authors: J. McCloskey, M. Lee, J. Saran)
74. TMS, February 2005, *Arsenic Removal from Mine and Process Waters by Lime/Phosphate Precipitation: Pilot Scale Demonstration,* San Francisco, CA (Presenter, J. McCloskey, Co-authors: **L.G. Twidwell**, M. Lee)
75. SME, March 2005, *Removal of Selenium Oxyanions from Mine Waters Utilizing Elemental Iron and Galvanically Coupled Metals*, J.D. Miller Symposium, Innovations in Natural Resource Systems, Salt Lake City, UT, (**L.G. Twidwell,** Co-authors: J.M. McCloskey, H. Joyce, E. Dahlgren, A. Hadden).
76. CIM, August 2005, *Point of Zero Charge (Pzc) And Double Layer Adsorption -An Equilibrium Calculation Approach*, COM 2005 - The Conference of Metallurgists & 35th Annual Hydrometallurgical, Calgary, Canada (Hsin-Hsiung Huang, **L.G. Twidwell**, C.A. Young).
77. CIM, August 2005, *Point of Zero Charge (Pzc) And Double Layer Adsorption -An Equilibrium Calculation Approach*, COM 2005 - The Conference of Metallurgists & 35th Annual Hydrometallurgical, Calgary, Canada (Presenter, Hsin-Hsiung Huang, Co-authors: **L.G. Twidwell**, C.A. Young).
78. CIM, August 2005, *Chemical Titration Simulation - An Equilibrium Calculation Approach*, COM 2005 - The Conference of Metallurgists & 35th Annual Hydrometallurgical, Calgary, Canada (Presenter, Hsin-Hsiung Huang, Co-authors: **L.G. Twidwell**, C.A. Young).
79. XITC'05, October 2005, *The TEMPER and Free Form Fabrication Titanium Initiatives at The Center for Advanced Mineral and Metallurgical Processing*, USA, International Titanium Conference Xi'an, Shaanxi, China (Presenter, **L.G. Twidwell**, Co-authors: C.G. Anderson, P.J. Miranda).
80. SME, February 2005, *The TEMPER and Free Form Titanium Fabrication Titanium Initiatives at The Center for Advanced Mineral and Metallurgical Processing,* Heavy Minerals Conference 2005, Florida (Presenter, P.J. Miranda, Co-authors: C.G. Anderson, **L.G. Twidwell**).
81. NWMA, December 2005, *The Removal of Arsenic from Aqueous Solution by Co-precipitation with Iron (III): An Update*, Northwest Mining Association, Spokane, WA (Presenter, **L.G. Twidwell,** Co-authors: R.G. Robins, J.W. Hohn)
82. COM, October 2006, *A Comparison of Ferrihydrite and Aluminum Modified Ferrihydrite for Removing Arsenate by Co-Precipitation*, Iron Control in Hydrometallurgy, CIM, Montreal, (Presenter, J. Hohn, Co-authors: **L.G. Twidwell**, R.G. Robins).
83. COM, October 2006, *The Control of Iron and Arsenic in the Treatment of Gold Bearing Enargite Concentrates*, Iron Control in Hydrometallurgy, CIM, Montreal, (Presenter, C.G. Anderson, C.G., Co-Author: **L.G. Twidwell**).
84. NWMA, December 2006, *Selenium Issues in the US Coal Industries* NWMA Annual Meeting, Tahoe, NV (Presenter, B. Park, Co-authors**:** J. McCloskey**, L.G. Twidwell**).
85. SME, February 2007, *Characterization of The Berkeley Pitlake II: Deep Water, Sediments and Pore Water*, SME Annual Meeting, Denver, CO (Presenter, C. Young**,** Co-authors**: L.G. Twidwell**, R. Berg).
86. SME, February 2007, *Characterization of The Berkeley Pitlake I: Surface Waters*, SME Annual Meeting, Denver, CO (Presenter, C. Young**,** Co-authors**: L.G. Twidwell**,, M. Bennett).
87. SME, MPD Division Meeting, Denver, *Enhanced Natural Processes for Remediation of the Berkeley Pitlake,* April 25, 2008, (Presenter: C. Young, Co-author: **L.G. Twidwell)**
88. Hydrometallurgy 2008, August 2008, *Removal of Cadmium, Copper, Nickel and Zinc from Aqueous Solution by Adsorption on Ferrihydrite and Long-Term Storage Stability of the Metal Loaded Product*, SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: **L.G. Twidwell**, Co-author: J. Leonhard)
89. Hydrometallurgy 2008, August 2008, *Free Energies from The Solubility of Solid Compounds Using Speciation Calculations,* SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: H.H. Huang, Co-authors: **L.G. Twidwell**, C.A. Young, R.N. Gow, J. McCloskey)
90. Hydrometallurgy 2008*, Pitlake Remediation by Slag Addition: Dual Ecosystem Enhancement*, SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: C. A. Young, Co-authors: K. Filius, E.A. Streich, D. Berg and **L.G. Twidwell**)

91. Hydrometallurgy 2008, *Spectroelectrochemical Investigation of the Reaction Between Adsorbed Cuprous Cyanide And Gold Thiosulfate Ions at Activated Carbon Surfaces,* SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: Courtney A. Young, Co-authors: Gretel K. Parker, Robert N. Gow, **Larry G. Twidwell** and Greg A. Hope)
92. Hydrometallurgy 2008, *Surface Water Characterization of The Berkeley Pitlake*, SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008 (C.A. Young, Co-authors: **L.G. Twidwell** and M. Bennett).
93. Hydrometallurgy 2008, *Removal of Selenium Oxyanions from Industrial Scrubber Waters Utilizing elemental Iron,* SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008 (Presenter: J. McCloskey, Co-authors: **L.G. Twidwell,** Brian Park).
94. Hydrometallurgy 2008, *Cuprous Cyanide Adsorption on Activated Carbon: Pretreatment for Gold Take-up from Thiosulfate Solutions*, SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008, (Presenter: Courtney A. Young, Co-authors: Robert N. Gow, **Larry G. Twidwell,** Gretel Parker, and Greg A. Hope).
95. REWAS, 2008, *Separation, Recovery And Fixation of Tin, Arsenic, Antimony, Mercury and Gold with Alkaline Sulfide Hydrometallurgy,* TMS, Cancun, October 2008, (Presenter: C. Anderson**,** Co-author: **L.G. Twidwell**).
96. REWAS, 2008, *Ferrihydrite and Aluminum-Modified Ferrihydrite Enhanced High-Density Sludge Treatment for Removing Dissolved Metals from Acid Rock Drainage Wastewaters,* TMS, Cancun, October 2008, (Presenter: J. Downey**,** Co-author: **L.G. Twidwell**)
97. The Kazakh National Technical University, Invitation, 2008, "Preservation of the Environment from Industrial Dusts", *Removal of Selenium Oxyanions from Industrial Scrubber Waters Utilizing Elemental Iron*, Almaty, Kazakhstan (Presenter; J. McCloskey, Co-authors: **L.G. Twidwell**, B. Park, and M. Fallon)
98. Hydrometallurgy 2008, *Removal of Selenium Oxyanions from Industrial Scrubber Waters Utilizing elemental Iron,* SME/TMS/CIM Fall Meeting, Phoenix, AZ, August 2008 (Presenter: J. McCloskey, Co-authors: **L.G. Twidwell**, Brian Park).
99. SPE, 2009, *Removal of Hazardous and Heavy Metals from Produced Water*, Abstract submitted SPE, Indonesia Conference 2009 (Presenter: C.H. Rawlins, Co-authors: **L.G. Twidwell**, J. McCloskey).
100. SME, MPPD, 2010, *Fundamental Procedures to Evaluate and Design Industrial Waste Water Metals Treatment Systems, Case Study Discussions*, SME, MPPD, Tucson, AZ (Presenter: J. McCloskey, J, Co-authors: **L.G. Twidwell**, H.H. Huang, L. Goldstien
101. SME, ICPC, 2010, *Enhancement of Montana Coal: Sodium Removal s and Technologies, Evaluations, and Development,* Lexington, KY (Presenter: **L.G. Twidwell**, Co-authors: Jay McCloskey, Sean Dudley)
102. SME, MPPD, 2010, *Fundamental Procedures to Evaluate and Design Industrial Waste Water Metals Treatment Systems, Case Study Discussions*, SME, MPPD, Tucson, AZ (Presenter: J. McCloskey, J, Co-authors: **L.G. Twidwell**, H.H. Huang, L. Goldstien)
103. SME, MPPD, Tucson, AZ Feb 2010, *Fundamental Procedures to Evaluate and Design Industrial Waste Water Metals Treatment Systems, Case Study Discussions*, (Presented by J. McCloskey, Co-authors**, L.G. Twidwell**, H.H. Huang, and L. Goldstien)
104. TMS, EPD, 2011, **Distinguished Lecture Award**, *The Removal of Arsenic, Selenium and Metals from Aqueous Solution by Iron Precipitation and Reduction Techniques,* TMS Annual Meeting, San Diego, CA, Feb 2011. (Presenter: **L.G. Twidwell***)*
105. SME, 2013, *Innovations in Chemical and Bacterial Water Treatment*, SME, Denver, CO (Presenter: J. McCloskey, Co-Authors, B. Park, **L.G. Twidwell**)
106. COM, 2014, Arsenic Hydrometallurgy: Fundamentals, Technologies, Applications (Presenter: C.G. Anderson, Co-Authors, **L.G. Twidwell**, R.G. Robins, K.D. Mills), CIM, Conference of Metallurgist, Vancouver, B.C. Canada September, 2014.
107. IMPC, 2016, *The Optimization of an Industrial Ammonium Jarosite Production Circui*t, (Presenter: C.G. Anderson, Co-Authors, C. Fleuriault, **L.G. Twidwell**), Quebec, Canada, DOI: 1013140/RG.2.2.33378.32962.
108. ICMR'98 Akita, October, 2017, Akita, Japan, *Stability Diagrams for Metal-Sulfur Systems Applied to Extractive Metallurgical Processes*, (Presenter, H.H. Huang, Co-Authors **L.G. Twidwell,** C.A. Young).
109. SME, 2018, *A Survey of Pyrometallurgical Arsenic Volatilization Techniques*, (Presenter: C.G. Anderson, Co-Author, **L.G. Twidwell**, SME Minneapolis.
110. MTECH. 2021. *Treatment of Arsenic-Bearing Minerals and Fixation of Recovered Arsenic Products: An Updated Review*. **L.G. Twidwell**, Professor Emeritus, Montana Technological University. DOI: 101340/RG.2.2.15550.00325.

Publications (Chronological: * designates peer review, **(Arsenic, Selenium, Thallium presentations are highlighted)**

treatment of arsenic, selenium, thallium solutions and sludges are highlighted in the following table)

*1. **Twidwell, L.G.**, and Larson, A. H., *The Influence of Selected Sulfides on the Decomposition Rate of Zinc Sulfate at 600°C.* Trans. Met. Soc. AIME Vol. 236, pp 1379-80, 1966.

*2. **Twidwell, L.G.** and A. H. Larson, *The Influence of Additive Elements on the Activity Coefficient of Sulfur in Liquid Lead at 600°C,* Trans. Met. Soc. AIME, Vol. 236, pp. 1414-1420, 1966.

*3. **Twidwell, L.G.**, *Thermodynamic Properties of Dilute Solutions in Liquid Bismuth – Part I.* Bulletin of the Bismuth Institute, Vol. 8, Supplement 6, Second Quarter, 1976, pp C52-C54.

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A GUIDE TO FIFTY YEARS OF RESEACH AT MONTANA TECH: THE TREATMENT OF ARSENIC, SELENIUM, THALLIUM, METAL BEARING SOLUTIONS AND WASTE SOLIDS (End of PART 1)

A GUIDE TO FIFTY YEARS OF RESEACH AT MONTANA TECH: PART 2 ELECTROPLATING AND ELECTROMACHINING SLUDGE (Presented in a separate document)

INTRODUCTION for Part 2

In addition to our arsenic/selenium/thallium research, EPA and NSF supported studies directed toward treating high value electroplating and electromachining hydroxide sludge materials (primarily we investigated ways to selectively recover iron, chromium, cobalt and nickel from a wide variety of industrially supplied hydroxide source material). A list of the studies with annotated comments is presented in a separate document 2022).