MWTP-84

FINAL REPORT—ARSENIC OXIDATION DEMONSTRATION PROJECT

MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY III, PROJECT 7

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U.S. Department of Energy
Federal Energy Technology Center
Pittsburgh, Pennsylvania 15236
Contract No. DE-AC22-96EW96405

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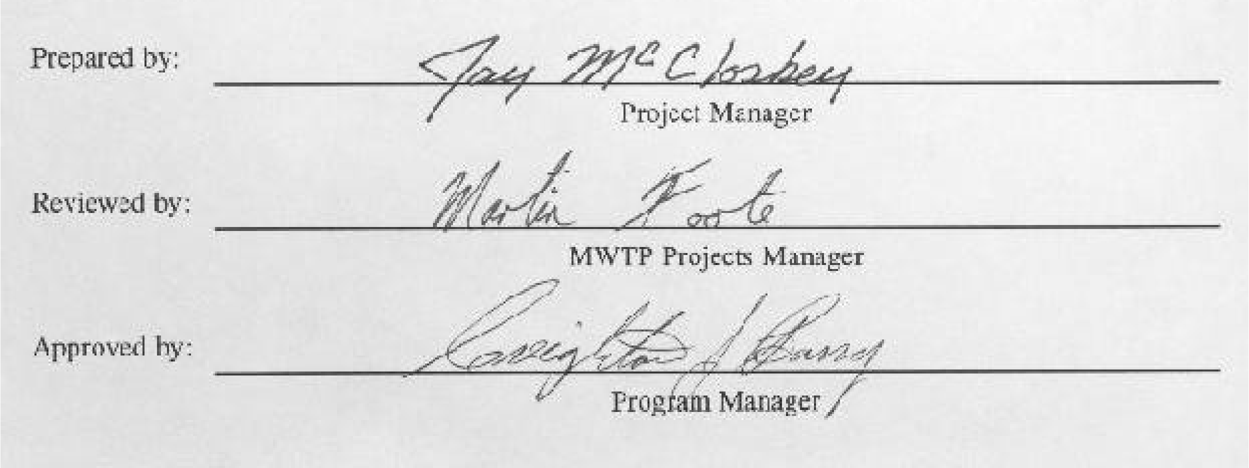

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FINAL REPORT—ARSENIC OXIDATION DEMONSTRATION PROJECT

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Foreword

Today, the mineral industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the U.S. Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. This document is a product of the research conducted by these two Federal organizations.

This document is the Final Report for EPA's Mine Waste Technology Program (MWTP) Activity III Project 7, Arsenic Oxidation Demonstration Project. The MWTP is a program developed through an Interagency Agreement between EPA and DOE. MSE Technology Applications, Inc., manages the MWTP and is responsible for the field demonstration activities and preparing this document. The information generated under this program provides a vital communication link between the researcher and the user community.

One of the objectives of the MWTP is to identify the types of mining wastes impacting the nation and the technical issues that need to be addressed. Other objectives of this program are: 1) address these technical issues through application of treatment technologies, 2) determine the candidates' technologies that will be tested and evaluated, and 3) determine the candidate waste form/sites where these evaluations will take place.

Executive Summary

This document is the Final Report for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP) Activity III Project 7, Arsenic Oxidation Demonstration Project. The MWTP is a program developed through an Interagency Agreement (IAG) between EPA and the U.S. Department of Energy (DOE). MSE Technology Applications, Inc. (MSE) manages the MWTP and owns/operates the MSE Testing Facility in Butte, Montana. MSE proposed and was granted funding for the Arsenic Oxidation Demonstration Project during the December 1994 IAG Management Committee Meeting.

Acidic metal-bearing water draining from remote, abandoned mines has been identified by the EPA as a significant environmental/health hazard in the Western United States. Many of these waters contain dissolved arsenic in the trivalent and pentavalent state. The arsenic problems in discharge streams are directly related to the EPA's Technical Issue *Mobile Toxic Constituents–Water*. The National Drinking Water Standard is 50 parts per billion (ppb). The World Health Organization revised the guideline for arsenic in drinking water from 50 to 10 ppb in 1993 (Ref. 1). The effective removal of dissolved arsenic(III) [As(III)] from water to concentrations of less than 10 ppb requires an oxidation step. Consequently, oxidants such as hydrogen peroxide (H_2O_2) or chlorine-based oxidants are generally used in a pretreatment step since the oxidation rate of dissolved As(III) by air (oxygen) is extremely slow.

The purpose of the Arsenic Oxidation Demonstration Project was to demonstrate alternative treatment technologies capable of oxidizing As(III) in mineral industry effluents to As(V) and to effectively immobilize the arsenic. Several technologies with potential application to treat the arsenic problem were presented in the MWTP Activity I, Volume 5, *Issues Identification and Technology Prioritization Report—Arsenic*. Each technology was screened and prioritized on the basis of their potential to reduce arsenic levels of mobility and toxicity in the mineral industry.

In January 1996, an agreement between the Australian Nuclear Science and Technology Organization (ANSTO) and MSE was signed for the demonstration of the ANSTO process to oxidize and immobilize arsenic. After a laboratory-scale test was completed to confirm the veracity of the claims for the oxidation process, three ANSTO officers, in collaboration with MSE staff, performed the pilot-scale demonstration in Montana in August–September 1996. This report addresses the results of the pilot demonstration project and the subsequent leachability testing of the arsenical residues produced during the demonstration. Researchers at ANSTO discovered that, in the presence of light and dissolved iron compounds, the oxidation rate of dissolved As(III) by oxygen can be increased by more than four orders of magnitude (Ref. 2). The oxidized arsenic can then be removed by an iron coprecipitation process, thus, effectively utilizing the photo-absorber to immobilize the arsenic.

In this project, the ANSTO processes to photo-oxidize, remove and immobilize arsenic were demonstrated using: (1) acid mine water from Susie Mine, an abandoned hardrock gold, silver, and lead mine located near Rimini, Montana that has an arsenic(III) concentration of about 12 part per million (ppm); and (2) a water leachate from arsenic-trioxide rich flue dust from past roasting of nickel ore in Western Australia. The U.S. Patent Office has granted a patent for the photo-oxidation process, U.S. Patent no. 5,688,378, *Photoassisted Oxidation of Species in Solution*.

The specific findings from the demonstration work listed according to the specific objectives of the project, which are essentially the claims for the technology, are listed below.

Objective 1.
To demonstrate that the photo-assisted oxidation process can oxidize at least 90% of the initial dissolved As(III) in the test streams.

- The project was successful in demonstrating the effectiveness of the photochemical process to oxidize dissolved As(III). Both sunlight and artificial light from ultraviolet (UV) lamps can be used to initiate and sustain the photochemical process. The completion of the oxidation process was confirmed by the analyses of arsenic in the residues produced during the demonstration: at least 97% of the arsenic was As(V).

- As previously determined at ANSTO, ferric chloride was the most effective iron compound to add to the reaction mixture to initiate the photochemical reaction. As a photo-absorber, it undergoes photolysis to produce reactive radicals with high oxidative potentials. Hydrochloric acid (HCl) is required to acidify the reaction mixture to pH less than 2 to 3 to keep the photo-absorber, iron(III) [Fe(III)], in solution. Sulfuric acid can be used but the rate of oxidation is slower in sulfate solutions.

- During photo-oxidation tests using acid mine water collected from the abandoned Susie Mine site, As(III) was preferentially oxidized in the presence of a large excess of dissolved iron(II) [Fe(II)] (Fe(II)/As(III) mole ratio of 22/1). In conventional treatment systems for oxidizing As(III), dissolved Fe(II), which is usually present, represents an extra chemical oxidant demand that has to be satisfied during the oxidation of As(III).

- Although it has been reported that there are hundreds of acid mine drainage waters containing arsenic in the Western United States, only seven sets of chemical composition data with arsenic and iron speciation analyses were available before this project commenced. The As(III) concentrations ranged from 150 to 11,420 ppb, while the Fe(II)/As(III) mole ratios ranged from 12 to 506. Of the seven sets of data, the highest As(III) concentration was that of Susie Mine water with an Fe(II)/As(III) mole ratio of 39/1.

- For acid mine waters with smaller concentrations of As(III) than that of Susie Mine water, smaller dosages of Fe(III) chloride and HCl would be required.

- Characterization of the hydraulic flow behavior of the UV lamp reactor used in the demonstration project (commercially manufactured in the United States) revealed a problem in the reactor design that caused short-circuiting within the reactor. Consequently, only the batch test results were used to calculate process economics.

- Analytical results produced by the MSE-HKM Laboratory and ANSTO personnel (in situ analysis in the field) were both used for the compilation of this report. It was noted, however, that the method for separating As(III) from As(V) using ion-exchange resins as used by the MSE-HKM Laboratory is adversely affected when As(V) in the sample is present at high concentrations or as iron arsenate colloidal particles. The method is designed primarily for trace amounts of arsenic in ground water.

Objective 2. To reduce the concentration of dissolved arsenic in the test water to a level under the drinking water limit for arsenic established by the World Health Organization of 10 parts per billion (ppb).

- The removal of oxidized As(V) after photo-oxidation from the test stream to residual levels of less than 10 ppb using iron coprecipitation was not achieved during the field demonstration with the equipment available. Three iron coprecipitation procedures using oxidized Susie Mine water performed during the field demonstration gave residual arsenic concentrations in the filtrate of 17, 35, and 53 ppb. However, the same coprecipitation and analysis procedure performed five times in the ANSTO analytical laboratory gave results ranging from 1 to 5 ppb.

- The coprecipitation process can be optimized to remove both arsenic and some heavy metals. The concentrations of chloride and sulfate in the treated water, however, may be greater than the regulatory discharge limits.

Objective 3. To render the arsenic-bearing precipitate generated by the flue dust and mine water tests environmentally stable.

- The arsenic-bearing solids produced by the iron coprecipitation process (with and without Portland cement solidification) met the requirements of both the EPA’s Toxicity Characteristic Leaching Procedure and another more specific leach test using aerated water lasting 3 months. The second more specific leach test is used to verify whether arsenic is present in the residues as iron/arsenate material, which is stable under storage conditions. Calcium arsenate compounds, which are subject to decomposition by dissolved atmospheric carbon dioxide, may form during the lime neutralization operation usually practiced in conjunction with the iron coprecipitation process.

Although there are limits to conclusions that can be drawn from a single-field demonstration, process economics on the application of the photochemical process to the treatment of acid mine water was calculated based on test results using Susie Mine water. It should be noted, however, that the cost data are approximate figures and several factors affecting the process economics are highly site-specific (e.g., the composition of the effluent to be treated, reagent and electric power costs, local climate, and the value of land occupied by solar ponds).

- The total cost (per thousand gallons of water) for arsenic oxidation of Susie Mine water is \$1.50 using a UV lamp reactor, or \$1.00 using solar ponds. Both the reagent and operating cost would be less for acid mine waters with lower concentrations of As(III).

- For comparison, the equivalent cost using calcium hypochlorite is \$1.75, or \$2.90 using potassium permanganate (H_2O_2, which is a cheaper oxidant, reacts too slowly with As(III) at room temperature to be considered). All the cost data were calculated based on the (bulk) price of reagents without consideration of transportation costs to remote mine sites. The operation and maintenance as well as the capital cost is based on a small plant of 15 gallons per minute (gpm) or a set of solar ponds of 22,000 gallons total capacity. For a given As(III) concentration, the cost of the required chemical oxidant would increase with an increase in the Fe(II)/As(III) ratios.

- Compared to the cost of alternative chemical oxidants such as calcium hypochlorite or hydrogen peroxide, the photochemical process is less attractive when used to oxidize As(III) in the hot flue dust leachate from treating flue dust with a hot leach process.

Despite the need for more survey data on the composition of acid mine waters in order to assess the more general application of the oxidation technology, the main conclusion that can be drawn from this project is that the photo-oxidation/iron coprecipitation process was successfully demonstrated to treat arsenical acid mine water and that the process economics appear to be very promising.

Acknowledgments

This document, the Arsenic Oxidation Demonstration Project Final Report, was prepared for the EPA NRMRL in Cincinnati, Ohio, and the DOE Federal Energy Technology Center (FETC) in Pittsburgh, Pennsylvania, by MSE under contract DE-AC22-96EW96405 and the Technology Developer, Australian Nuclear Science and Technology Organization (ANSTO) and the Cooperative Research Centre for Waste Management and Pollution Control Limited (CRC). The Arsenic Oxidation Demonstration Project was conducted under the Mine Waste Technology Program (MWTP) funded by the EPA. The MWTP is jointly administered by EPA and DOE through an Interagency Agreement. MSE manages the MWTP and owns/operates the MSE Testing Facility in Butte, Montana.

Mr. Roger Wilmoth from NRMRL served as EPA MWTP Program Manager, Mr. David Ferguson from NRMRL served as the EPA Technical Project Manager, and Mr. Melvin Shupe from DOE served as DOE Technical Program Officer. Dr. Des Levins served as the ANSTO Project Manager, Dr. Ging Khoe served as the ANSTO Technical Project Manager, Geoff Tapsell served as the ANSTO Field Technical Project Manager. Mr. Creighton Barry served as the MSE Program Manager, Dr. Martin Foote served as the MSE MWTP Projects Manager, and Mr. Jay McCloskey served as MSE's Technical Project Manager. The organization and execution of the MWTP Arsenic Oxidation Demonstration Project was a collaborative effort between the participants mentioned above.

Further recognition is due to ANSTO for writing their Arsenic Oxidation Demonstration Project report, which was utilized almost in its entirety in this report.

In addition to the people listed above, the following agency and contractor personnel contributed their time and energy by participating in the Arsenic Oxidation Demonstration Project and preparing this document.

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Contents

Page

Contents (cont.)

Tables

Tables (cont.)

Tables (cont.)

Figures

Figures (cont.)

Figures (cont.)

Page

Figures (cont.)

Acronyms, Abbreviations, and Chemical Symbols

ANSTO	Australian Nuclear Science and Technology Organization
As	arsenic
As(III)	arsenic(III), arsenite
As(V)	arsenic(V), arsenate
atm	atmospheres
BDAT	best demonstrated available technology
BLB	black light blue (lamp) wavelength
cm	centimeter
cm^2	square centimeter
CRC	Cooperative Research Centre for Waste Management and Pollution Control Limited
DO	dissolved oxygen
DOE	U.S. Department of Energy
E_H	oxidation-reduction potential
EPA	U.S. Environmental Protection Agency
Fe	iron
Fe(II)	iron(II)
Fe(III)	iron(III)
FETC	Federal Energy Technology Center
FOB	freight on board
g	grams
g/L	grams per liter
gpm	gallons per minute
H_2H_2	hydrogen peroxide
HCl	hydrochloric acid
IAG	Interagency Agreement
ICP	inductively coupled plasma (spectrophoto)
ICP-AES	inductively coupled plasma atomic emission spectroscopy
J	joule
kg	kilogram
kW	kilowatt
kWh	kilowatt hours
L	liter
L/min	liters per minute
MDSL	Montana Department of State Lands
mg/L	milligrams per liter
ml	milliliter
mm	millimeter
Montana Tech	Montana Tech of the University of Montana
MSE	MSE Technology Applications, Inc.
mV	millivolts
mW	milliwatt

Acronyms, Abbreviations, and Chemical Symbols (Cont.)

MWTP	Mine Waste Technology Program
nm	nanometer
NRMRL	National Risk Management Research Laboratory
ppb	parts per billion
ppm	parts per million
QA	quality assurance
QA/QC	quality assurance/quality control
QAPP	quality assurance project plan
scfm	standard cubic feet per minute
Se	selenium
TCLP	toxicity characteristic leaching procedure
UV	ultraviolet
UVA	near-ultraviolet component of light
W	watt
W/L	watts per liter
µg/L	micrograms per liter
µM/L	micromoles per liter

1. Introduction

This document is the Final Report for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP) Activity III Project 7, Arsenic Oxidation Demonstration Project. The MWTP is a program developed through an Interagency Agreement (IAG) between EPA and the U.S. Department of Energy (DOE). MSE Technology Applications, Inc. (MSE) manages the MWTP and owns/operates the MSE Testing Facility in Butte, Montana. MSE proposed and was granted funding for the Arsenic Oxidation Demonstration Project during the December 1994 IAG Management Committee Meeting.

The purpose of the Arsenic Oxidation Demonstration Project was to demonstrate alternative treatment technologies capable of oxidizing arsenic(III) [As(III)] in mineral industry effluents to arsenic(V) [As(V)], then to effectively immobilize the arsenic. Several technologies with potential application to treat the arsenic problem were presented in the MWTP Activity I, Volume 5, *Issues Identification and Technology Prioritization Report—Arsenic*. Each technology was screened and prioritized on the basis of its potential to reduce arsenic levels of mobility and toxicity in the mineral industry.

The analytical methods and pilot-scale treatment testing conducted for this study were consistent with EPA's requirements outlined in the project-specific Quality Assurance Project Plan (QAPP) for the Removal of Arsenic from Waste Solutions as Storable Stable Precipitates (Ref. 3). This final report describes the work that was conducted and summarizes the technical results that were obtained to evaluate treatment technologies for mineral industrial wastewaters. Refer to the QAPP (Ref. 3) for detailed descriptions of the process operations.

In January 1996, an agreement between Australian Nuclear Science and Technology Organization (ANSTO) and MSE was signed for demonstrating the ANSTO process to oxidize and immobilize arsenic. ANSTO has considerable experience in the chemistry of arsenic and heavy metal removal from waste effluents. After a laboratory-scale test was completed to confirm the veracity of the claims for the oxidation process, three ANSTO officers, in collaboration with MSE staff, performed the pilot-scale demonstration in Montana in August–September 1996. This report addresses the results of the pilot demonstration project and the stability testing of the arsenical residues produced during the demonstration.

The U.S. Patent Office has granted a patent for the photo-oxidation process, U.S. Patent no. 5,688,378, *Photoassisted Oxidation of Species in Solution*.

1.1 Scope of the Problem

Acidic metal-bearing water draining from remote, abandoned mines has been identified by the EPA as a significant environmental/health hazard in the Western United States. Many of these waters contain dissolved arsenic in the trivalent and pentavalent state (Ref. 4).

Arsenic compounds and solutions are also frequently an unwanted by-product of the mining and extraction of metals such as copper, gold, lead, and nickel. Their production will continue to grow as high-grade ores with low-arsenic content are depleted, and the processing of sulfide ores with high arsenic content becomes increasingly common. A more notable example of arsenic-bearing wastes from processing of such ores is the flue dust from roasting and smelting. It is one of the most concentrated sources of arsenic trioxide. Large quantities of flue dust from past and current mineral-processing operation are being kept in temporary storage pending the development of safe disposal methods.

The U.S. National Drinking Water Standard is 50 parts per billion (ppb). Due to concerns for cancer risk associated with arsenic, the World Health Organization revised the guideline for arsenic in drinking water from 50 to 10 ppb in 1993 (Ref. 1). The effective removal of dissolved As(III) from water to concentrations of less than 10 ppb requires an initial oxidation step prior to effective precipitation. Furthermore, As(III) compounds are more environmentally mobile than those of As(V). Consequently, since the oxidation rate of dissolved As(III) by air is extremely slow, oxidants such as hydrogen peroxide (H_2O_2) or chlorine-based oxidants are used in a pretreatment step to obtain effective arsenic removal and immobilization.

Researchers at ANSTO discovered that, in the presence of light and dissolved iron compounds, the oxidation rate of dissolved As(III) by air [dissolved oxygen (DO)] can be increased by more than four orders of magnitude (Ref. 2). The oxidized arsenic can then be removed by an iron adsorptive coprecipitation process, thus, effectively utilizing initial photo-absorber to immobilize the arsenic. This early research was funded in Australia by the Cooperative Research Centre for Waste Management and Pollution Control Limited (CRC), an organization established by the Australian Government to advance science and technology through cooperative research of universities, companies, and research institutions.

1.2 Demonstration Objectives

The primary objective of this project was to assess the effectiveness of ANSTO processes to photo-oxidize As(III), and remove and immobilize the oxidized arsenic using an iron coprecipitation process. More specifically, the objectives of this project have been defined as listed below:

C To demonstrate that the photo-assisted oxidation process can oxidize at least 90% of the initial dissolved As(III) in the test streams.

C To reduce the concentration of dissolved arsenic in the test water to a level less than the drinking water limit for arsenic established by the World Health Organization of 10 ppb.

C To render the arsenic-bearing precipitate generated by the flue dust and mine water tests environmentally stable in accordance with regulatory criteria. The dewatered and solidified precipitate will be subjected to leachability testing using EPA's Toxicity Characteristic Leaching Procedure (TCLP) in which the concentration of arsenic in the TCLP leachate will be less than the limit of 5 parts per million (ppm).

1.3 Process Description

A general schematic diagram of the processes included in this project is shown in Figure 1-1. Dissolved As(III) in the test solutions is converted to As(V) using the ANSTO photo-assisted oxidation process in which dissolved inorganic iron is used as the light absorber. For test streams that are deficient in dissolved iron, inorganic iron salts such as ferric chloride were added as a photoabsorber.

Two light sources were used during the demonstration: sunlight and low-pressure mercury lamps. The photo-oxidation process was performer in a batch-wise and flow-through manner using:

– solar troughs and ponds; or
– an Ultrox photo-reactor fitted with 24 low-pressure mercury vapor lamps of 65-watt (W) capacity each.

In this report, reference to arsenic(III) or As(III) will include all arsenite species in which the arsenic is present in the trivalent oxidation state, and reference to arsenic(V) or As(V) will include all arsenate species in which the arsenic is present in pentavalent oxidation state. Similarly, iron(II) or Fe(II) refer to ferrous species of divalent oxidation state, and iron(III) or Fe(III) refer to ferric species of trivalent oxidation state.

1.3.1 Light-Assisted Oxidation of As(III)

Thermodynamically, dissolved oxygen in water in ambient conditions is capable of oxidizing As(III). The reported kinetics data, however, indicate that the oxidation rate is extremely slow. (Ref. 5) reported that the rate has a complex dependence on pH: in acid region the rate is decreased as the pH is raised from 2 to 5.5.

However, even at pH 2 at pO_2 of 0.2 atmosphere (atm) at 25EC, only 9% of the initial As(III) concentration of 100 micromoles per liter (FM/L) [7.5 milligrams per liter (mg/L)] was oxidized in 100 days. Johnson and Pilson (Ref. 6) also reported an extremely slow rate of oxidation in seawater (pH 8.2): 0.023 FM [1.7 micrograms per liter (Fg/L)] of As(III) per year.

Figure 1-2 shows that while As(III) alone is not oxidized in the presence of sunlight, the oxidation reaction proceeds rapidly at a pH around 3 in the presence of dissolved iron. Compared to the rate reported by Eary and Schramke (Ref. 5), ANSTO engineers discovered that the rate of oxidation of As(III) was increased by more than four orders of magnitude using dissolved iron(III) [Fe(III)] as a photoabsorber.

The photolysis reactions of Fe(III) in water involve the transfer of one electron from the complexed ligand, such as organic, hydroxide, or chloride species, to the Fe(III)-centered orbital forming Fe(II) and a free radical (Refs. 7, 8, and 9). The subsequent reaction of the free radical with As(III) or dissolved oxygen produces photochemical chain reactions that result in the oxidation of As(III) and, sometimes, Fe(II) as well.

$$\begin{gathered} Fe^{3+}(OH)^- \text{----}^{hv}\text{---->} Fe^{2+} + OH^- \\ FeCl^{2+} \text{----}^{hv}\text{---->} Fe^{2+} + Cl^- \end{gathered} \tag{1-1}$$

Experimental results show that the rate of oxidation of As(III) in the ANSTO process increases with the increase in the net light power input to the reaction mixture (Figure 1-3). Consequently, it is essential that the electrical power input to the ultraviolet (UV) lamp reactor and the photon input to the reaction mixture are measured accurately during the demonstration.

Considerable research has been undertaken to characterize the arsenic photo-oxidation reaction. It was found that the oxidation rate is generally enhanced by the decrease in pH and an increase in chloride concentration. Since the kinetics of the oxidation reaction is not directly affected by the initial As(III) concentration, the process can be used to treat streams with high or low initial arsenic concentrations.

1.3.2 Removal of As(V) Using Iron Adsorptive-Coprecipitation

According to a recent EPA report (Ref. 10), the best demonstrated available technology (BDAT) for removing dissolved arsenic and heavy metals is chemical precipitation. Coprecipitation with excess iron is usually practiced because of the availability of iron at low/no cost and also in order to meet the low limits for dissolved contaminants (Ref. 11).

Test work performed in ANSTO laboratories using acid mine water samples showed that the concentration of arsenic in the filtrate, after they were neutralized with lime to pH 7, was greater than 10 ppb unless all of the initial arsenic was present as As(V) (Ref. 12).

1.3.3 Immobilization of Arsenic as Ferric/Arsenate Solid

Bench-scale studies in ANSTO laboratories indicated that dried arsenic-bearing hydrous ferric oxide precipitate and the cement-solidified monoliths easily passed EPA’s TCLP (Ref. 13) as well as a long-term leach test using aerated water (developed at ANSTO). These compounds represent a promising waste form for arsenic disposal. This is supported by the findings from a long-term monitoring program of ferric/arsenate precipitates in the Inco's Copper Cliff tailings dump (Ref. 14). The presence of ferric/arsenate material in medieval mining dumps that have existed for over 500 years is testimony to the high stability of these compounds under normal weathering conditions (Ref. 15).

1.3.4 Leachability Testing

The aerated-water test was developed because some arsenic-bearing solids that had already passed TCLP failed when they were placed in water containing dissolved carbon dioxide. Iron/arsenate compounds are immune to reactions with dissolved carbon dioxide. However, other metal arsenates, such as calcium- and zinc-arsenate, which may form during the lime neutralization step, are not stable in the presence of dissolved carbon dioxide. For example, calcium arsenate can be converted to calcium carbonate, and release arsenic, due to the reaction with atmospheric carbon dioxide (Ref. 16).

1.4 Site Description

1.4.1 Rimini

The demonstration was performed at the Valley Forge/Susie Mine site in Rimini, Montana, located approximately 15 miles west of Helena, Montana. The Susie Mine site is located in the center of town and occupies a small city lot adjacent to Ten Mile Creek. Rimini's primary road runs through the property. Figure 1-4 is the Rimini site location and vicinity map site plan.

1.4.1.1 Site History

In the late 1800s, Rimini was a trade center for a mining district that produced gold, silver, zinc, and lead. The town consists of one long street lined with many false-front frame buildings and a second street parallel to and behind it, also filled with houses and cabins. Rimini is one of the oldest lead-zinc camps in Montana. Placers above Rimini were worked during the 1870s, 1880s and from 1900 to 1903. Mining in the area has been abandoned since 1920.

1.4.1.2 Site Characteristics

The Susie Mine is an abandoned gold mine that was reclaimed under Montana Department of State Lands (MDSL) Abandoned Mine Reclamation Program. The mine portal was closed and the tailings dump immediately outside the portal was capped and vegetated. Water is discharging from the tailings dump at a rate of approximately 5 gallons per minute (gpm) through a 6-inch-diameter plastic pipe. The water flows under the road through an 8-inch culvert and continues above ground on the west side of the road until it enters Tenmile Creek. A large 20 by 30 foot (ft) canvas tent was erected to house the equipment for the ANSTO/MSE demonstration. The area where the tent was located and the demonstration was held was a reclaimed mine tailings dump. Figure 1-5 illustrates the solar reactors as they were situated during the demonstration.

1.4.2 MSE Testing Facility

The field demonstration was moved to the MSE Testing Facility Resource Recovery Building to conduct the photoreactor tests. The facility is located approximately 3 miles south of Butte, Montana (see Figure 1-4). Figure 1-5 shows the photoreactor as it was set up during the demonstration at the MSE Testing Facility.

1.4.3 MSE-HKM Laboratory

All quality assurance (QA) inorganic chemical analyses, with the exception of long-term leach testing, for the samples collected were conducted at the MSE-HKM Laboratory, which is located approximately ¼-mile south of the MSE Testing Facility. Long-term leach testing was performed at ANSTO in Australia following the demonstration.

1.5 Project Schedule and Operation

Formal field testing began on August 5, 1996 and concluded on September 19, 1996. Preliminary laboratory testing was performed by ANSTO in Australia and additional optimizing laboratory testing was performed at the MSE Testing Facility prior to going to the field. The field demonstration was split into two phases: (1) solar testing; and (2) photoreactor testing. The scheduling of the field demonstrations was governed by the need to perform the solar tests first to take advantage of the late summer sunlight and the scheduled delivery of the Ultrox photoreactor (Ultrox reactor) in September 1996. The schedule for tasks associated with the Arsenic Oxidation Demonstration Project was very aggressive and is presented in Table 1-1.

Because of legal complications over the use of the Susie Mine site, the solar test program was completed, and the demonstration project was moved to the MSE Testing Facility where the photoreactor with Susie Mine water testing was completed on August 26, 1996.

ANSTO personnel, in collaboration with MSE staff, carried out the scheduled test work as well as arsenic analyses. Analytical results produced by ANSTO personnel and the MSE-HKM Laboratory are used in this report.

After all testing was completed, arsenic-bearing filter cakes produced from the demonstration project were shipped to Australia and tested for leachability at ANSTO laboratories in Sydney from December to February 1997.

1.6 Project Organization and Responsibilities

1.6.1 MWTP

The MWTP is funded by EPA and is jointly administered by EPA and DOE through an IAG. MSE owns/operates the MSE Testing Facility and manages the MWTP. The MWTP's primary objective is to advance the understanding of engineering solutions to national environmental issues resulting from past practices in the mining and smelting of metallic ores.

The MWTP consists of the following six activities:

Activity I:
Montana Tech of the University of Montana (Montana Tech) will develop a data base of information on technical issues, mine waste forms, treatment technologies, and characterized mine waste sites.

Activity II:
Montana Tech will develop a generic QAPP for the MWTP as a whole and the pilot- and bench-scale projects conducted under Activities III and IV.

Activity III:
MSE will conduct large pilot- or field-scale demonstrations of applicable treatment technologies.

Activity IV:
Montana Tech will conduct small bench- or pilot-scale research projects on remediation technologies that show promise for treating mine wastes.

Activity V:
MSE will prepare documentation and conduct technology transfer for the MWTP.

Activity VI:
Montana Tech will develop the educational component of the MWTP.

Under Activity III, MSE conducts large pilot/field-scale demonstrations of innovative technologies for the remediation of mine waste. This project is the MWTP Activity III, Project 7, Arsenic Oxidation Demonstration Project.

1.6.2 Project Management

An overall MWTP project organization chart and a general description of the project responsibilities for the MWTP activities are presented in this Final Report (see Figure 1-6). Specific EPA, DOE, and MSE project officers and their respective responsibilities for Activity III, Project 7 are listed below.

***EPA Project Officer*—**Roger Wilmoth: Responsible for all MWTP projects.

***EPA Technical Project Manager*—**Dave Ferguson: Responsible for EPA project management for MWTP and reviewing and approving the final project report.

***DOE Project Officer*—**Mel Shupe: Responsible for DOE participation in the MWTP and reviewing and approving the final project report.

***NRMRL QA Associate*—**Kim McClellan: Responsible for reviewing and endorsing the QAPP.

***MSE Program Manager*—**Creighton Barry: Responsible for senior review of all project plans and deliverables and for ensuring that the project objectives are achieved within schedule and budget constraints.

MSE Senior Project Manager—Martin Foote: Responsible for all MWTP projects at the MSE level. Informs the Program Manager of the project status and of any technical/administrative/ contractual/financial issues and proposed resolutions.

MSE Project Manager—Jay McCloskey: Responsible for ensuring that the project is conducted according to the appropriate plans and that all project activities are documented in a project file.

MSE Project Test Engineer—Dick Harned: Responsible for developing process equipment design, equipment installation, and site logistics.

MSE Program Support Manager—Vince Tonc: Responsible for all aspects of program support including safety and health and quality assurance/quality control (QA/QC).

MSE Project QA Manager—Ken Reick: Responsible for reviewing and submitting QA Reports to the Project Manager and for reviewing QA section(s) of project reports.

MSE Project QA Officer—Helen Joyce: Responsible for developing the project QAPP and auditing test personnel and equipment and for submitting audit findings to the QA Manager.

MSE-HKM Laboratory Manager—Kevin Kissell: Responsible for ensuring that all analytical data meets quality objectives and for reviewing all laboratory reports.

MSE-HKM Laboratory QA Officer—Pat Seccomb: Responsible for reviewing all analytical data associated with the project and submitting findings to the QA Manager.

ANSTO Project Manager—Dr. Ging Khoe: Responsible for ensuring that the project is conducted according to the specified plans, that the technology is demonstrated, that it meets the project objectives, and that all project activities are documented in a project file.

A project organization chart delineating lines of authority is presented in Figure 1-6.

1.6.3 Communications

Formal external communications shall originate from and be received by the MWTP Program Manager. Formal internal project communications shall be accomplished through program review meetings and routine weekly, monthly, and annual reporting. Weekly project meetings will be held to discuss the project progress, problems, scheduling, and overall status. Written minutes shall be taken at each meeting and distributed to project personnel and managers.

Laboratory testing, including quality control data and documentation, shall be reported to the Project Manager on a continual basis. Upon completion of field testing, the Laboratory Manager shall submit a Final Report, complete with QA/QC documentation, to the Project Manager.

The QA Manager shall submit monthly QA reports summarizing laboratory and test site activities to the Project Manager. Corrective actions and QA reporting requirements are discussed in the QAPP (Ref. 3).

Table 1-1. Demonstration task schedule.

Date	Task
11/01/94	White paper prepared
12/14/94	White paper presented and approved at IAG Management Committee Meeting
11/07/95	Funding received to start project
12/01/95	Request for proposal sent to ANSTO
01/11/96	Received proposal, initial offer from ANSTO
02/15/96	Signed ANSTO contract
03/28/96	Visited ANSTO, discussed laboratory results and developed process design
04/15/96	ANSTO submitted laboratory-scale test report
05/15/96	ANSTO submitted process design report
06/30/96	NEPA/CX documentation approved, water discharge approval acquired
07/31/96	Site access agreements approved
07/08/96	Draft QAPP submitted
07/15/96	Began installation and fabrication at demonstration site
08/01/96	Project field test plan approved
08/05/96	Field demonstration began at Rimini (solar process demonstration)
08/25/96	Completed solar testing, started moving equipment to the MSE Testing Facility to test photoreactor
09/05/96	Began photoreactor testing
09/19/96	Completed photoreactor testing
10/15/96	Completed treating demonstration process water
02/28/97	Completed leach testing
06/30/97	Draft final report submitted

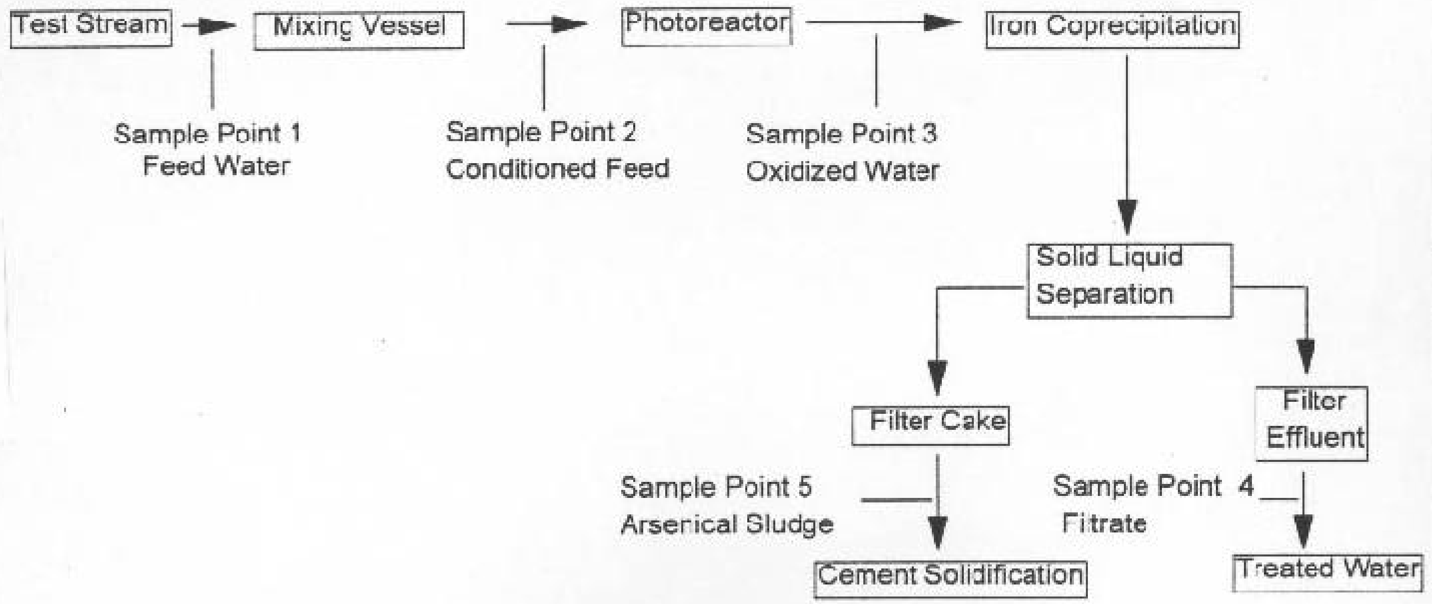

Figure 1-1. Photochemical oxidation and coprecipitation process flow diagram.

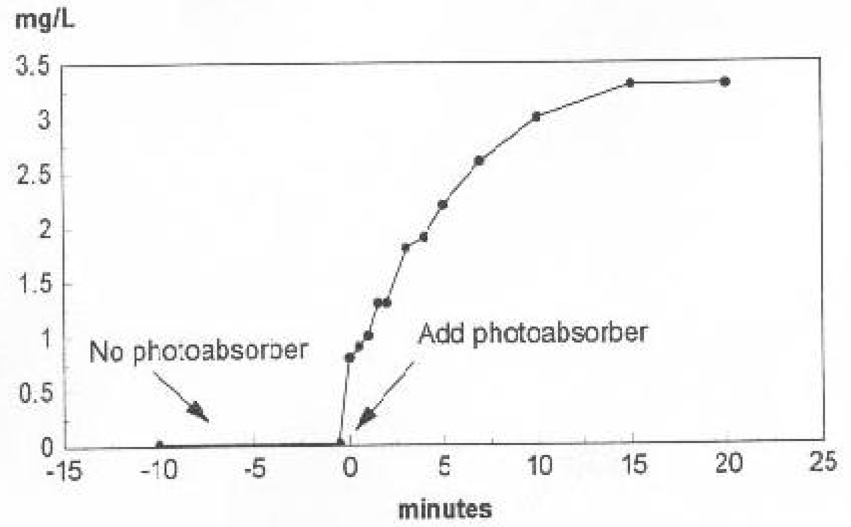

Figure 1-2. As(V) concentration in demineralized water as a function of time in the absence and presence of Fe(III) photo-absorber. Initial arsenic (III) concentration 3 mg/L, Fe(III) 28 mg/L as chloride, near-ultraviolet component of light (UVA) energy input 0.5 watts per liter (W/L).

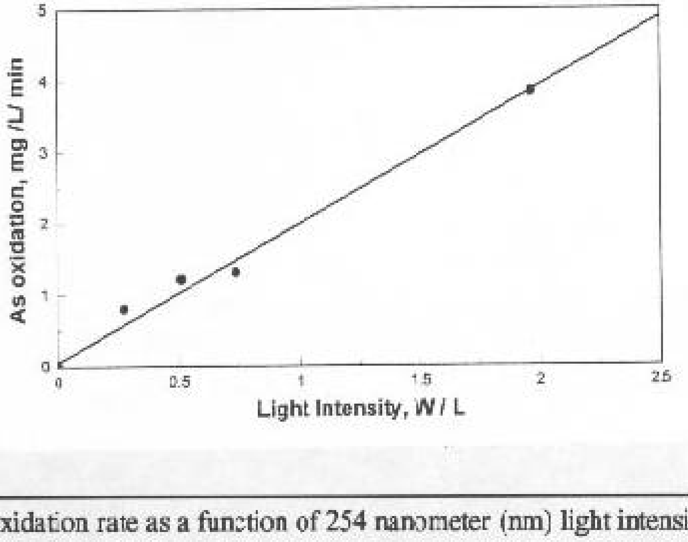

Figure 1-3. Arsenic oxidation rate as a function of 254 nanometer (nm) light intensity. pH 1, As(III) 50 mg/L, Fe(II) 74 mg/L as chloride.

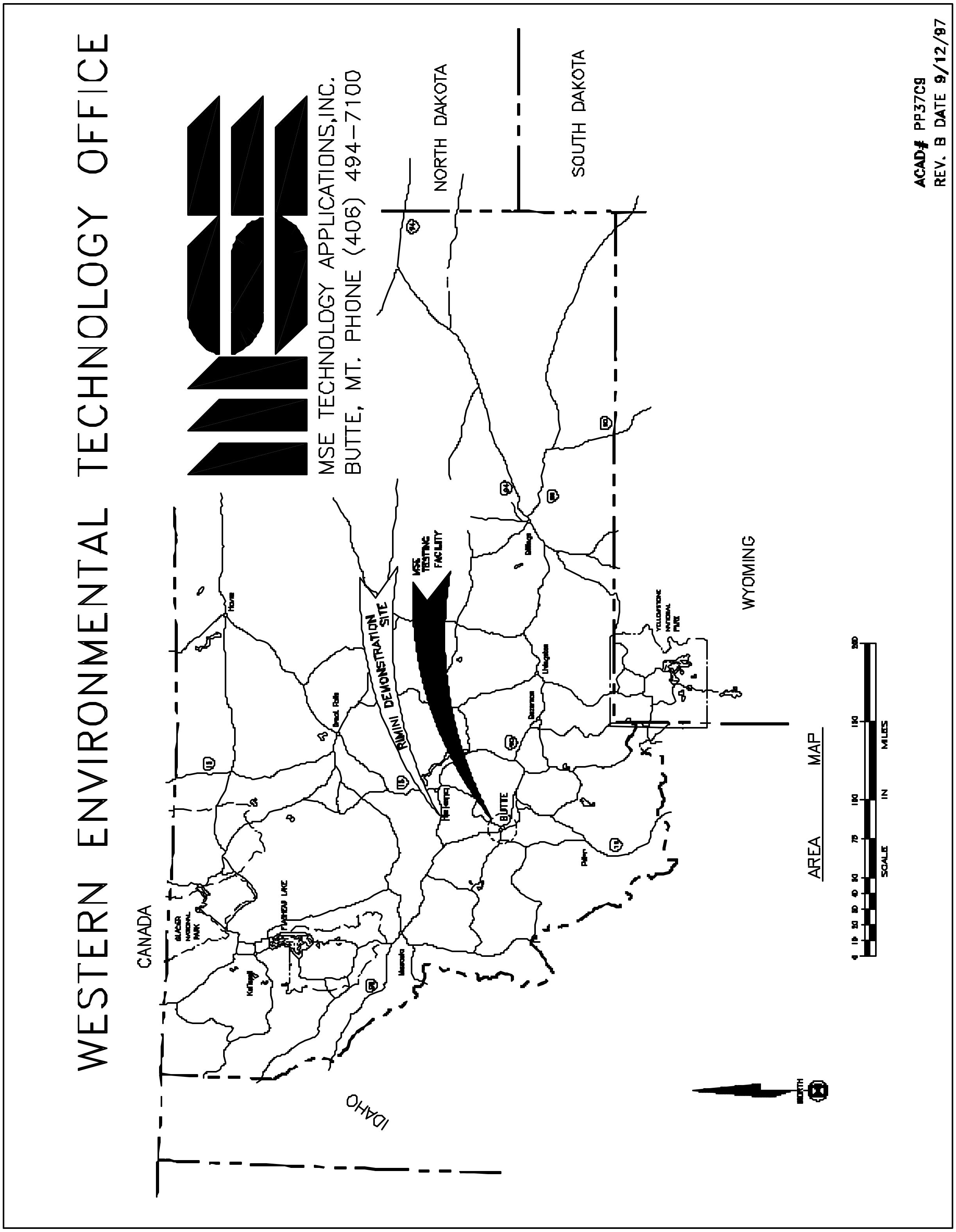

Figure 1-4. Rimini site location and vicinity map site plan.

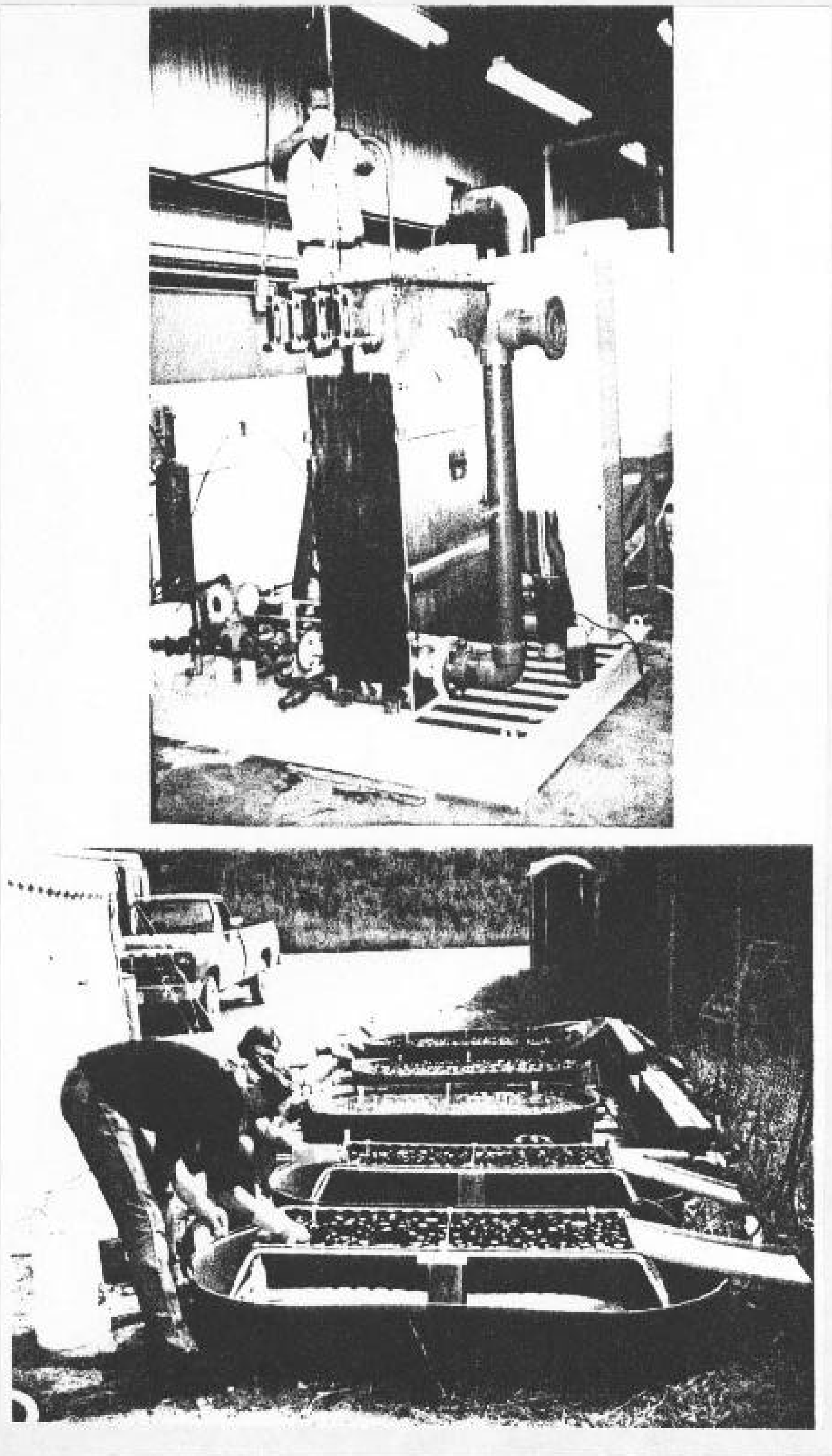

Figure 1-5. Photoreactor as it sat during the demonstration at the MSE Testing Facility.

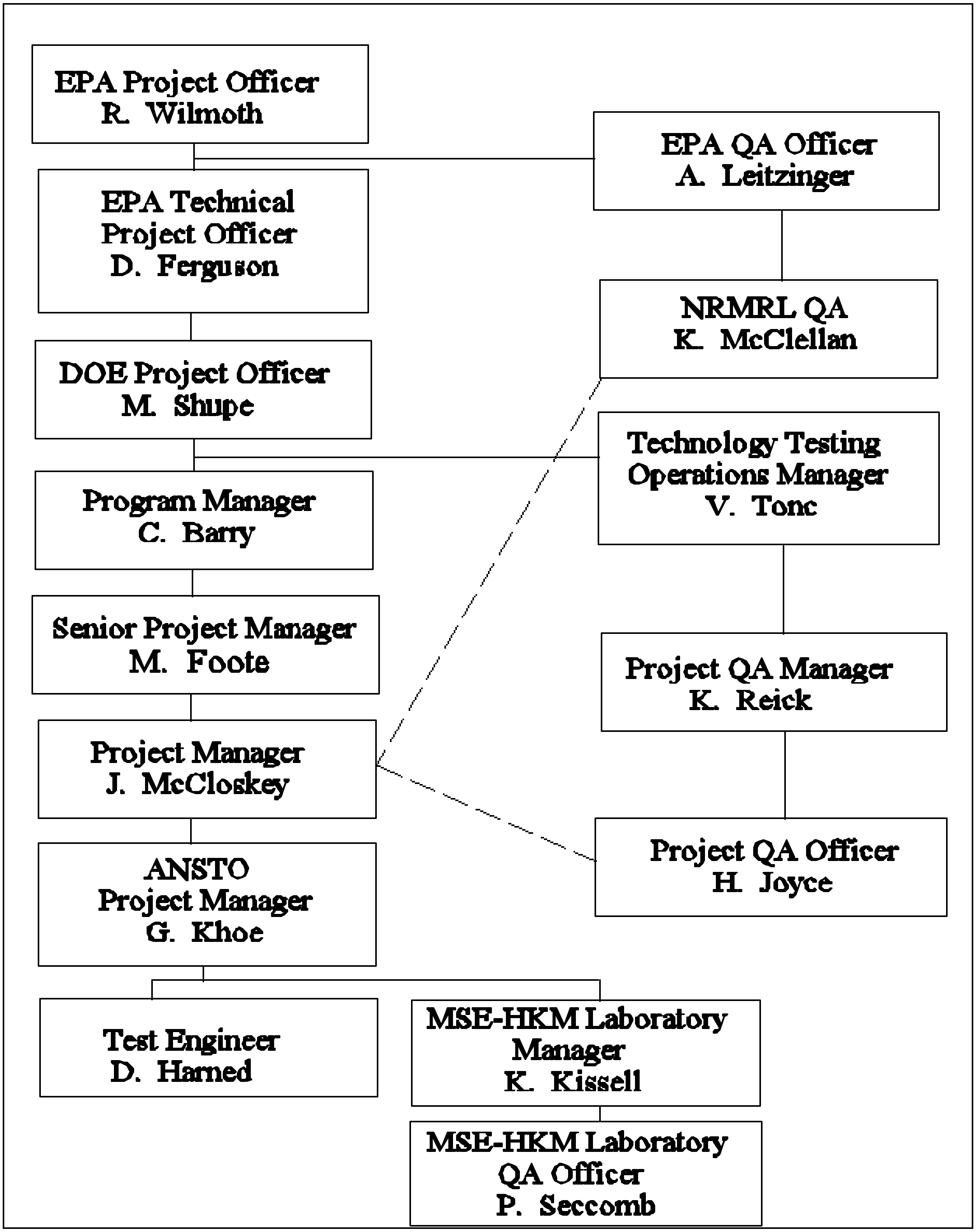

Figure 1-6. Arsenic Oxidation Demonstration Project organizational chart.

2. Process Equipment

The general schematic diagram of the processes included in this project is shown in Figure 1-1. As noted, two aqueous streams were used during the demonstration: Susie Mine water and water leachate of nickel roaster flue dust. Detailed process diagrams for the various unit operations can be found in Section 4 and also in the Process Design Report issued in June 1996 (Ref. 17).

2.1 Bench-Scale Test Apparatus

Figure 2-1 is a schematic diagram of the 1.1 liter (L) photoreactor fitted with a black light blue (lamp) wavelength (BLB). The BLB lamp is used as a simulation of the near-UV component of sunlight (wavelength 350 nm).

The schematic diagram of the UV lamp reactor is shown in Figure 2-2. A 15-W low-pressure mercury lamp that produces >90% of its light output at 254 nm is fitted in this reactor unit. The 1.7-L unit is designed to represent a miniaturized unit cell of a commercially produced Ultrox photoreactor.

2.2 Solar Ponds

The solar ponds used in the demonstration are light-weight polypropylene cattle feed troughs (Figure 1-5). Air sparging is achieved with porous plastic/rubber tubing.

Two types of solar reactors were used for the demonstration. Ninety-gallon solar ponds were used for the batch test runs using flue dust leach liquors. Smaller, 22-gallon solar troughs were used to treat acid mine water in both batch and continuous flow modes.

Flue Dust Leach Liquor:

Operation: Batch
Volume: 105 gallons (400 L)
Pond Size: 20 feet^2, 9 in. deep [1.8 meters^2, 20 feet^2, 9 in. deep [1.8 meters^2, 220 millimeters (mm) deep] 2 standard cubic feet per minute
Air Flow Rate: (SCFM)(60 liters per minute^{-1})

Operation: Batch or Continuous
Volume: 2 x 22 gallons (170 L total)
Pond Size: 2 x 7 feet^2, 8 in. deep (2 x 0.63 m^2, 200 mm deep)
Air Flow Rate: 2 SCFM (60 liters per minute^{-1}) per pond

2.3 Ultrox Reactor

The UV Reactor Module is a self-contained, stand-alone unit providing a UV source for the reaction mixture (Figure 1-5). The reactor unit contains 24, 65-W duty, lamps housed in quartz sleeves. Low-pressure, mercury arc lamps that emit UV predominantly in the 254-nm range are used. The lamps are mounted vertically in the reactor in four chambers, six lamps to a chamber. Power to each lamp is monitored on the reactor control panel. Flow is by gravity from one chamber to the next, with air sparging introduced at the bottom of each chamber. Air flow to each chamber is indicated by individual flowmeters that are part of the reactor system. The head of liquor in the reactor is approximately 5-feet. A variable speed influent feed pump and feed flowmeter were installed on the reactor skid as part of the supply, as well as sparger air filtration and pressure regulation. The UV reactor, manufactured by Ultrox, is constructed of Inconel 625 with Hastelloy C-276 air spargers. Engineering drawings of the Ultrox reactor are not given here because they are confidential property of the US Filter Company.

The reactor unit was operated in a batch mode for the demonstration to treat flue dust leach liquor. In this mode, the contents of the reactor were filled by pumping 150 gallons of feed liquor from the feed preparation tank using the reactor influent pump. When the reactor was full, power and air were turned on, and the solution was irradiated for the appropriate time. Samples were taken during the run from the chamber sample valves.

The reactor unit was operated in both batch and continuous flow mode for treating acid mine water.

2.4 Iron Adsorptive-Coprecipitation and Filtration Apparatus

The bulk precipitations were carried out in a 1,000-gallon tank fitted with stirrers and air spargers. Following precipitation, the slurries were left to settle. The underflows were then filtered using a filter press.

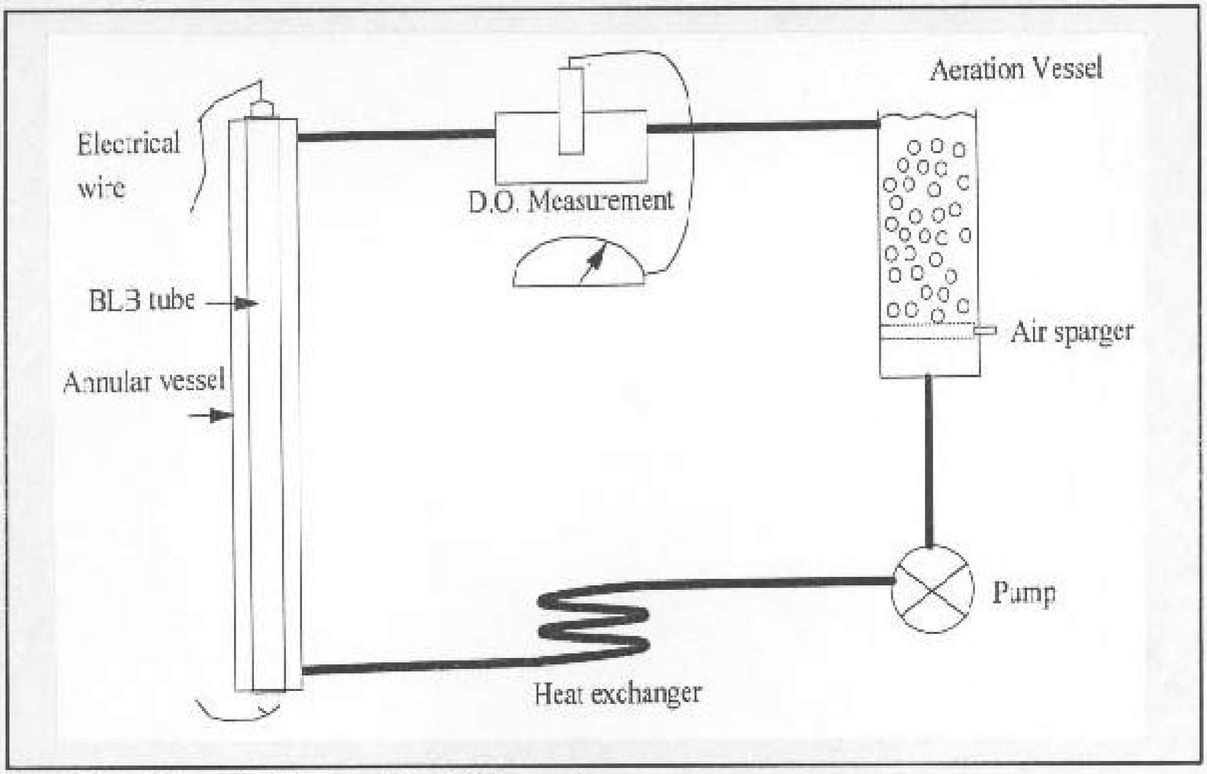

Figure 2-1. Schematic diagram of the BLB apparatus.

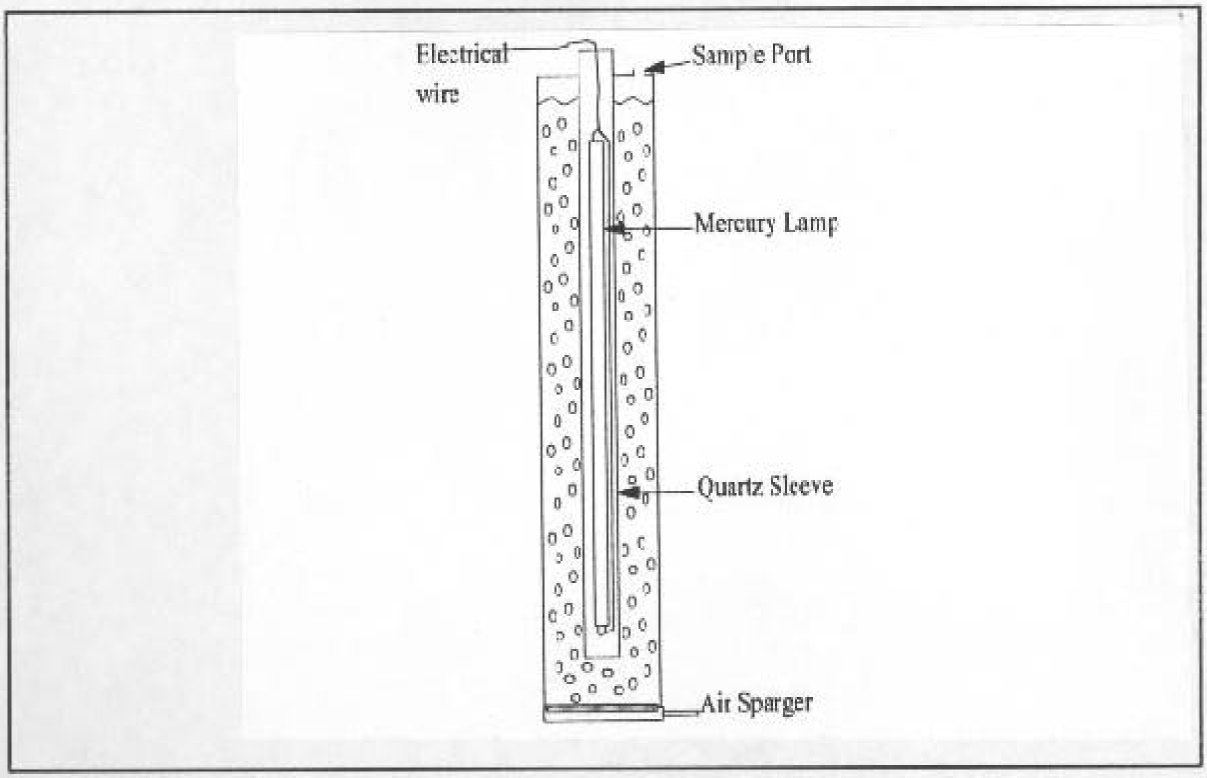

Figure 2-2. Schematic diagram of the UV apparatus with a low-pressure mercury arc lamp.

3. Bench-Scale Tests Using Susie Mine Water

Bench-scale testing using actual Susie Mine water was performed at ANSTO laboratories in May 1996. However, the composition of the Susie Mine water samples sent to Sydney changed during shipment, namely a proportion of the Fe(II) compound in the samples was oxidized and converted to Fe(III) hydroxide precipitate, which removed some of the dissolved arsenic. Consequently, bench-scale testing using Susie Mine water was repeated at the MSE-HKM Laboratory to determine the optimal dosage of acid [hydrochloric acid (HCl)] and iron (ferric chloride) for the demonstration test work at Rimini.

Two bench-scale photoreactors that were designed and manufactured at ANSTO laboratories were used for the tests at MSE. They were fitted with a 20-W BLB or a 15-W, low-pressure mercury lamp. The first was used to simulate tests using solar ponds and the second the Ultrox reactor.

The acid mine water was collected in 20-L plastic containers and filtered through a glass fibre filter paper (0.6–0.8 micron porosity) immediately before use.

3.1 Tests Using the BLB Reactor (350 nm)

BLB fluorescent tubes are commonly used to simulate the near ultraviolet component of sunlight. They emit a band of radiation from 300 to 400 nm that is centered at 350 nm. Light of these wavelengths corresponds to the near ultraviolet region of sunlight that represents about 5% of the total solar energy. Previous experiments at ANSTO showed that, despite the fact that visible light is predominant in sunlight, the ultraviolet component is responsible for half of the reaction rate in oxidizing As(III) to As(V) using appropriate conditions.

Figure 2-1 is a schematic diagram of the reactor. Because of the difference between the frequency and voltage of the electricity supply in the United States and Australia, the actual utilizable light energy produced by the lamp was measured at the MSE-HKM Laboratory using ferrioxalate actinometry (see Analytical Methods, Appendix A). If it is assumed, for calculation purposes, that the light was monochromatic with a wavelength of 350 nm, then the net light power input to the reactor would be 2.57 W/L. The path length for light in the reactor was 9.6 millimeters (mm).

Various quantities of HCl and Fe(III) chloride were added to 1.1-L lots of Susie Mine water for each test to give reaction mixtures as listed in Table 3-1. For each test, several samples, 5 milliliters (ml) each, were removed from the reaction mixture during illumination and analyzed for As(V) using the molybdenum-blue colorimetry method (Appendix A). Within each test, the concentration of As(V) increased at an approximately constant rate until all the detectable As(III) was exhausted. Therefore, the oxidation rate was calculated from the slope of a linear regression between the As(V) concentration and illumination time before 90% of the initial As(III) was oxidized.

Total arsenic in the samples was determined by preoxidizing the solution with permanganate and following the same colorimetry procedure (Appendix A). The sum of the As(III) and As(V) concentrations remained constant between each test at 11.4 mg/L. The final As(V) concentration in several of the tests also ranged from 11.1 to 12 mg/L indicating that essentially all of the As(III) initially present had been oxidized.

The initial concentration of As(V) was always less than 0.7 mg/L despite the tests being conducted over several days with one bulk supply of Susie Mine water sample. This confirms that no significant arsenic oxidation occurred in the bulk sample during storage in the dark.

The absorbencies (optical density) of the test mixtures at 300, 350, and 400 nm were determined in 1 centimeter (cm) quartz cuvettes using a UV-visible spectrophotometer. Because the bench-scale photoreactors had a much shorter path length than those found in the solar pond, some photon losses (the portion unabsorbed by the reaction mixture) would have occurred. Therefore, reaction rates were corrected for these losses using the absorbance measurement of the reaction mixtures at 350 nm. The absorbance of the sample with no HCl could not be measured as precipitation had occurred before the spectrophotometer was inibated.

The concentration of Fe(II) was determined at the beginning and end of each experiment. The initial concentrations did not vary from 180 to 193 mg/L indicating that Fe(II) in the bulk sample, like As(III), did not vary significantly during storage in the dark.

The Fe(II) concentration increased significantly during the tests with low acid addition and high Fe(III) concentrations. In these experiments, since the amount of Fe(III) reduced exceeded the amount of As(III) oxidized, ferric ion was considered to be the rate controlling oxidant. In contrast, where high amounts of HCl and lower concentrations of Fe(III) were used, the Fe(II) concentration fell during each test. In these cases, oxygen was the active oxidant.

The addition of HCl increased the arsenic oxidation rate in a near linear manner as shown in Figure 3-1. It would have been misleading to use pH on the X-axis as both the chloride and hydrogen ion concentrations were increased by adding of HCl. Previous studies at ANSTO have shown that both ions increase the rate of arsenic oxidation.

The effect of Fe(III) chloride addition on the rate of arsenic oxidation is shown in Figure 3-2. Up to 195 mg/L of iron was added resulting in a corresponding chloride addition of up to 370 mg/L. Since HCl was also added to the mixtures at 1.08 and 0.36 grams per liter (g/L), the resultant background chloride concentrations were 1,060 and 350 mg/L, respectively. At the higher acid concentration, the chloride added with the iron addition was insignificant, thus, only iron is shown on the X-axis of Figure 3-2.

The rate of arsenic oxidation was shown to increase as the concentration of Fe(III) was increased, especially at the higher acid dosage. Because the photon losses at the higher acid dosage were significant, the corrected oxidation rates were calculated and also plotted in Figure 3-2. The corrected curve has a low slope indicating that, as occurred in the experiment with less acid addition (0.36 g/L HCl), the reaction rate was only slightly dependent on the Fe(III) addition.

Fe(III) is 1,000 times more effective in absorbing near ultraviolet light than is Fe(II). In addition, previous studies at ANSTO showed that Fe(II) in the absence of Fe(III) poorly promotes arsenic oxidation. The addition of the first 56 mg/L Fe(III) was sufficient to effectively start and sustain the photochemical reaction. The subsequent higher Fe(III) additions produced little beneficial effect.

3.2 Tests Using Low-Pressure Mercury Lamp (254 nm)

Figure 2-2 is a schematic diagram of the low-pressure mercury lamp reactor. The lamp is of similar construction to the 65-W lamps used in the Ultrox reactor. These lamps, commercially used in germicidal applications, have quartz envelopes that transmit 254 nm light without the 195 nm light. Because they do not give out light of 195 nm wavelength, that convert dissolved oxygen into ozone, they are also termed non-ozone producing. In the present work, it is important that non-ozone producing lamps are used so the iron-based, photo-oxidation process can be investigated in the absence of ozone.

The light power input to the reaction mixtures, as determined using ferrioxalate actinometry, was

3.39 W/L. This light power input is higher than the 0.96 W/L found in the Ultrox reactor. Consequently, where identical reaction mixtures are used, the photo-oxidation reaction should occur 3.5 times faster in the bench-scale unit than in the Ultrox reactor (see Figure 1-5).

Unlike the tests with the BLB, it was not necessary to add Fe(III) (Figure 3-3) because there was a greater amount of Fe(III) in the bulk Susie Mine water sample, i.e., about 20 mg/L (Table 3-2), and Fe(II) was converted to Fe(III) during the photo-oxidation process. Furthermore, as noted above, Fe(III) is about 1,000 times more effective at absorbing light at 254 nm wavelength compared to Fe(II).

For QA purposes, the total amount of arsenic and iron in the filtrate after reagent addition were determined by the MSE-HKM Laboratory using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method. These results are listed in Table 3-2. A comparison between the total arsenic analyses ICP-AES and the As(V) as determined by the ANSTO colorimetry method indicates that essentially all of the As(III) was oxidized at the end of each test.

The effect of added acid on the arsenic oxidation rate is shown in Figure 3-4. For all the Fe(III) additions used, increasing the acid dosage from 0.36 to 1.1 g/L increased the oxidation rate. However, further addition of HCl indicated that an optimum acid dosage was between 1.1 and 2.2 g/L. Previous chemical modeling work at ANSTO showed that in high acid concentrations, more iron is present in the uncomplexed state. Compared to the uncomplexed Fe(III), complexed Fe(III) species such as the hydroxo- and chloro-complexes appear to be more effective as photo-initiators of the oxidation process.

3.3 Adsorptive-Coprecipitation of Oxidized Arsenic with Iron

The iron coprecipitation tests were carried out to demonstrate that the procedure can be used effectively to remove dissolved As(V) to a residual concentration of less than 10 ppb. The concentration of arsenic and other analytes in the sample of Susie Mine water after photo-oxidation are in Table 3-3. HCl was added to adjust the pH to 1.5 on-line. The relatively high initial arsenic concentration in the sample was due to the fact that it was taken from the last fraction of the bulk sample, and some of the initial arsenic was concentrated in the iron hydroxide solids that precipitated during storage.

Five 100-ml samples were taken for precipitation tests at different pH levels. No extra Fe(III) was added, and the pH of each sample was adjusted to levels between pH 5 and 8.5 with a 30% lime slurry while the mixtures were rapidly stirred. Because of the slow hydrolysis reactions of Fe(III) (Ref. 18), the samples were left to equilibrate for 3 hours before the final pH was recorded as listed in Table 3-2.

The solids were removed by filtration through a 0.45 micron membrane filter paper. The analyses of these filtrates are also shown in Table 3-3.

No extra iron was added because the initial iron/arsenic mole ratio in the Susie Mine water was 12.6 to 1. The residual arsenic concentrations in the filtrates were reduced to between 1 and 4.4 ppb. It appears as though the low arsenic levels are due to adsorption on ferric oxyhydroxide (ferrihydrite) even though some of the arsenic may have been precipitated as a calcium arsenate. These results agree with previous adsorption studies (Ref. 11) that indicated that an iron/arsenic mole ratio of 10 to 1 resulted in residual arsenic about 20 ppb in the pH range 4 to 6 when the initial As concentration was 300 mg/L.

The concentrations of heavy metals and other analyses in the filtrates are also given in Table 3-3. Cadmium, zinc, and manganese were also removed when the pH was raised above pH 7. Therefore, the optimal pH for removing arsenic and heavy metals is 7 to 8.4.

Table 3-1. Reagent addition, arsenic speciation, absorbance and Fe(II) determination in Susie Mine water test solutions illuminated with light from a BLB lamp.

HCl, g/L	0.36	1.08	2.16	3.6	0	0.36	1.08	1.08	1.08	0.36
pH	2.09	1.5	1.2	1.00	2.64	2	1.5	1.52	1.49	2.1
Fe(III) add	100	100	100	100	195	195	195	57	138	57
Time (min)	As(V) mg/L									
0	0.4	0.6	0.5	0.4	0.4	0.4	0.2	0.5	0.7	0.2
5		3.1	5.3	7.5	1.2	1.8	3.1		3.0	
10	2.6	5.2	8.3	10.2	1.9	2.7	5.7	3.8	5.1	2.0
15		6.8	9.9	11.1	2.6	3.9	7.6		6.9	3.3
20	4.2	8.2	10.7	11.3	3.6	4.9	9.1	6.6	8.3	4.6
30	5.8	10.0	11.6	11.4	4.4	6.7	10.9	8.4	10.1	
40	7.2	11.1	11.5	11.4	5.4	8.1	11.6	9.7	10.9	5.6
50	8.4	11.2	12	11.4	6.2	9.2	11.4	10.4	11.1	6.6
Total As	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.4	11.8
As oxidation rate mg/min	0.16	0.38	0.78	1.40	0.12	0.18	0.49	0.26	0.41	0.12
Corr rate	0.16	0.44	0.88	1.53	0.12	0.18	0.51	0.37	0.44	0.12
Abs, 300 nm	4.21	3.12	2.78	2.42	4.23*	5.05	4.37	1.99	3.92	4.59
Abs, 350 nm	2.64	0.91	0.97	1.11	1.36*	1.66	1.60	0.57	1.19	2.39
Abs, 400 nm	0.15	0.04	0.05	0.01	0.07*	0.09	0.07	0.02	0.06	0.12
Abs C.F.*	1.0	1.2	1.1	1.1	1.1	1.0	1.0	1.4	1.1	1.0
Time (min)	Fe(II) mg/L									
0	185	193	188	187	184	191	183	186	185	180
50	189	183	177	178	236	230	210	183	195	185

*Precipitation had occurred making measurement unreliable.

Table 3-2. Reagent addition, arsenic speciation, absorbance and Fe(II) determination Susie Mine water test solutions illuminated with light from a low-pressure mercury lamp.

HCl, g/L	0.36	1.08	2.2	3.6	0	0.36	0.36	.36	0.36	1.08	1.08	1.08
pH	2.02	1.57	1.4	1.15	3.08	1.97	1.96	1.96	1.98	1.56	1.57	1.6
Fe(III) add	0	0	0	0	0	25	50	100	150	150	100	25
Time (min)	As(V) mg/L											
0	0.1	0.1	0.2	0.3	0.0	0.3	0.5	0.3	0.4	0.2	0.4	0.3
2	1.6	2.8	3.7	2.1	1.2	2.0	2.3	2.1	2.4	3.1	3.2	3.0
4	3.2	5.4	6.3	4.0	1.8	3.7	4.0	3.9	4.1	5.0	5.0	5.2
7	5.4	8.0	8.4	6.8	2.2	5.7	5.8	5.8	5.9	6.1	6.2	6.7
10	7.1	9.3	9.0	7.6	3.0	6.9	7.0	7.1	6.8	6.3	6.7	7.2
15	8.9	10.0	9.3	8.9	4.2	7.8	7.7	7.4	7.3	6.5	6.7	7.4
20	9.7	10.2	9.4	9.1	6.7	8.0	7.9	7.6	7.6	6.5	6.6	7.4
30	10.2	10.4	9.7	9	7.5	8.3	8.1	7.7	7.7	6.5	6.8	7.5
Total As	10.2	10.2	9.2	8.9	6.8	8.31	7.84	7.27	7.63	6.32	6.39	7.26
Total Fe	209.	197.	184.	184.0	184.0	211	231	269	345	259	213	201
As oxidation	0	0	0	0.76	0.26	0.67	0.77	1.03	0.78	1.18	1.16	1.23
rate mg/min	0.60	1.13	1.95									
Abs, 254 nm	129	1.22	1.39	1.44	1.93	2.55	3.67	5.40	4.89	4.47	4.09	2.48
Time (min)	Fe(II) mg/L											
0	182	181	166	166	162	151	150	147	145	118	128	147
40	165	163	150	149	152	141	141	141	143	114	121	138

Table 3-3. Arsenic and other analyses in the initial Susie Mine water and after filtration using membrane of 0.45 micron porosity.

		Susie Water	Filtrates				
pH		1.5	5.15	5.87	6.44	7.05	8.44
As	ppb	38500	4.4	2.7	1.6	1	2.6
Al	mg/L	4.045	1.69	1.25	1.03	1.06	1.19
Ni	mg/L	0.105	0.07	0.045	0.025	0.08	0.12
Cd	mg/L	2.74	0.495	0.305	0.28	<0.2	<0.2
Mo	mg/L	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Na	mg/L	24.45	21.1	22.15	22.8	22.9	22.5
Cu	mg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	mg/L	333.5	<0.2	<0.2	<0.2	<0.2	<0.2
Mn	mg/L	19.6	15.55	15.5	14.45	14.4	2.585
Zn	mg/L	66	53.5	50.5	33.9	22.85	< 0.1
Mg	mg/L	82	78.5	80.5	82.5	84.5	76.5
Ca	mg/L	227.5	1525	1565	1620	1665	1690

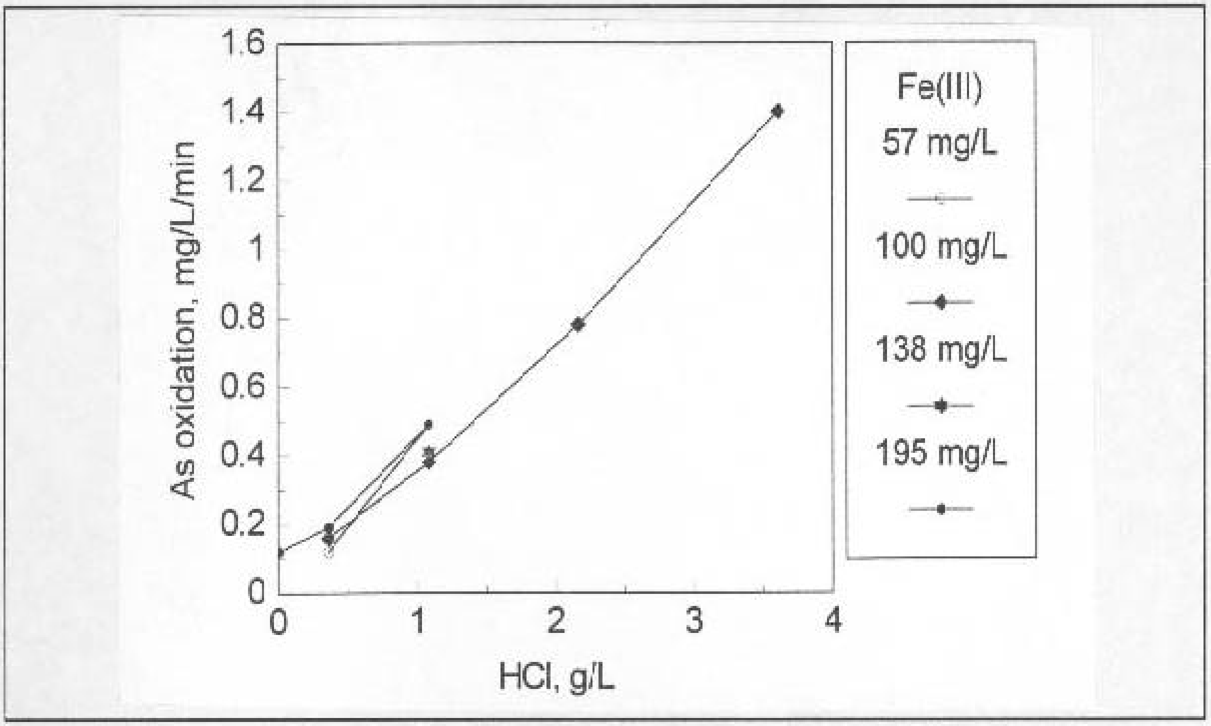

Figure 3-1. Arsenic oxidation rate in the BLB reactor as a function of acid addition for four different Fe(III) dosages.

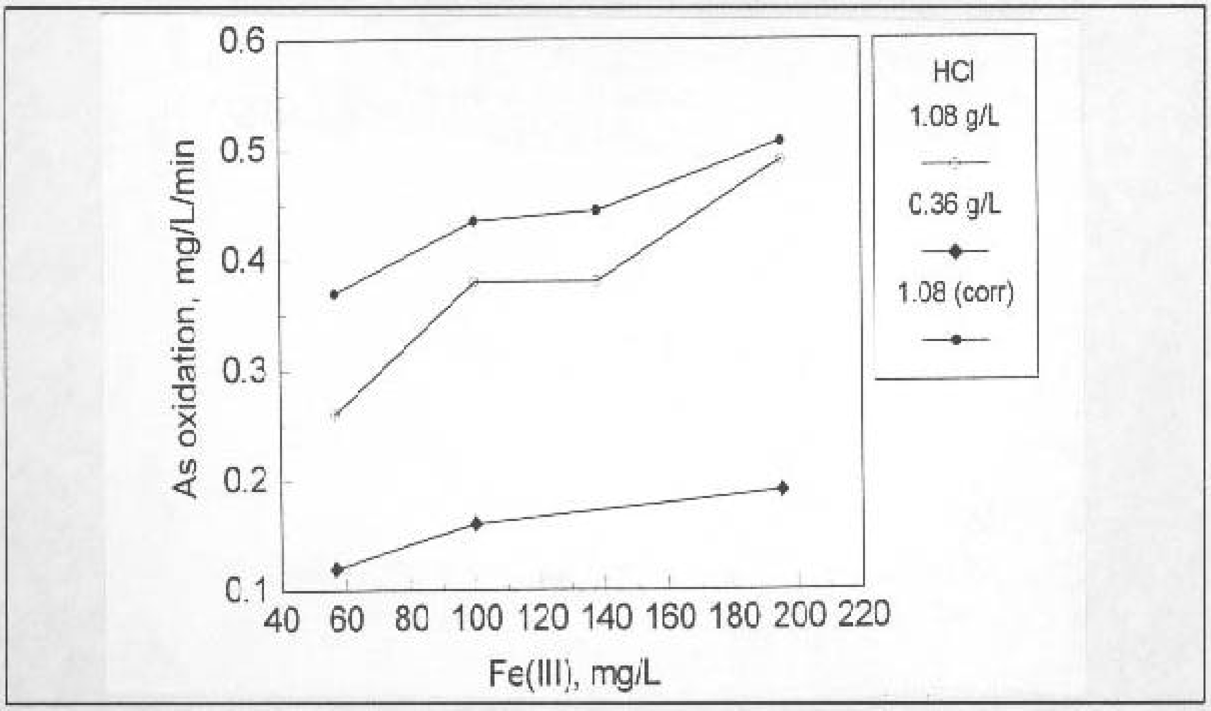

Figure 3-2. Arsenic oxidation rate in the BLB reactor as a function of Fe(III) addition for two different acid dosages. The oxidation rates corrected for photon losses (unabsorbed) at the higher acid dosage are also shown.

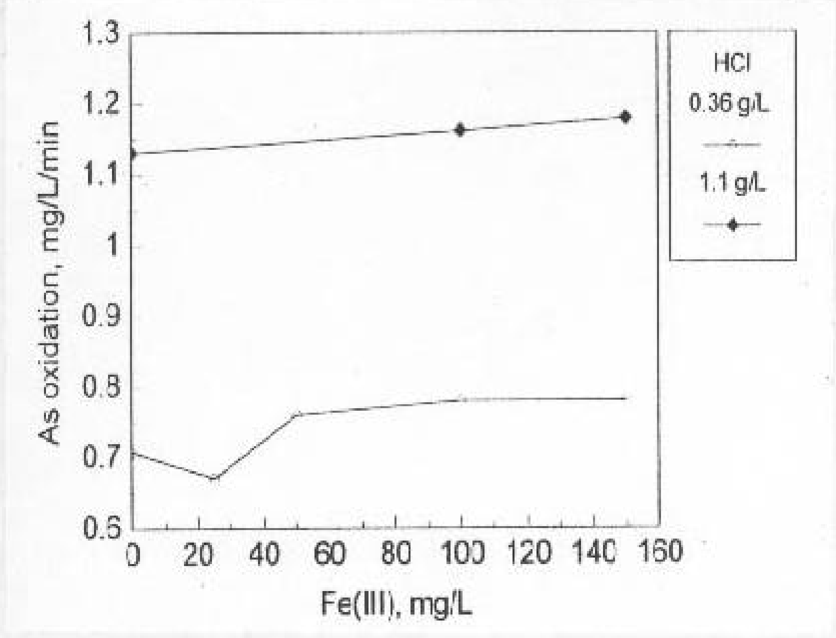

Figure 3-3. Arsenic oxidation rate in the low-pressure mercury lamp reactor as a function of Fe(III) addition for two different acid dosages.

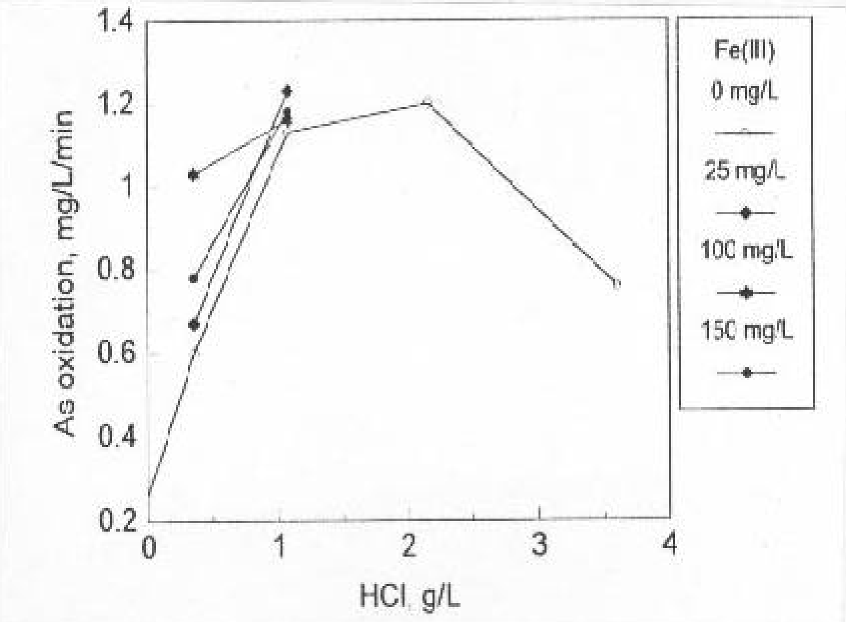

Figure 3-4. Arsenic oxidation rate in the low-pressure mercury lamp reactor as a function of acid addition for four different Fe(III) dosages.

4. Photo-Oxidation of Arsenic

As noted in Section 1, the demonstration test work was commenced at the Susie Mine site in early August 1996. Test experiments using solar ponds were performed first to take advantage of the late summer sunlight and also because of the later than scheduled delivery of the Ultrox reactor in September 1996.

Because of legal complications over the use of the Susie Mine site, the demonstration project was moved to the MSE Testing Facility in Butte, Montana, on August 26, 1996. Approximately 2,000 gallons of Susie Mine water was collected and stored in a dark tank at the facility to complete the second phase of the demonstration using the Ultrox reactor.

Chemical Analysis

Since the primary objective of this project was to demonstrate whether As(III) was effectively oxidized by the photochemical process, the arsenic speciation analysis, namely the accurate measurements of As(III) and/or As(V) concentration, was critically important. Two analytical methods were used for arsenic speciation:

- The separation of the two arsenic species using ion-exchange resins. This method (Ref. 19) was used by the MSE-HKM Laboratory. A number of inconsistencies were noted with the analytical results, especially when As(V) was present as colloidal iron arsenate particles (see Section 4.1.2).

- The determination of As(V) by the colorimetry method (Ref. 6) was used by ANSTO personnel in the field (see Appendix A).

The analytical results from both arsenic speciation methods are used in this report.

The procedures for sampling and for using both analytical methods were subjected to rigorous QA/QC checks as shown in Appendix A. In a similar way to dissolved arsenic, dissolved iron is also subjected to oxidation/reduction reactions during the photo-chemical process. The methods for iron speciation are also in Appendix A.

As an additional check, total iron and arsenic concentrations was determined by the MSE-HKM Laboratory using an ICP-AES. The ICP-AES and ANSTO procedures used unfiltered samples; therefore, they would have accounted for both dissolved and solid arsenic and iron. The MSE-HKM Laboratory arsenic-speciation procedure was applied to filtered samples and reported only dissolved arsenic and iron.

4.1 Tests Using Solar Ponds

4.1.1 Solar Batch Tests Using Susie Mine Water

A schematic for solar batch tests using Susie Mine water is shown in Figure 4-1. The feed water for all the solar batch tests was drawn from the abandoned Susie Mine at one time and stored in a dark 1,000-gallon tank. After batch 1 (no reagent added, see below) was completed, a small amount of HCl was added to the tank to reduce the pH to 3. Various amounts of Fe(III) chloride and HCl, for each test, were then mixed with 95 L of the Susie Mine water in a batch preparation tank before being pumped into the solar pond. Air was supplied to the ponds from a compressor through a sparging pipe. Samples were then collected periodically and submitted to the MSE-HKM Laboratory for analysis. ANSTO personnel also collected samples for iron and arsenic speciation that were completed immediately, for process control purposes. Some of the tests were interrupted due to the lack of light at the end of the day and resumed the following morning. In these instances, the air supply was turned off and the pond was covered with a dark tarpaulin overnight.

Because the bulk storage tank was filled only once and stirred during removal of the water for each batch experiment, the arsenic concentration in the feed mixtures should not have varied. The total arsenic concentration determined by the MSE-HKM Laboratory ICP-AES and ANSTO on the feed mixtures for each batch were 14.5 ± 1.4 and 16.0 ± 0.8 mg/L, respectively (from Tables 4-1 and 4-3). The MSE-HKM Laboratory analysis of dissolved arsenic was calculated by adding the concentrations of dissolved As(III) and As(V) determined during speciation and found to be 12.7 ± 2.7 mg/L. The errors were calculated as the standard deviation of all the analyses provided by each method. It can be seen that the ANSTO results gave the least standard deviation and provided a satisfactory agreement with the MSE-HKM Laboratory ICP-AES results.

As noted above, a small amount of HCl was added to the bulk storage tank to lower the pH value from 4.9 to 2.5 to prevent Fe(II) oxidation. Consequently, the initial Fe(II) concentration did not vary significantly between tests. Fe(II) reacts significantly with oxygen in air at pH values greater than 4 to form amorphous Fe(III) hydroxide, which removes arsenic from solution.

Analysis of the background metals Al, Cd, Zn, Ca, and Na in the prepared feed solutions before and after some sunlight exposure are listed in Table 4-1. The calcium concentrations ranged from 211–229 mg/L in the feed solutions indicating that the bulk storage tank was well mixed (sodium ranged from 19.3 to 22.7 mg/L). At the end of the tests, the analyzed calcium concentrations varied from 223–232 mg/L (sodium ranged from 19.3–22.7). The similarity of these two ranges of calcium concentrations indicates that evaporation from the ponds was not significant. No significant variation in the concentrations of Al, Cd, or Zn occurred between batches or during each test. No attempt was made here to demonstrate whether these metals affect the rate of arsenic oxidation. Previous work at ANSTO indicated that they did not influence the photochemical process.

The results from analysis of the anions, chloride, and sulfate are also listed in Table 4-1. The sulfate concentrations varied from 1080–1160 mg/L in the initial feed solutions and during each test. Fundamental studies at ANSTO revealed that the presence of sulfate decreases the arsenic oxidation rate. However, as its concentration did not vary, this effect was not apparent in this work. The chloride concentration varied since Fe(III) was added since its chloride salt and HCl was used to adjust the pH. Although the effect of chloride on the arsenic oxidation was not isolated from that of pH or Fe(III) here, previous ANSTO work demonstrated that chloride enhances the rate of arsenic oxidation. The effect in the absence of sulfate was apparent in the test results on flue dust oxidation described in Section 4.1.2. However, the presence of sulfate did reduce the positive effect of increasing the chloride concentration in the Susie Mine water.

Batch Test Results

Eleven solar batch tests were carried out: Batch test 1 was performed to determine whether the oxidation reaction proceeds without any reagent additions; batch test 11 was performed with near-optimum reagent additions but without light; the other nine tests were conducted with different additions of Fe(III) chloride and HCl using the bench-scale experimental results as a guide. The sequence in which the batch tests were conducted was based on the weather and the availability of sunlight and the expected duration of the tests (from bench-scale test results given in Section 3).

The concentrations of HCl and iron added to each batch are listed in Table 4-2. Arsenic speciations were carried out at several time intervals and are listed in Table 4-3. Iron speciation was also undertaken periodically, and the results are listed in the tables. Field measurements of pH, Eh, dissolved oxygen, and temperature were recorded during each experiment and are in Table 4-4.

Batch Test 1

In the first batch test using Susie Mine water, no reagents were added to the water before it was pumped into the solar pond. In Figure 4-2, the concentration of dissolved As(III) and As(V) determined by the MSE-HKM Laboratory are shown as a function of the time of day. The on-site determination of total As(V) concentration by ANSTO personnel is also shown. The fourth set of data points show the solar flux measured at 1 minute intervals throughout the test. In Figure 4-3, As(III) and As(V) concentration in the Susie Mine water are shown as a function of cumulative absorbed sunlight UVA energy for solar batch test 1.

There was no change in the concentration of As(III) or As(V) indicating that no arsenic oxidation occurred.

The dissolved and total iron concentrations were both about 200 mg/L before the test and did not vary throughout the test indicating that no iron precipitation had occurred. The oxidation state of the iron was found to be all Fe(II). This is confirmed by the low Eh measurement of 230 millivolts (mV) (relative to the Ag/AgCl electrode) despite the high dissolved oxygen concentration. In fact, measurements of the actual dissolved oxygen concentrations showed that the reaction mixture was fully saturated with oxygen aerated throughout the test, i.e., dissolved oxygen readings close to the saturation concentration range of 6.2 to 7.8 mg/L for Rimini (elevation of more than 5000 feet) at a temperature of 16 to 25 EC.

The absorbance (optical density) of the initial reaction mixture, as measured using a UV-visible spectrophotometer, was found to be 0.42 at 350 nm and 0.07 per cm at 400 nm. Previous studies at ANSTO indicated that Fe(II) is ineffective at absorbing light and promoting the oxidation of arsenic.

Arsenic oxidation in Susie Mine water with HCl and ferric chloride but without sunlight (Batch Test 11)

To demonstrate the necessity of light for the oxidation reaction to proceed, Fe(III) chloride and HCl were added to the Susie Mine water in sufficient quantities and then placed in the solar pond and aerated at night. From Figure 4-4, it can be seen that no oxidation of the arsenic occurred. When the same reagent concentrations were used in the presence of sunlight (Batch 7), all the initial As(III) was oxidized in less than 4 hours.

ANSTO analyses indicated that virtually no change in the Fe(II) or Fe(III) concentration had occurred.

The effect of acid and iron addition on the rate of arsenic oxidation in Susie Mine water exposed to sunlight (Batch Tests 2–10)

Nine solar batch tests were carried out with different additions of Fe(III) chloride and HCl using the bench-scale experimental results as a guide. As discussed above, the sequence in which batch tests 2 to 10 were conducted was based on the weather and the availability of sunlight and the expected duration of the tests. The results presented in Figures 4-5 to 4-13 are based on three sets of tests of three different iron additions with three different acid dosages within each set as given in Table 4-2.

From Figures 4-5 to 4-13 and Table 4-3, it can be seen that the combination of Fe(III) as a photoabsorber, sunlight as an energy source, and oxygen as an oxidant resulted in the complete oxidation of As(III).

During the batch tests, the solar flux varied with the position of the sun and with the extent of cloud cover. Further variability was introduced by a slight smoke haze, at high altitude, produced from forest fires in Washington state. Hence, it is not possible to directly compare the reaction rates of tests performed at different times.

To provide a comparison between tests carried out at different times, it is necessary to express the progress of arsenic oxidation as a function of absorbed sunlight energy. Consequently, the solar flux readings in milliwatts (mW) of UVA/square centimeters (cm^2) was converted to UVA energy dosage, namely the cumulative dose of UVA sunlight energy in joule (J/cm^2), by adding the energy absorbed in every minute of the elapsed time using equation [4-1]. The solar flux readings were taken every minute, and it is assumed that the solar flux remained constant during each minute time interval.

$$CumulativeDose = \int_0^t SolarFlux(mW/cm^2) \times 60/1000 \tag{4-1}$$

The oxidized arsenic concentrations as a function of the cumulative absorbed sunlight energy are shown in Figure 4-3. The oxidation rates were calculated from the slope of the linear regression and are expressed as mg/L per J/cm^2. These rates can be used to compare tests performed at different times. The time taken to complete the oxidation can be found in Table 4-3 and are summarized in Table 4-2.

The slope of each line was determined from the time elapsed between the beginning of the experiment and when 90% of the arsenic was oxidized. The data points after 90% of the arsenic was oxidized were not used, as the inclusion of points after oxidation was complete would have resulted in the underestimation of the oxidation rate. It was necessary to continue the experiments after the oxidation was completed to verify that complete oxidation had occurred.

The rate of disappearance of As(III) should equal the rate of appearance of As(V) if no precipitation of the arsenic occurs. The dissolved and total iron results were similar, indicating that no iron precipitate had formed during the tests; hence, all the arsenic would have remained in solution. The disappearance and appearance rates are within 10% of each other for batch tests 3, 4, 6, 7, and 9. The other batches, however, show greater variations.

No such check could be performed on the ANSTO field data as only As(V) was determined. However, the ANSTO data, compared to those of MSE, are more consistent, and smooth trends are apparent in Figures 4-5 to 4-13.

From Figure 4-14, it can be seen that the rate of arsenic oxidation is proportional to the concentration of HCl addition. The fastest oxidation rate occurred in batch test 4 where the arsenic was oxidized at a rate of 5.5 mg/L per minute and the oxidation reaction was completed in 1 hour (Figure 4-15).

The different completion times for the same value of absorbed sunlight energy (Figure 4-15) highlighted the fact that it is necessary to use absorbed sunlight energy in order to compare results of tests performed at different times. The results of bench-scale tests (Section 3) were used to plan the batch tests such that their duration was no longer than 6–9 hours.

The addition of Fe(III) increased the oxidation rate; the effect was more pronounced when the iron dosage was increased from 180 to 270 mg/L. There was no significant change when the dosage was increased from 110 to 180 mg/L.

No change in the Fe(II) concentration occurred during the tests, indicating that As(III) was "selectively" oxidized in the present work. Conventional oxidation processes would have required additional chemical oxidants to oxidize Fe(II) before As(III) could be oxidized.

The temperature of the solution and its pH, Eh, and dissolved oxygen concentration were determined in the field and are listed in Table 4-5. The temperature of each reaction mixture rose as it was exposed to the hot sun and fell overnight in cases where experiments were performed for more than 1 day.

4.1.2 Solar Batch Tests using Flue Dust Leachate

Three solar batch tests were performed concurrently. Figure 4-16 is a schematic for the solar vat flue dust leachate batch tests using Susie Mine water. The feed liquors were prepared in the solar ponds by diluting the concentrated flue dust leachate with local well water and adding Fe(III) chloride, HCl, and sodium chloride. Reagents were added to the three feed liquors in the amounts shown in Table 4-6. The Fe(III) content of batches 1, 2, and 3 were 430 mg/L. The chloride concentrations were 3,700, 1,370, and 3,900 mg/L, respectively; the nominal pH value was 1 for batch test 1 and 2 and for batch tests 2 and 3.

During the tests, a precipitate formed in batch tests 2 and 3, and it was noted that the cloudiness of the ponds was proportional to the amount of arsenic oxidized, indicating that the generation of As(V) was causing the precipitation. At the end of the test, the bottom of the 8-inch deep pond could not be seen clearly. However, the dissolved iron concentration determined in the filtrate from a 0.45 micron membrane did not decrease throughout the tests indicating that the solids were present as colloidal material that could pass through the filter membrane.

The As(III) and (V) analyses provided by the MSE-HKM Laboratory were both so inconsistent that only the As(III) results are shown in Figure 4-17. The As(V) concentrations shown in the figure were obtained in the field by ANSTO personnel. The concentration of As(III) and (V) determined during the three batch tests are shown as a function of the cumulative dose of sunlight, which was calculated in the same manner as in Section 4.1.3. Total As(III) initially present was completely oxidized in 10, 48, and 24 hours of sunlight during batch tests 1, 2, and 3, respectively. The rate of arsenic oxidation remained constant, with respect to the energy absorbed, throughout each test despite the falling As(III) concentration. This is advantageous for the process since complete oxidation of the final/residual proportion of the As(III) can be readily achieved. The rate of oxidation with respect to time was observed to fall when the sun weakened at the end of each day.

The inconsistencies in the As(III) and (V) analyses provided by the MSE-HKM Laboratory may be explained as follows: the ion-exchange method for arsenic speciation used (Ref. 19) was developed primarily for trace amounts of arsenic in groundwater samples. Consequently, it may be affected if As(V) in the samples is present in significant concentrations such that its precipitation or complexation into neutral species occurs (the dilution of samples may not readily dissolve the colloidal ferric/arsenate). In the vicinity of the ion-exchange resins, As(V) species are to be present mainly as dissociated charged species and As(III) as undissociated neutral species. In this case, some As(V), which was present as uncharged colloidal particles, passed unretained through the ion-exchange column as do neutral As(III) species. This would have the effect of an underestimation of the As(V) and an overestimation of the As(III) concentration; the error would occur in a randomized manner because some of the colloidal iron-arsenate particles might be mechanically intercepted by the column. The data shown in Figure 4-17 appear to support this hypothesis, i.e., the determined concentrations of As(III) were random and much greater than expected at the end of batch tests 2 and 3 (with precipitation) as compared to those of Test 1 (no precipitation).

The ANSTO field determination of total As at the beginning of each test was 427, 439, and 423 mg/L for batch tests 1, 2, and 3, respectively (Table 4-7). This is in close agreement with the MSE-HKM Laboratory ICP-AES result of 390, 410, and 391 mg/L (dissolved arsenic), respectively. The MSE-HKM Laboratory data for dissolved As(III) + As(V) showed a standard deviation of 30% for batch tests 2 and 3. The fact that As(V) and As(total) analyses were found to be the same at the conclusion of the tests indicates the completion of the photo-oxidation reaction.

The background metal concentrations shown in Table 4-5 do not vary within each test indicating that the replacement of well water lost due to evaporation was effective and so evaporation does not account for the variability of the arsenic analysis. The error in the MSE-HKM Laboratory analyses is random.

The amount of arsenic oxidized, from the slope of each graph, was 3.19, 0.86 and 1.70 mg/L per J/cm^2 for the respective batches. Given that the area of the ponds was 18,600 cm^2 with a volume of 400 L, this corresponds to an absolute amount of arsenic being 60, 16, and 32 mg/kilojoule. For a typical solar flux of 4 mW/cm^2, this corresponds to 16.1, 4.3, and 8.5 grams (g) of arsenic being oxidized every hour in the pond.

The arsenic oxidation rate was most rapid in the first batch since it had the lowest pH and highest chloride concentration. No precipitation occurred during this test. The second batch displayed the slowest rate since the pH was higher and the chloride concentration was low. The addition of sodium chloride to the third test demonstrated that, for high chloride to sulphate ratios, chloride will accelerate the reaction rate. The anion concentrations were checked and are listed in Table 4-5.

Well water was used to replace water in each pond due to losses caused by evaporation. Sulfate was present in the well water used. The introduction of this sulfate into the pond water resulted in an increase in the sulfate concentration.

The Fe(II) present in all of the tests would have been produced in situ by the reduction of the added Fe(III). From Table 4-7, it can be seen that only a small amount of Fe(II) (about 15 mg/L) was produced in batch test 1. At the higher pH of batch tests 2 and 3, the Fe(II) concentration increased to 225 mg/L. If As(III) and Fe(III) were to react directly as a redox couple, this would account for 10 mg/L of As(V) in batch test 1 and 150 mg/L of As(V) in batch tests 2 and 3. Because over 400 mg/L of arsenic were oxidized, clearly, oxygen, not iron, is the major oxidant in this reaction. The high concentration of dissolved oxygen listed in Table 4-8 indicated that the spargers were adequately replenishing the oxygen used, and oxygen mass transfer is not a problem.

4.1.3 Hydraulic Flow Testing of the Solar Ponds

Hydraulic flow testing was carried out to characterize the hydraulic behavior of the solar ponds when being used as a continuous flow reactor, i.e., to measure the extent of short circuiting and back mixing when the solar ponds were used as a flow through reactor.

Three baffles were fitted into each pond to minimize short circuiting and back mining. The liquor flowed under the first and third baffle and over the second. As the air from the spargers traveled across the flow direction of the water, the bubbles were not expected to promote back mixing or to cause short circuiting.

Phosphorus, which was added as sodium hydrogen phosphate, was chosen as a physical tracer as it was easily analyzed by the same spectrophotometric method used for As(V). To perform each test, the solar ponds were filled with water, and the prescribed flow rate was maintained. All of the phosphorus was added to the inlet at once, and the movement of the phosphorus through the ponds was monitored. The results are shown in Figure 4-18.

The hydraulic flow testing was performed in Australia using water from the Crystal mine. Because this water only contained about 1 mg/L of arsenic, a relatively short residence time was used for the tracer test, i.e., 17 minutes for a flow rate of 2.6 gpm. From Figure 4-18, the mean residence time was 15 minutes, and the percentage of phosphorus passing through the ponds before the mean was 27%. The above tracer test results were used to guide the operation of the continuous flow tests using Susie Mine water.

Because of the need for a larger sunlight collection area for treating Susie Mine water, two of the solar ponds were converted for continuous flow tests by mounting them so that the water would cascade from one to the other.

4.1.4 Solar Continuous Flow Tests Using Susie Mine Water

Because of a time constraint, only two continuous flow tests were performed: Test 1 to demonstrate the completeness of oxidation and Test 2 to demonstrate the effect of higher flow rate.

A second lot of the feed mixture used for batch test 2 was prepared for use in the first continuous test. The mixture for the second continuous test was identical to that of batch test 7. From Table 4-1 it can be seen that the sample matrix is the same between the corresponding liquors used for the batch and continuous testing.

A schematic for the solar continuous flow method is shown in Figure 4-19. The feed mixtures were pumped into the solar pond at 0.75 gpm for Tests 1 and 2 starting at 11:00 am. The distribution of arsenic species throughout the reactor was then determined at noon, 1:00, 2:00, and 3:00 pm as shown in Table 4-9. The As(V) concentrations in the samples taken at the various ports are given in Figure 4-21 for Continuous Flow Test 1 and Figure 4-24 for Test 2. The ANSTO chemical analysis of water in Test 1 was affected by a constant positive error such as would be caused by contamination of the analytical reagent. Separate plots of the As(III) concentrations are shown in Figures 4-22 and 4-25.

The continuous tests were performed on fairly cloud-free days as can be seen from the solar flux readings shown in Figures 4-20 and 4-23 with an average solar flux of 3.612 mW/cm^2 for Test 1 and 3.906 mW/cm^2 for Test 2. If these tests had been conducted in batch mode, the first test would have taken 26 minutes to complete, and the second would have taken 2:12 hours to complete. These completion times were calculated from the time taken to complete Batches 2 and 7, namely 3:30 and 2:30 hours, respectively, with corresponding average solar fluxes of 0.646 and 2.468 mW/cm^2 (taking into account the difference in the solar flux readings). Previous work at ANSTO showed that the arsenic oxidation rate is proportional to the intensity of light.

The flow rate of 0.75 gpm for Test 1 was chosen to give a calculated residence time of 1 hour. The average percent As(V) at the outlet was calculated in Table 4-9 and found to be 95.5% (ANSTO result 97.5%) for Test 1 and the residual As(III) was found to be 1%. Such a high degree of conversion would be expected given that the residence time was 2.3 times larger than that required to complete the reaction.

In contrast, in Test 2, only 83.9% (ANSTO result 81.4%) of the arsenic was oxidized at the outlet, and 11.3% remained as As(III). In this case, the residence time is 0.4 times that required for the batch reaction. Complete conversion would have been possible at the same flow rate if 3 more ponds had been added to the system.

The efficiency of Test 1 could have been improved by increasing the flow rate until just before As(III) was found at the outlet. However, as the time required for the arsenic oxidation varied with the intensity of sunlight, it would have needed a great amount of time to obtain the optimum flow rate by continually monitoring and adjusting the flow rate accordingly.

The field measurements in Table 4-10 were similar to those made for the batch tests with the exception of temperature. A consistent rise in temperature occurred as the reaction mixture flowed through the pond.

4.2 Tests Using Ultrox Reactor

4.2.1 Determination of Light Power Input to the Ultrox Reactor

Actinometry was used to determine the efficiency of the fluorescent lamps. The reduction of Fe(III) by oxalate during illumination with ultraviolet light has been well characterized and has a quantum efficiency of 1.25, i.e., for each mole of photons absorbed, 1.25 moles of Fe(II) is produced (Ref. 7).

The Ultrox reactor was filled with 570 L of 0.006 M $K_3Fe(C_2O_4)_3$ and the pump was used to circulate the reaction mixture. The conversion of Fe(III) to Fe(II) as a function of illumination time is shown in Figure 4-26. Fe(II) was produced at a constant rate of 8.514 mg/L per minute. As the light from the lamps consists mainly of a monochromatic line of 254 nm wavelength, the rate of Fe(II) production can be converted to light power (1 mole of 254 nm photons have 4.709×10^5 joules of energy) and was found to be 546 W. The Ultrox unit is fitted with 24 lamps with nominal power of 65 W each so the total power consumed by the lamps would have been 1560 W. Therefore, the electrical efficiency of the lamps was 35%.

4.2.2 Batch Tests using Susie Mine Water

Because the Ultrox tests were performed at the MSE Testing Facility in Butte rather than at the Rimini mine site, 2,000 gallons of Susie Mine water was transported by truck to the MSE Testing Facility. A schematic of the Ultrox batch or continuous flow system is shown in Figure 4-27. The pH of the water was reduced to 2.5 with HCl at the Susie Mine site to limit iron oxidation, and light was excluded where possible. The feed for each test was prepared by adding HCl and/or Fe(III) chloride as shown in Table 4-12. Elemental analyses of batches 1 to 3 are given in Table 4-11. The prepared feed liquor was then pumped into the Ultrox reactor before the lights were turned on at time 0. Two sets of tables are shown in Table 4-12 (in a chronological order and in the order of increasing acid additions with and without Fe(III) additions). The second ordering of batch tests were used to sequence the graphs showing the progress of oxidation reaction with time (Figures 4-28 to 4-34). These figures and the data given in Table 4-13 were used to estimate the completion of the As(III) oxidation process.

Figures 4-35 and 4-36 show the oxidation rate in the Susie Mine water as a function of acid and ferric chloride additions.

Since arsenic analysis was performed by both MSE and ANSTO personnel, there are two sets of results given in Table 4-12. The oxidation rates using ANSTO results were calculated based on the total As(V) and dissolved As(V) analyses.

The results shown in Table 4-12 indicate that without iron addition, there is an optimum point when the addition of HCl was 0.27 g/L. With 100 mg/L of Fe(III) added, the added acid increased the oxidation rate. However, for the same amount of acid added, the added Fe(III) did not increase the rate of arsenic oxidation. In fact, it resulted in slightly lower rates. This was observed during bench-scale tests (Section 3): there was no benefit by adding extra Fe(III) during the oxidation of arsenic in Susie Mine water (with some of its ferrous content oxidized) using low-pressure mercury lamps.

The total concentrations of background metals are listed in Table 4-1. These elements are present in the same concentration found when Susie Mine water was used for the solar tests. Where no iron was added (batches 1, 3, 4, and 6), the total concentration of iron remained the same as was present for the solar tests (about 200 mg/L). However, from Tables 4-13 and 4-3, it can be seen that during transport from Rimini to Butte half of the iron(II) was oxidized. Nevertheless, no further oxidation of Fe(II) occurred in the storage tank between each of the batches and continuous experiments conducted at the MSE Testing Facility. Some of the iron precipitate redissolved when HCl was added. The precipitate did not have a significant adverse effect on the arsenic analysis performed by ANSTO since it was dissolved by the sulfuric acid in the analytical reagents.

The on-line measurements for the Ultrox batch tests using Susie Mine water are listed in Table 4-14. The temperature throughout these tests remained at the ambient temperature found in the bulk storage tank. The presence of Fe(III) resulted in high Eh values, and the dissolved oxygen measurements indicate that the spargers supplied sufficient oxygen for the reactions.

The Ultrox reactor was fitted with a power meter that recorded the total electricity consumption of the entire rig. Electricity operates both the lamps in the reactor, that have a nominal power rating of 1,560 W, and the liquor flow control pump of 550 W. An insignificant amount of power was also used by the flow control meter. The pump was used to recirculate the liquor during batch tests and to fill and drain the reactor between batches. During all these operations, it was operated at a fraction of full power.

Periodic checks of the power meter over a 5-hour period showed that the average power consumption was 1,750 W. The majority of power meter readings taken during test runs were not correct (i.e., negative power consumption and too high and too low figures). Consequently, an average constant electric power consumption of 1,750 W was used for process cost calculation.

During each batch test, the reaction mixture was recycled through the reactor at 5 gpm to ensure that no stagnant liquor or unilluminated body of liquor was present within the reactor.

4.2.3 Batch Tests using Flue Dust Leachate

The elemental analyses of the flue dust leachate are given in Table 4-15. A schematic of the batch method for Ultrox treatment of flue dust leachate is shown in Figure 4-37. The concentrated flue dust leachate was diluted in two lots, and Fe(III) chloride and HCl were added as listed in Table 4-16. The first batch was clear throughout the test but a thick cream-colored precipitate of Fe(III) arsenate formed during the second test. Samples were taken and speciated for arsenic by the MSE-HKM Laboratory. The results are given in Table 4-17 and are plotted in Figures 4-38 and 4-39.

The MSE-HKM Laboratory analyses for batch test 1 indicate that the oxidation reaction stopped when apparently only 50% of the initial As(III) was oxidized. In batch test 2, only 50% of the As(III) was oxidized after 42 hours. These liquors were subsequently removed from the Ultrox reactor, combined, and coprecipitated with iron hydroxide as detailed in Section 5. Speciation analysis of the dried solids at ANSTO for total arsenic (34.75 mg/g) and As(V) (34.47 mg/g) indicate that over 99% of the arsenic was pentavalent (oxidized) (Table 6-1). Also, if 600 mg/L of As(III) were present during the precipitation, then the residual arsenic left in solution would have been tens of mg/L not ppb (the oxidation step is performed for this very reason). Because it was highly unlikely for the arsenic to oxidize during precipitation, these observations place doubt on the MSE-HKM Laboratory arsenic speciation results. As noted in Section 4.1.2, the arsenic speciation analysis using the ion-exchange method (Ref. 19) used by the MSE-HKM Laboratory may be affected by high concentrations of As(V).

The initial total arsenic concentrations determined by ANSTO were 1,430 and 1,700 mg/L (dissolved + suspended arsenic) for batch tests 1 and 2, respectively. These are similar to that determined by the MSE-HKM Laboratory ICP-AES, that is 1210 and 1410 mg/L (dissolved). The dissolved As(III) + As(V) determined from the MSE-HKM Laboratory arsenic speciation were 1,100 for both batches.

During batch test 1, the ANSTO analysis for arsenic was performed on unfiltered samples as it was done elsewhere in the work reported here. However, the extensive precipitate formed in batch test 2 settled within the Ultrox reactor causing an uneven distribution of As(V) throughout the reactor. When the As(V) analysis was performed on unfiltered samples, the results (not reported here) were scattered. Since As(III) was not incorporated in the precipitate, it remained evenly distributed; so when dissolved As(III) was chosen as the analyte, the smooth progress of the oxidation reaction became apparent. The total dissolved arsenic was found to steadily decreased confirming that arsenic was incorporated in the precipitate. Some on-line measurements are given in Table 4-18.

4.2.4 Hydraulic Flow Testing of the Ultrox Reactor

Hydraulic flow testing of the Ultrox reactor was carried out using the same method that was applied to the solar ponds. Since sample ports were installed to allow monitoring of all four chambers, the concentration of phosphorus was determined half way through each chamber and at the outlet. The progress of the phosphorus through the reactor operating at 2 gpm is shown in Figure 4-40.

At 2 gpm the residence time in the reactor is calculated from the reactor volume of 150 gallons to be 75 minutes. The mean residence time for the phosphorus was found to be about 50 minutes. Also, 61% of the phosphorus came through the reactor before the calculated residence time confirmed that most of the liquid was short circuiting through the reactor. The test was repeated at 10 gpm, which should have resulted in a residence time of 15 minutes. However, 54% of the phosphorus passed through before this time.

The first and final baffle plates in the reactor had drainage notches cut out of their base. The holes were 0.56 square inches and allowed all the chambers to have an even liquid level while the reactor was being filled or drained. Once the reactor was filled, no liquid should have flowed through these notches as the desired flow path is over the top of these baffles.

The rapid appearance of phosphorus at the outlet in both tracer tests seemed to indicate that a significant amount of liquor was traveling straight through the drainage notches across the floor of the reactor without passing the lights. Therefore, it was decided to seal the notches and repeat the tracer tests. The results of these tests are shown in Figures 4-41.

The calculated residence times were not changed by the modification, and it was found that 62% and 40% (at 2 and 10 gpm, respectively) of the phosphorus passed through the reactor before the expected residence time. The modification, therefore, had not significantly improved the flow characteristics of the reactor. However, there was a reduction in the amount of phosphorus appearing before the first sample was taken. In the 2 gpm tests, the amount of phosphorus appearing before 15 minutes was reduced from 2.9 to 1.2%, and the reduction at 3 minutes for the 10 gpm test was from 2.9 to 0.9%.

4.2.5 Continuous Flow Tests using Susie Mine Water

The first continuous test of the Ultrox reactor with Susie Mine water was conducted before the modification was made to the reactor. HCl was added at 0.36 g/L to the Susie Mine water to produce a feed mixture identical to that used for batch test 1 in which the reaction was completed in 30 minutes. A flow rate of 5 gpm was chosen that resulted in a calculated residence time of 30 minutes. However, given the poor performance during tracer testing, complete oxidation was not expected to occur. The reagent additions are summarized in Table 4-19.

During the first continuous test, the total arsenic in the water was 14.1 mg/L, and the feed water contained 8.6 mg/L As(V). From Figures 4-42 and 4-43 and Table 4-20, it can be seen that the concentration of As(V) increased as the liquid flowed through the reactor. However, at the outlet > 1.7 mg/L of As(III) remained unoxidized (Table B11, Appendix B). This would be due to short circuiting that resulted in some of liquor not being exposed to the light for the 30 minutes required for complete oxidation. The iron speciation is given in Table 4-21.

The feed mixture for the second continuous test was prepared by mixing the partially oxidized water from Test 1 with the remaining Susie Mine water in the bulk storage tank. Further HCl was added to maintain the concentration of 0.36 g/L. The test was conducted at a flow rate of 3 gpm after the notches in the reactor were sealed. Figure 4-44 shows the As(V) concentrations during this test. This resulted in a calculated residence time of 50 minutes. The feed liquor contained 10.5 mg/L of As(V) and

12.4 mg/L of total arsenic. The effluent from the reactor contained 12 mg/L of As(V). Because only 1.9 mg/L of the arsenic required oxidizing, the time required would have been 4.4 minutes during a batch operation. However, ten times this time was chosen as the calculated residence time to ensure complete oxidation (Table B11).

The on-line measurements taken during these tests are shown in Table 4-22.

Table 4-1. Elemental analysis of test feed mixtures used for solar batch and continuous tests using Susie Mine water.

Sample	Ca mg/L	Na mg/L	Zn mg/L	Al mg/L	Cd mg/L	Fe mg/L	As mg/L	Chloride mg/L	Sulfate mg/L
Batch 1									
1	215	21.4	63.3	3.01	0.508	192	12.2		
5	232	22	68.5	2.77	0.542	200	9.82		
Batch 2									
1	211	22.7	60.2	3.27	0.494	357	15.7		
6	223	22.6	65.1	3.42	0.522	375	14.9		
Batch 3									
1	229	21.5	66.6	3.45	0.52	301	16.1		
2								698	1130
8	239	23.2	70	3.61	0.555	312	15.8	720	1190
Batch 4									
1	221	20.8	62.7	3.27	0.523	489	16.3		
3								4490	994
8	227	20.4	65.5	3.39	0.54	496	14.9	4600	1100
Batch 5									
1	226	21.1	66.5	3.4	0.522	399	15.1	899	1120
13	229	21	67.9	3.62	0.566	402	15.7	912	1090
Batch 6									
1	221	20.9	64.8	3.35	0.518	464	14.9	1050	1020
	223	20.6	66	3.52	0.553	479	15.5	1110	889
Batch 7									
1	217	19.6	63.2	3.36	0.545	390	15.6	1710	1050
8	228	20.6	66.9	3.59	0.571	404	14.7	1750	1110
Batch 8									
1	219	19.3	63.7	3.38	0.551	494	14.6	1890	1050
9	221	20.7	64.7	3.52	0.559	489	14.1	1970	1070
Batch 9									
1	219	20.1	63.5	3.45	0.537	292	14.7	1510	1060
7	229	21.1	66.7	3.64	0.563	303	14.1	1550	1130
Batch 10									
1	218	20.3	62.2	3.47	0.539	290	14.4	3840	1160
6	224	20.5	64.2	3.57	0.553	295	13.5	3840	1110
Batch 11									
1	224	22.1	64.1	3.55	0.56	308	14.7	2040	1080
3	232	20.9	67.8	3.59	0.587	432	13.8	1710	1060

Sample/Port									
Cont 1									
1/A	223	20.4	62.8	3.48	0.536	353	13.5	3300	1080
1/E	228	21.2	64.3	3.56	0.564	360	13.4	3270	977
4/A	227	20.3	64.5	3.54	0.54	361	13.4	3240	1090
4/E	223	20.3	63.3	3.48	0.536	349	13.1	3280	1090
Cont 2									
1/A	223	21.8	64.2	3.54	0.561	397	13.2	1700	1030
1/E	224	22	64.5	3.58	0.563	397	12.9	1700	1040
3/A	222	22.1	64	3.55	0.566	394	13	1690	829
3/E	226	22.3	65.2	3.61	0.578	401	13.1	2110	1030

Table 4-2. Reagent additions for solar batch tests using Susie Mine water.

Batch Test	Iron Addition mg Fe/L	Acid Addition g HCl/L	Time to Completion (Hour)
1 (no reagent added)	0	0	did not oxidize
11 (performed at night)	200	1.08	did not oxidize
3	98	0.36	6.5
9	110	1.08	4
10	110	3.24	2
5	180	0.36	9.5
7	180	1.08	4
2	180	3.24	5
6	270	0.36	6
8	270	1.08	3.6
4	270	3.24	1

Table 4-3. Absorbed solar energy, arsenic and iron speciation during solar batch tests using Susie Mine water.

Date	Time	Hours	Energy J/cm^2	As mg/L	As(V) mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1							
Aug 11	12:00	0:00	0	17.6	5.70		15
Aug 11	14:00	2:00	13.19		5.80		11.3
Aug 11	18:00	6:00	34.79	17.2	7.74		8.28
Batch 2							
Aug 11	13:10	0:00	0	16.99	5.70	202.00	172
Aug 11	13:30	0:20	0.51		6.12		176
Aug 11	14:00	0:50	2.9		11.00		
Aug 11	18:00	5:00	24.4		17.60	195.00	181
Batch 3							
Aug 12	11:30	0:00	0	16.3	5.88	203.00	94
Aug 12	12:30	1:00	12.35		8.17		96
Aug 12	13:30	2:00	26.27		10.21		97
Aug 12	14:30	3:00	39.91		12.02		98
Aug 12	15:30	4:00	51.94		14.29		99
Aug 12	18:00	6:30	71.98		16.21	205.00	105
Batch 4							
Aug 12	14:50	0:00	0		5.13	194.00	270
Aug 12	15:05	0:15	3.06		10.50		258
Aug 12	15:20	0:30	5.98		12.90		265
Aug 12	15:35	0:45	8.76		15.10		268
Aug 12	15:50	1:00	11.42		16.10		269
Aug 12	16:05	1:15	13.9		16.30		260
Aug 12	16:20	1:30	16.21		16.40	188.00	254

Date	Time	Hours	Energy J/cm^2	As mg/L	As(V) mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 5							
Aug 13	11:30	0:00	0	17.01	5.13	198.00	193
Aug 13	12:30	1:00	12.78		8.29		183
Aug 13	13:30	2:00	24.57		10.96		185
Aug 13	14:30	3:00	32.54		12.23		178
Aug 13	15:30	4:00	36.63		14.77		189
Aug 13	16:30	5:00	39.2		14.95		184
Aug 13	11:30	7:00	53.6		15.81		190
Aug 13	14:00	9:30	72.5		16.87	198.00	187

Table 4-3. Absorbed solar energy, arsenic and iron speciation during solar batch tests using Susie Mine water. (cont.)

Date	Time	Hours	Energy J/cm^2	As mg/L	As(V) mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 6							
Aug 13	11:30	0:00	0	16.99	5.34	198.00	290
Aug 13	12:30	1:00	12.78		9.56		274
Aug 13	13:30	2:00	24.57		12.38		260
Aug 13	14:30	3:00	32.54		13.61		276
Aug 13	15:30	4:00	36.63		15.89		268
Aug 13	16:30	5:00	39.17		16.26		273
Aug 14	10:30	6:00	46.7		15.77		269
Aug 14	11:00	6:30	50.4		15.77	197.00	273
Batch 7							
Aug 14	11:30	0:00	0	15.92	4.29	190.00	189
Aug 14	12:30	1:00	6.74		8.08		190
Aug 14	13:30	2:00	14.47		11.65		193
Aug 14	14:30	3:00	24.97		14.60		192
Aug 14	15:30	4:00	35.59		15.89		199
Aug 14	16:30	5:00	42.46		15.82		198
Aug 14	17:30	6:00	47.52		15.8	185.00	200
Batch 8							
Aug 14	15:00	0:00	0	15.39	5.08	186.00	285
Aug 14	15:30	0:30	5.54		9.59		290
Aug 14	16:00	1:00	9.22		11.30		288
Aug 14	16:30	1:30	12.41		12.33		293
Aug 14	17:00	2:00	15.12		13.47		282
Aug 14	17:30	2:30	17.47		14.65		290
Aug 14	11:00	3:40	26.1		15.25		
Aug 14	12:00	4:40	37.1	15.97	15.95	190.00	
Batch 9							
Aug 15	10:30	0	0	15.39	5.01	187.00	110
Aug 15	11	0:30	4.537		5.93		106
Aug 15	11:30	1:00	9.843		8.39		110
Aug 15	12:00	1:30	15.49		11.22		115
Aug 15	12:30	2:00	20.29		12.07		115
Aug 15	13:30	3:00	31.95		14.10		118
Aug 15	14:30	4:00	43.85	15.97	14.90	180.00	117
Batch 10							
Aug 15	14:30	0:00	0	15.1	3.00	188.00	109
Aug 15	15:00	0:30	2.924		6.63		105
Aug 15	15:30	1:00	9.98		12.50		112
Aug 15	16:00	1:30	16.09		14.04		113
Aug 15	16:30	2:00	21.14		14.53		113
Aug 15	17:00	2:30	25.25		14.70	175.00	115
Batch 11							
Aug 15	21:00	0:00	0	15.1	2.68	189.00	195
Aug 15	22:00	1:00	0		2.91		
Aug 15	23:00	2:00	0		2.80	186.00	190

Table 4-4. Field measurements during solar batch tests using Susie Mine water.

Date	Time	Sample	Temperature °C	pH	Eh mV vs Ag/AgCl	Dissolved Oxygen (DO) mg/L	UV mW/cm^2
		Batch 1					
8/11/96	12:10	1	17.5	4.93	109	7.2	
8/11/96	13:00	2	22	4.66	226	6.6	
8/11/96	14:55	3	25	4.54	218	6.2	2.26
8/11/96	15:27	4		1.31			1.03
8/11/96	17:00	5	26	4.22	239	6.6	1.96
8/12/96	13:30	6	27	3.88	318	5.6	3.15
		Batch 2					
8/11/96	13:00	1	17	1.37	476	7.5	2.64
8/11/96	14:00	2	19	1.35	481	7.1	1.69
8/11/96	14:55	3	21	1.3	498	7.0	2.77
8/11/96	15:27	4	23	1.22	494	6.8	1.03
8/11/96	17:00	5	24	1.2	496	6.6	1.96
8/11/96	18:00	6	24	1.21	495	6.6	1.78
		Batch 3					
8/12/96	11:30	1	18	1.87	472	7.5	2.59
8/12/96	12:30	2	22	1.89	459	6.5	2.91
8/12/96	13:30	3	24.7	1.85	484	6	3.15
8/12/96	14:30	4	27	1.78	478	7	3.28
8/12/96	15:30	5	27	2.1	486	6	3.31
8/12/96	16:30	6	27	2.05	486	6	
8/12/96	17:00	8	27	2.27	485	6.3	3
		Batch 4					
8/12/96	14:35	1	19	1.3	494	10.5	3.29
8/12/96	14:50	2	19.7	1	490	7.2	3.3
8/12/96	15:05	3	20.3	1.2	499	7	3.31
8/12/96	15:20	4	21.7	1.4	504	6.8	3.31
8/12/96	15:35	5	22.3	1.5	498	8.2	3.3
8/12/96	15:50	6	23	1.4	500	6.6	3.29
8/12/96	16:05	7	23.9	1.5	498	6.2	3.27
8/12/96	16:20	8	24	1.4	498	6	3.25
		Batch 5					
8/13/96	11:30	1	16.5	1.84	471	7.0	1.91
8/13/96	12:30	2	21	2.06	486	6.5	2.55
8/13/96	13:30	3	23	2.1	493	5.8	2.74
8/13/96	14:30	4	25.5	2.1	493	6.2	2.63
8/13/96	15:30	5	25	2.08	490	7.4	2.36
8/13/96	16:30	6	24	2.09	491	6.4	2.11
8/14/96	9:30	7	16	1.9	453	8.0	1.77
8/14/96	10:30	8	18	2	454	7.0	2.05
8/14/96	11:30	10	20	2	459	7.2	1.99
8/14/96	12:30	11	21	2.04	478	6.4	1.96
8/14/96	13:30	12	22	2.12	481	6.6	2
		Batch 6					
8/13/96	11:30	1	16.5	1.83	481	7.0	1.91
8/13/96	12:30	2	20.5	2.02	493	6.2	2.55
8/13/96	13:30	3	22.5	2.03	511	5.9	2.74
8/13/96	14:30	4	24.5	2.04	507	6.2	2.63
8/13/96	15:30	5	24.5	2.03	504	7.6	2.36
8/13/96	16:30	6	24	2.07	503	6.2	2.11
8/14/96	9:30	7	16	1.86	485	7.6	1.77
8/14/96	10:30	8	18.5	1.91	488	7.0	2.05
8/14/96	11:00	9	19.5	1.93	488	6.7	2.06

Table 4-4. Field measurements during solar batch tests using Susie Mine water. (cont.)

Date	Time	Sample	Temperature EC	pH	Eh mV vs Ag/AgCl	Dissolved Oxygen mg/L	UV mW/cm^2
		Batch 7					
	11:30	1	17	1.62	450	5.8	1.99
8/14/96	12:30	2	17.5	1.72	480	6.6	1.96
8/14/96	13:30	3	20	1.74	477	6.8	2
8/14/96	14:30	4	22.5	1.7	481	6.6	2.17
8/14/96	15:30	5	24	1.61	491	6.4	2.24
8/14/96	16:30	7	25	1.69	496	6.2	2.24
8/14/96	17:30	8	24.5	1.68	479	6.3	2.15
8/14/96							
		Batch 8					
8/14/96	15:00	1	20	1.71	485	6.4	2.23
8/14/96	15:30	2	20	1.67	487	7.0	2.31
8/14/96	16:00	3	22	1.78	482	6.2	2.3
8/14/96	16:30	4	21.2	1.78	497	7.0	2.24
8/14/96	17:00	5	22	1.69	500	6.4	2.21
8/14/96	17:30	6	22	1.69	482	7.0	2.15
8/15/96	10:00	7	16.5	1.51	471	7.4	2.05
8/15/96	11:00	8	19	1.59	478	7.3	2.6
8/15/96	12:00	9	22	1.72	499	6.5	3.05
		Batch 9					
8/15/96	10:30	1	16	1.8	449	5.4	2.47
8/15/96	11:00	2	18	1.6	468	7.0	2.6
8/15/96	11:30	3	19	1.58	488	7.4	2.93
8/15/96	12:00	4	21	1.68	476	6.5	3.05
8/15/96	12:30	5	22	1.8	471	6.8	2.9
8/15/96	13:30	6	25	1.8	473	6.0	3.02
8/15/96	14:30	7	26	1.75	477	6.0	3.14
		Batch 10					
8/15/96	14:30	1	19	1.5	450	4.2	3.14
8/15/96	15:00	2	20	1.71	450	6.7	2.92
8/15/96	15:30	3	22	1.6	472	6.4	3.03
8/15/96	16:00	4	22.5	1.48	470	6.42	3.07
8/15/96	16:30	5	24	1.49	472	6	3.05
8/15/96	17:00	6	25	1.6	481	5.8	2.99

Table 4-5. Elemental analysis of flue dust leachate taken from the solar ponds at different times during three batch tests.

Sample	Ca mg/L	Na mg/L	Zn mg/L	Al mg/L	Cd mg/L	Fe mg/L	As mg/L	Chloride mg/L	Sulfate mg/L
Batch 1									
1	71.1	13.2	8.61	0.18	0.028	437	394	3790	314
8	68.4	11.6	8.86	0.11	0.021	408	363	3690	480
Batch 2									
1	70.6	12	8.6	0.19	0.027	444	410	1370	290
10	69.3	12.6	9.57	0.1	0.019	436	400		
16	74.6	15.2	10.4	0.17	0.04	438	414		
Batch 3									
1	72.3	1760	9.07	0.16	0.02	441	391	3910	292
12	73.4	1720	9.68	0.13	0.034	392	355	3990	642

Table 4-6. Reagent additions to the flue dust leachate for solar batch tests.

Batch	FeCl3.6H2O g	NaCl g	pH	Pond Volume L	Fe(III) mg/L	Cl- mg/L
1	1000	nil	1	400	430	3700
2	1000	nil	2	400	440	1370
3	1000	2210	2	400	440	3900

Table 4-7. Absorbed solar energy, arsenic and iron speciation during solar batch tests using flue dust leachate.

Date	Time	Hours	Energy J/cm^2	As mg/L	As(V) mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1							
Aug 09	16:30	0:00	0.0	427	22	0.0	328
Aug 10	9:00	1:30	12.7		53		
Aug 10	13:00	4:30	53.6		174	20.8	
Aug 10	13:30	5:00	61.3		186		
Aug 11	10:00	9:20	114.7		391	16.7	
Aug 11	14:00	13:20	141.9		422	14.5	320
Aug 11	18:00	17:20	163.5	420	420	15.3	321
Batch 2							
Aug 09	16:00	0:00	0.0	439	15	0.0	308
Aug 10	9:00	2:00	12.8		22.4	20.4	
Aug 10	13:00	6:00	53.7		62	56.6	
Aug 11	10:00	9:30	115.4		137	70.9	
Aug 11	14:00	12:30	142.7		171		
Aug 11	18:00	16:30	164.3	448	187	225.5	294
Aug 12	12:30	19:30	191.5		219		
Aug 12	18:00	24:30	251.0	461	295	61.9	
Aug 13	14:00	28:30	290.0	462	299		
Aug 13	16:00	30:00	298.9	457	315	45.9	
Aug 14	17:30	36:00	391.7	445	362	35.8	320
Aug 15	17:00	42:00	465.0	460	414	28.7	
Aug 16	16:30	48:00	536.0	468	469	24.8	
Batch 3							
Aug 09	16:00	0:00	0.0	423	20	30.2	
Aug 10	9:00	2:00	12.8		31	0.0	
Aug 10	13:00	6:00	53.7		97	66.7	306
Aug 11	10:00	9:30	115.4		212	54.5	
Aug 11	14:00	12:30	142.7		263	46.3	
Aug 11	18:00	16:30	164.3		301	36.5	315
Aug 12	12:30	19:30	191.5		341	23.5	
Aug 12	18:00	24:00	251.0	452	437	22.3	
Aug 13	14:00	28:00	290.0	455	448	21.4	310
Aug 13	16:00	30:00	298.9	435	435		

Table 4-8. Field measurements during solar batch tests using flue dust leachate.

	Temperature °C	pH	Eh mV vs Ag/AgCl	Dissolved Oxygen mg/L	UV mW/cm^2
Batch 1					
1	19	1.3	582	78%	
2					2.4
3	19.3	1.25	575	72%	3.96
4	26	1.31	590	5.2	3.71
5	27.5	1.36	590	7.8	
6	22.5	1.08	566	6.2	2.02
7	25.5	1.29	560	6.3	1.78
8	26	1.21	591	6.2	
Batch 2					
1	24	1.81	609	82%	
2					2.4
3	19.8	1.79	591	80%	
4	26.5	1.9	594	5.8	3.96
5	29	1.85	573	6.4	3.71
6	23	1.63	554	6.3	
7	26	1.74	539	6.2	2.02
8	27	1.67	564	6.1	1.78
9	23	1.36	534	6.5	
10	27.8	2.01	565	7.2	3
11	26	1.8	555	6.2	2.7
12	25	1.81	442	6.4	2.22
13	25	1.74	536	6.4	2.15
14	27	1.89	530	5.8	2.99
15	28	1.3	550	5.6	3.12
Batch 3					
1	22	1.88	595	82%	
2					2.4
3	19.5	1.83	577	80%	
4	26	1.85	576	5.6	3.96
5	29	1.78	561	6.6	3.71
6	23	1.63	546	6.3	
7	26	1.71	542	6.2	2.02
8	27	1.67	560	6.1	1.78
9	22	1.36	537	6.4	
10	27.5	1.89	576	7	3
11	26	1.7	560	6.5	2.71
12	25	1.77	583	6.3	2.22

Table 4-9. As(V) concentrations during continuous solar flow tests using Susie Mine water.

Test 1 Time	12:00	13:00	14:00	15:00
Port				
A	11.0	13.0	13.3	10.6
B	17.3	17.6	18.1	17.4
C	18.5	19.2	19.3	19.0
D	21.0	20.9	21.4	21.0
E	21.8	21.4	21.8	21.5
			As(T) = 21.99, 21.89, 22.12	
Test 2				
A	5.7	4.3	3.1	3.2
B	7.4	7.3	6.6	6.5
C	8.0	8.3	6.9	7.5
D	10.4	10.6	10.6	10.3
E	10.5	11.0	11.2	10.8
			As(T) = 13.4, 13.2, 13.4, 13.4	

Table 4-10. Field measurements during solar continuous flow test using Susie Mine water.

Sample/Port	Temperature °C	pH	Eh mv vs Ag/AgCl	Dissolved Oxygen mg/L	UV mW/cm2
Test 1					
1/A	17	1.24	493	4.9	3.03
1/E	21	1.05	499	6.7	3.03
2/A	19.5	1.33	476	6.4	3.26
3/A	22	1.08	486	5.8	3.58
3/E	18	1.27	477	6.5	3.58
4/A	21	1.26	484	6	3.44
4/E					3.44
Test 2					
1/A	16	1.52	474	7.1	3.85
1/E	18	1.46	478	7.4	3.85
2/A	17	1.64	493	7.2	3.35
2/E	19	1.67	496	7	3.35
3/A	20	1.77	488	6.8	3.64
3/E	20	1.68	492	8	3.64
4/A	18.5	1.54		7	3.56
4/E	20	1.51		6.5	3.56

Table 4-11. Elemental analysis of test mixtures used for batch tests using Susie Mine water in the Ultrox reactor.

Sample	Ca mg/L	Na mg/L	Zn mg/L	Al mg/L	Cd mg/L	Fe mg/L	Chloride mg/L	Sulfate mg/L
Batch 1								
1	228	19.7	63	3.58	0.548	190	442	1020
7	230	20.2	63.3	3.65	0.546	189	441	977
Batch 2								
1	227	20.3	63.9	3.68	0.557	284	686	886
7	225	20.3	63.2	3.65	0.549	285	696	955
Batch 3								
1	244	20.2	67.5	4.01	0.554	219	1310	958
7	244	20.6	66.8	4.03	0.564	213	1390	823

Table 4-12. Reagent additions for Ultrox batch tests using Susie Mine water.

Batch	HCl g/L	Add Fe(III) mg/L	Rate (MSE) mg/L/min	Rate (ANSTO) mg/L/min	
				Total	Dissolved
1	0.36	0	-0.24[1]	0.44	0.48
2	0.36	100	0.23	0.38	0.34
3	1.08	0	0.35	0.51	ND
4	0.27	0	0.30	0.67	0.67
5	1.08	100	0.29	0.45	0.44
6	0.11	0	0.52	0.27	0.28
7	0.11	100	0.40	0.24	0.24
6	0.11	0	0.52	0.27	0.28
4	0.27	0	0.30	0.67	0.67
1	0.36	0	-0.24	0.44	0.48
3	1.08	0	0.35	0.51	ND
7	0.11	100	0.40	0.24	0.24
2	0.36	100	0.23	0.38	0.34
5	1.08	100	0.29	0.45	0.44

[1] Not included in cost calculation.

Table 4-13. Arsenic and iron speciation during Ultrox batch tests using Susie Mine water.

Minutes	As(V) Total mg/L	As(V) Dissolved mg/L	Arsenic mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1					
0	7.1	4.5	16.5		
15	13.6	11.6			
30	16.2	14.0			
45	16.5	14.2			
60	16.2	14.3			
75	16.5	14.3			
90	16.6	14.3			
slope	0.438	0.477			
Batch 2					
0	7.1	6.1	15.4	39	258
5	8.6	7.5			
10	11.3	10.1			
20	14.5	12.8			
30	15.2	14.0		122	172
40	15.4	14.5			
50	15.4	14.5			
slope	0.377	0.343			
Batch 3					
0	7.3	7.0	15.2	133	105
5	9.8				
10	12.8				
15	14.8				
20	15.0				
30	16.5			127	86
40	16.2	15.2			
slope	0.513				
Batch 4					
0	6.8	6.5	15.2	108	145
5	10.5	10.4			
10	13.5	13.2			
15	14.7	14.1			
20	15.2	15.2			
30	15.2	15.3		128	79.6
slope	0.670	0.667			
Batch 5					
0	6.8	6.9	15.2	126	176
5	9.4	9.5			
10	11.7	11.6			
15	13.5	13.5			
20	14.6	14.6			
25	14.9	15.1			
30	15.2	15.2		129	161
slope	0.448	0.436			
Batch 6					
0	7.1	6.8	14.7	109	153
10	10.1	9.8			
20	12.6	12.3			
30	13.9	13.6		98	109
45	14.7	14.3			
60	14.8	14.4			
75	14.7	14.4			
slope	0.274	0.278			
Batch 7					
0	6.1	5.6	12.4	139	152
10	8.8	8.3			
20	10.8	10.4			
30	11.8	11.2		142	150
45	12.3	11.8			
60	12.4	12.0			
75	12.4	11.9			
slope	0.236	0.239			

Table 4-14. On-line measurements during Ultrox batch tests using Susie Mine water.

Sample	Temperature °C	pH	Eh mV vs Ag/AgCl	Dissolved Oxygen mg/L	Energy kW/hr
Batch 1					
1	20.5	2.2	480	6.00	36.85
2	20.5	2.2	480	6.00	
3	21.5	2.2	483	5.80	
4	22.0	2.2	483	5.80	
5	22.2	2.2	487	5.80	
6	22.5	2.2	485	5.80	
7	22.8	2.2	479	5.65	29.7
Batch 2					
1	21.0	2.0	486	7.80	30.1
2	21.0	2.0	486	7.80	
3	21.0	2.0	487	7.80	
4	21.5	2.0	484	7.80	
5	22.0	2.0	485	8.00	
6	22.0	2.0	485	6.00	
7					31.9
Batch 3					
1	24	1.6	482	8.60	32.3
2	24	1.6	479	8.40	
3	23	1.6	479	8.40	
4	23	1.6	479	8.40	
5	23	1.6	480	8.40	
6	23	1.6	482	8.40	
7	23	1.6	483	6.50	34.7
Batch 4					
1	19.5	2.2	456	8.60	35.1
2	19.75	2.2	452	8.40	
3	20.0	2.3	451	8.40	
4	20.0	2.3	451	8.40	
5	20.2	2.3	452	8.40	
6	21.0	2.3	454	8.40	
7	21.0	2.3	457	6.50	38.4
Batch 5					
1	19	1.7	487	6.10	39.1
2	19	1.7	487	6.10	
3	19	1.7	487	6.10	
4	19	1.7	487	6.20	
5	20	1.7	487	6.10	
6	20	1.7	487	6.10	
7	20	1.7	483	6.10	40.9
Batch 6					
1	17.5	2.6	455	6.80	41.1
2	17.0	2.6	454	6.80	
3	17.0	2.6	452	6.70	
4	18.0	2.6	452	6.60	
5	18.5	2.6	452	6.60	
6	18.8	2.6	452	6.80	
7	19.1	2.6	453	6.40	43.2
Batch 7					
1	18.5	2.5	479	6.80	44.5
2	18.5	2.5	478	7.00	
3	19.0	2.4	478	7.00	
4	19.0	2.4	477	7.00	
5	19.2	2.4	478	6.60	
6	20.0	2.4	479	6.60	
7	20.1	2.4	479	6.60	47.3

Table 4-15. Elemental analysis of flue dust test mixtures during testing in the Ultrox reactor.

Sample	Ca mg/L	Na mg/L	Zn mg/L	Al mg/L	Cd mg/L	Fe mg/L	As mg/L	Chloride mg/L	Sulfate mg/L
Batch 1									
1	21	1.79	0.996	0.15	0.021	213	1210	4390	329
7	26.2	2.13	2.54	0.22	0.036	221	1200	4230	563
Batch 2									
1	24.5	1.95	1.2	0.12	0.018	229	1410	1360	437
11	26	2.02	1.2	0.17	0.005	56	1180	1250	227

Table 4-16. Reagent additions to the flue dust leachate for Ultrox batch tests.

Batch	HCl g/L	Fe(III) mg/L
1	3.6	200
2	0.36	200

Table 4-17. Arsenic and iron speciation during Ultrox batch tests using flue dust leachate.

Hours	As(T) mg/L	As(V) mg/L	As(III) mg/L	Fe(II) mg/L	Fe(III) mg/L
Test 1					
0		22		9.7	190
3:30		464		19.4	
7:30		971		17.7	
11:30		1429		21.3	
15:30		1470		11.8	
19:30		1390		10.1	
Test 2					
0	1693	161	1532	18.1	199
4*	*1693*	*417*	*1275*	*22.3*	
8	1707	640	1067	12.0	
12	1601	735	865	10.4	
16*	*1440*	*798*	*641*	*10.1*	
20	1443	1009	434	9.5	
24	1440	1219	221	4.7	
28	1305	1296	-9	2.5	
32	1255	1265	9	3.6	

*These results have been swapped from the original record, it appears that samples were labeled incorrectly.

Table 4-18. On-line measurements during Ultrox batch tests using flue dust leachate.

Sample	Hours	Temperature °C	pH	Eh	Dissolved Oxygen mg/L	Energy kWh
Batch 1						
1	0:00		1.4			56.1
1	0:00					
2	3:30					
3	11:30	33	1.4			
4	15:30	35				
5	19:30	37				
7	19:30	38				89.6
Batch 2						
1	0:00		1.8			90.4
1	0:00					
2	4:00					
3	8:00					
4	12:00	35				
5	16:00	37.5				
6	20:00	39.5				156.1
7	24:00	39				
8	28:00					
9	32:00	40				
10	36:00					
11	40:00	40				
Blk						

Table 4-19. Reagent additions to Susie Mine water for Ultrox continuous tests.

Test	HCl g/L	Add Fe(III) mg/L
1	0.36	0
2	0.36	0

Table 4-20. Arsenic and iron speciation during Ultrox continuous tests using Susie Mine water.

	As(V) mg/L		
Port Hours	1:00	1:30	2:00
Test 1			
Feed	9.0	8.4	8.5
1	9.7	9.5	9.6
2	10.9	11.3	11.3
3	11.7	11.9	11.8
5	12.5	12.2	12.3
	As(T)+14.1		
Test 2			
Feed	10.53		10.63
1	11.73		11.67
2	11.9		11.87
3	12.07		11.93
4	11.97		12.03
	As(T)=12.36		

Table 4-21. Iron speciation during Ultrox continuous tests using Susie Mine water.

Hours		Feed			Outlet	
	Fe(II) mg/L	Fe(III) mg/L	Fe(T) mg/L	Fe(II) mg/L	Fe(III) mg/L	Fe(T) mg/L
1	4.71	180	184.71	66	146	212
1.5	4.47	187	191.47	69	145	214
2	4.55	182	186.55	70	143	213

Table 4-22. On-line measurements during Ultrox continuous tests using Susie Mine water.

Sample	Port	Temp °C	pH	Eh mV vs Ag/AgCl	DO mg/L	Power kWh
Test 1						
1	4	20.5	2.2	475	6	51.5
2	4	21	2.1	474	6	
4	4	21	2.1	474	6.2	55.7
Test 2						
1	4	18	2.3	539	6.8	164.9
2	4		2.2			
4	4	18	2.2	543	6.8	173.90*

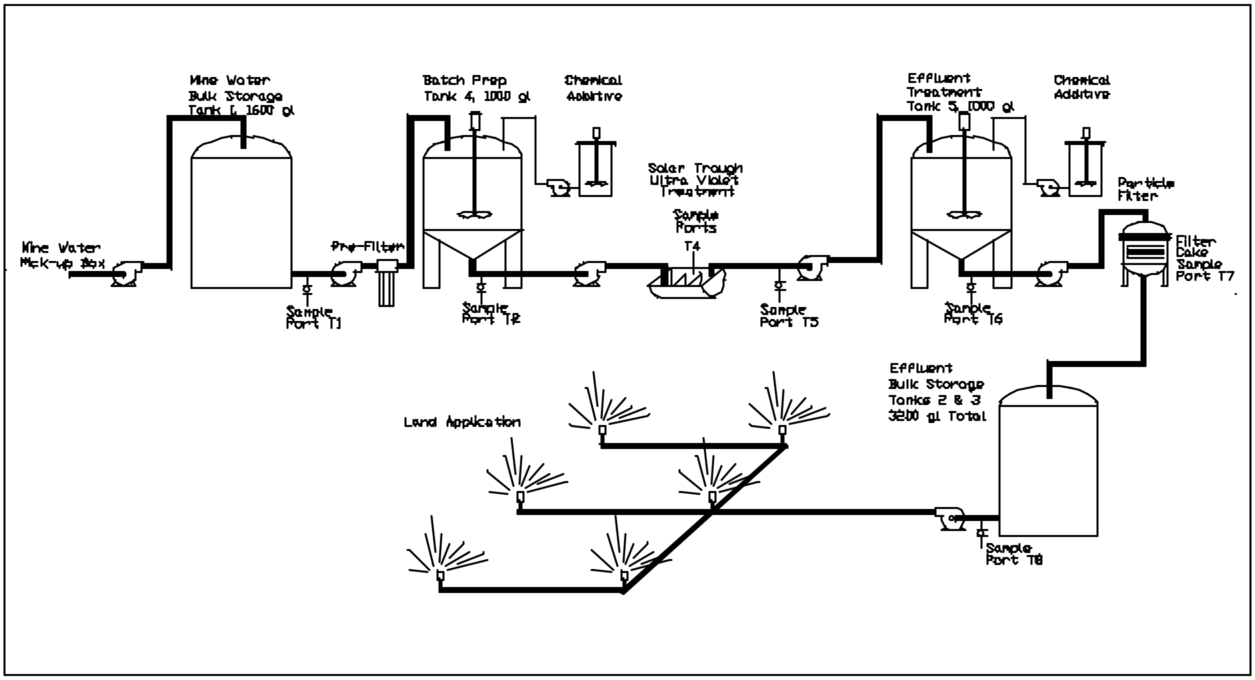

Figure 4-1. Solar trough arsenic oxidation and removal, batch method.

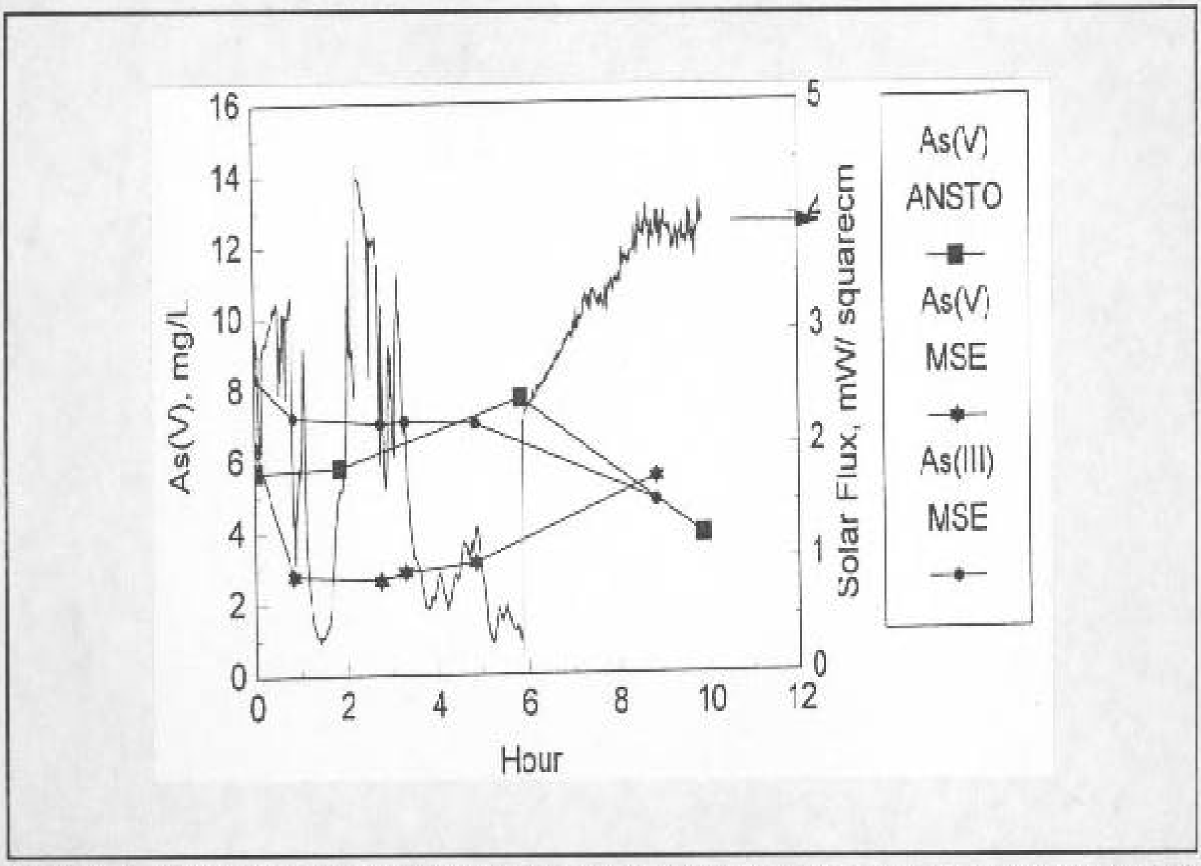

Figure 4-2. As(III) and (V) concentrations in the Susie Mine water as a function of time during solar batch test 1 (no additional reagents). UVA solar flux measurements which reflect cloud interference and time of day are also shown.

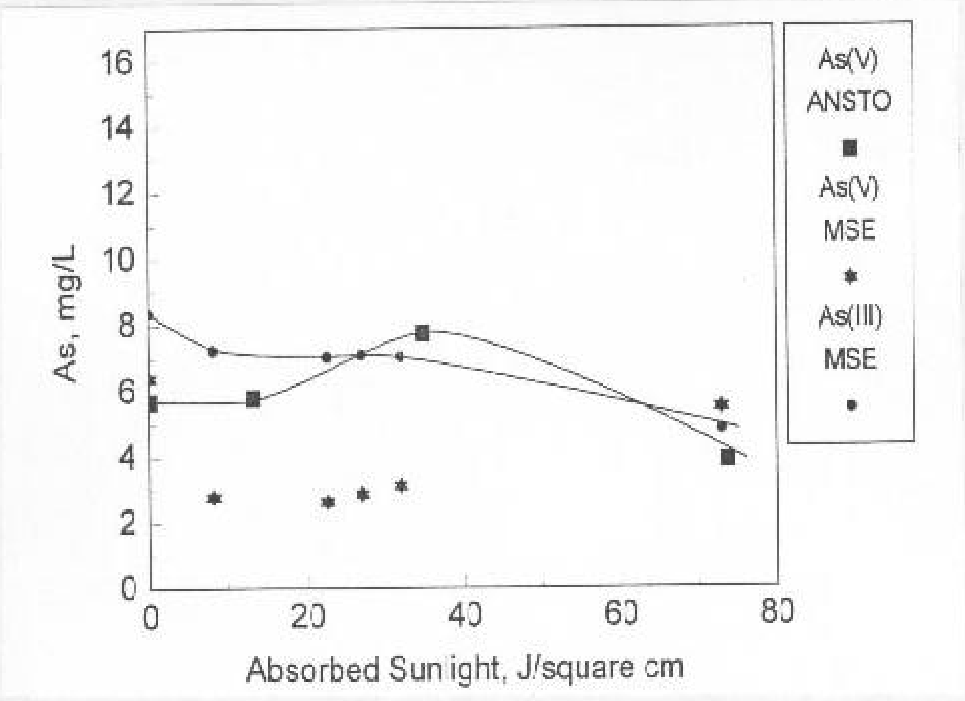

Figure 4-3. As(III) and (V) concentrations in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 1.

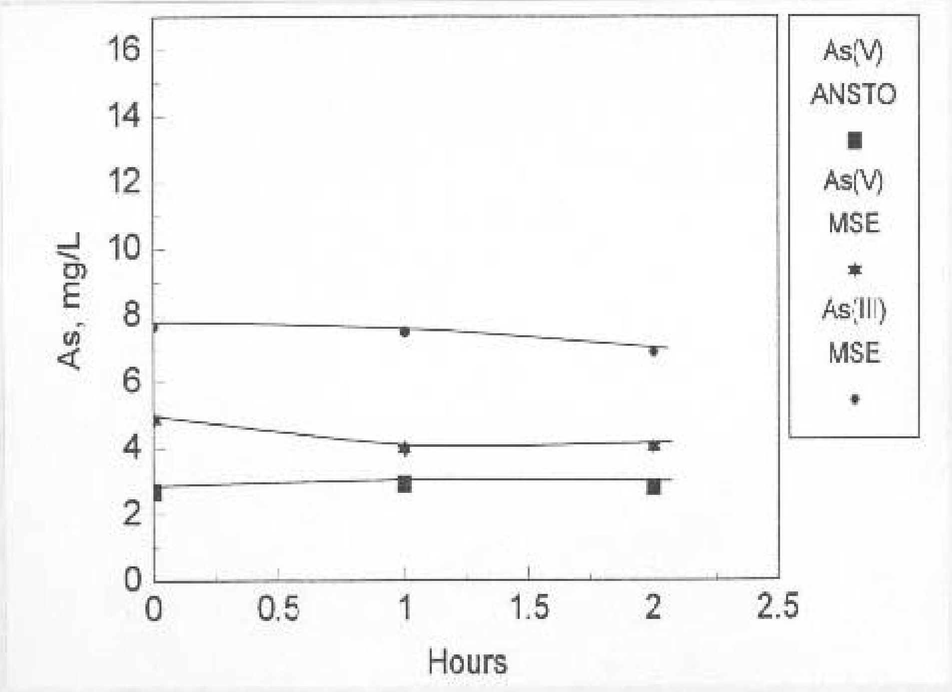

Figure 4-4. As(III) and (V) concentrations in the Susie Mine water as a function of time during the night for solar batch test 11.

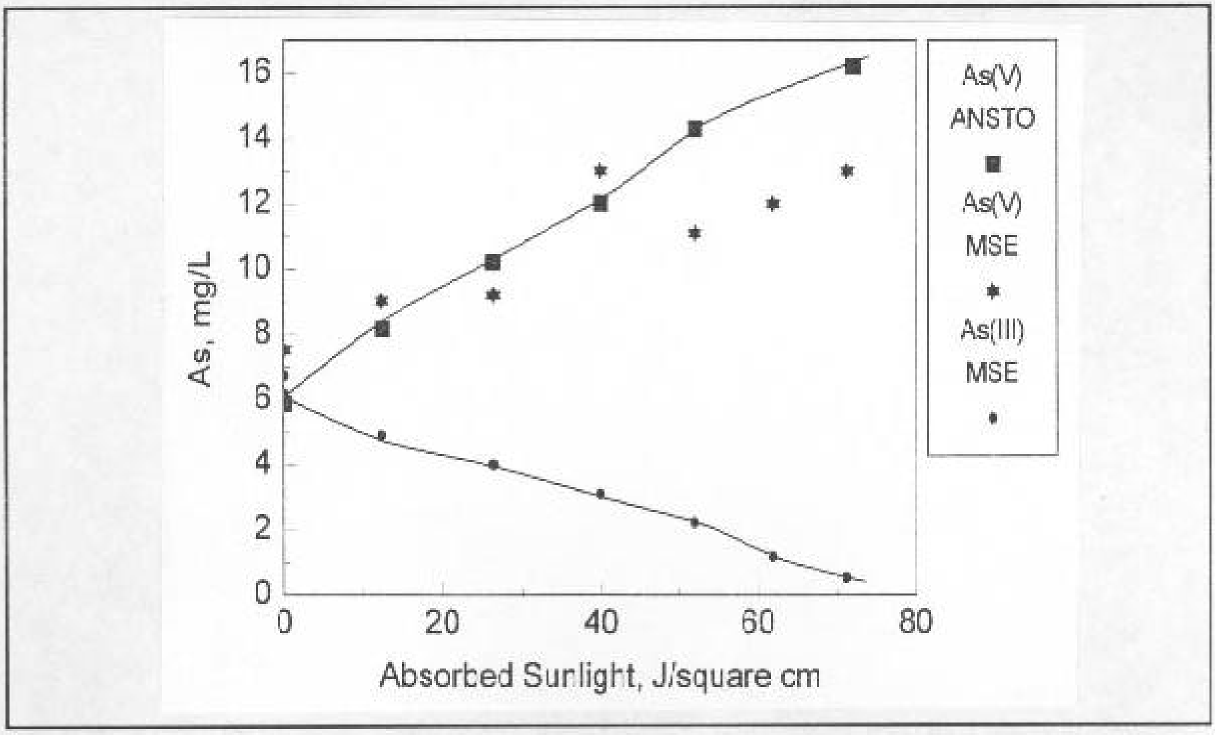

Figure 4-5. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 3.

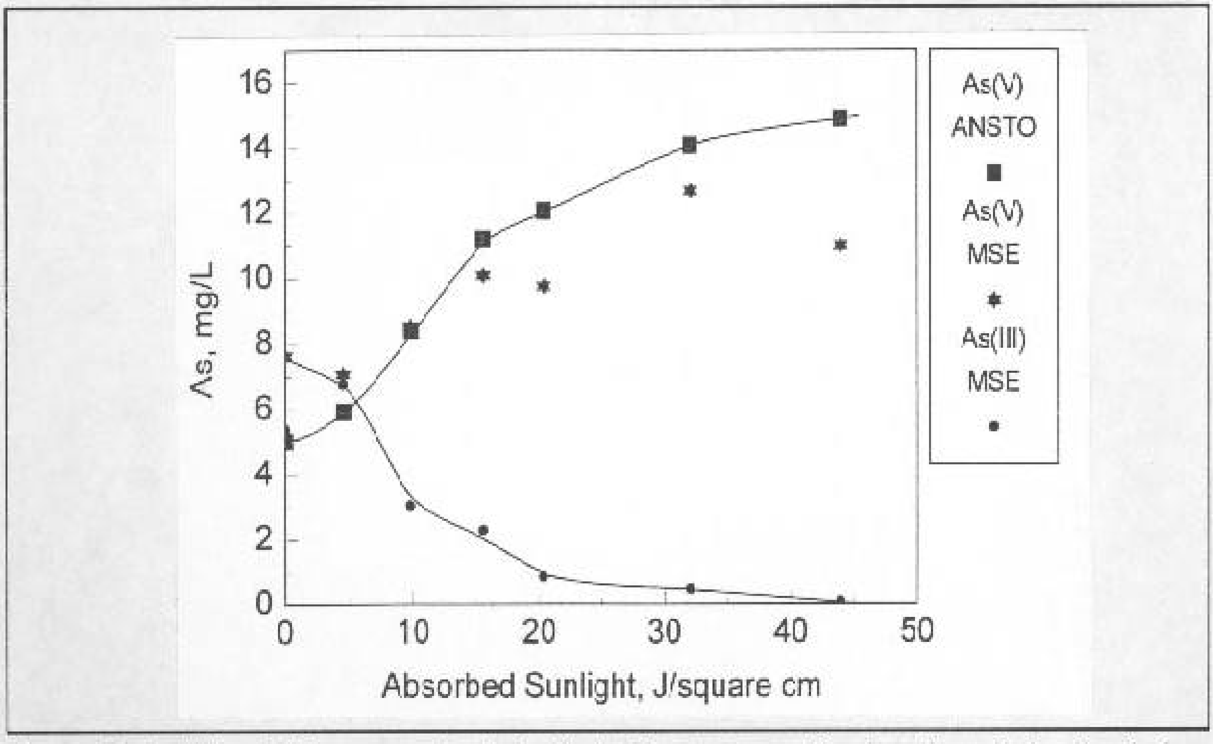

Figure 4-6. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 9.

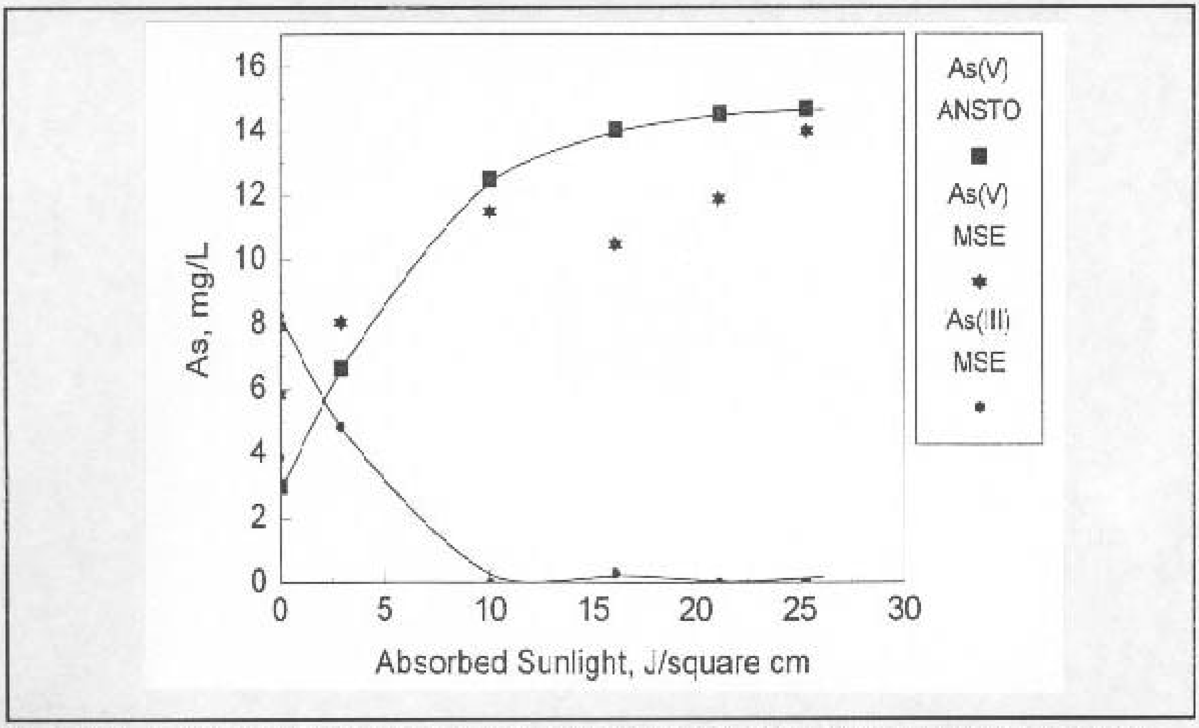

Figure 4-7. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 10.

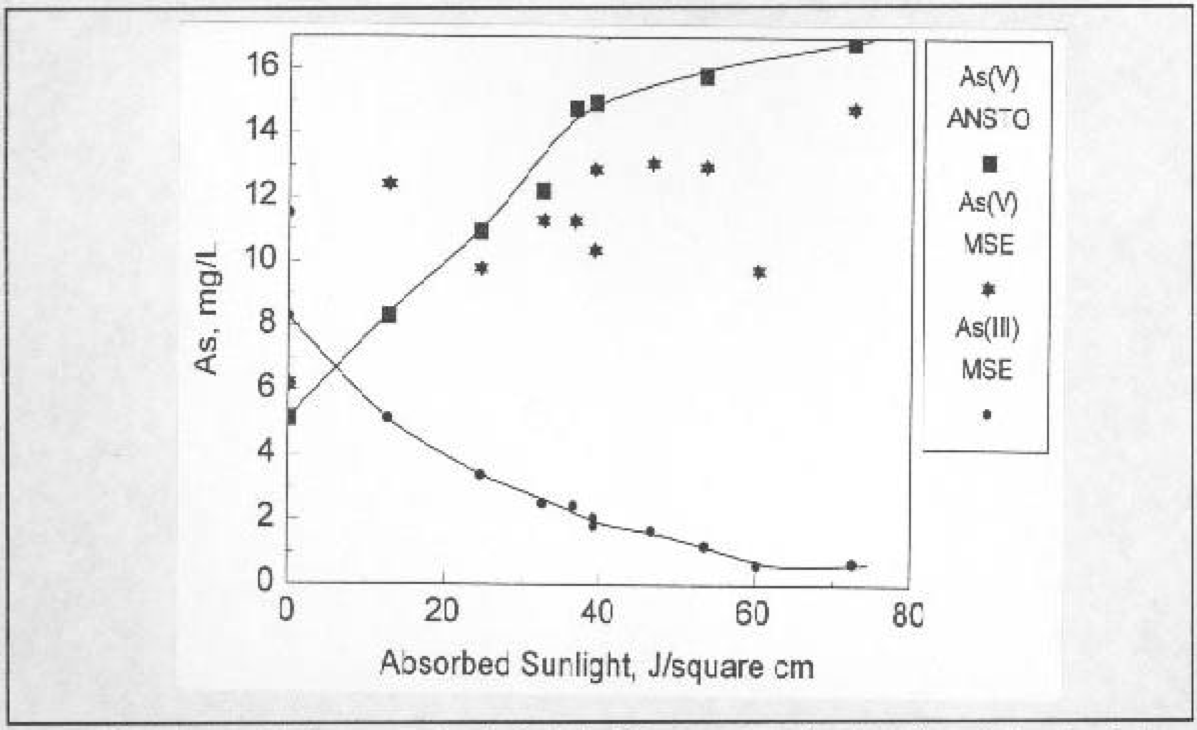

Figure 4-8. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 5.

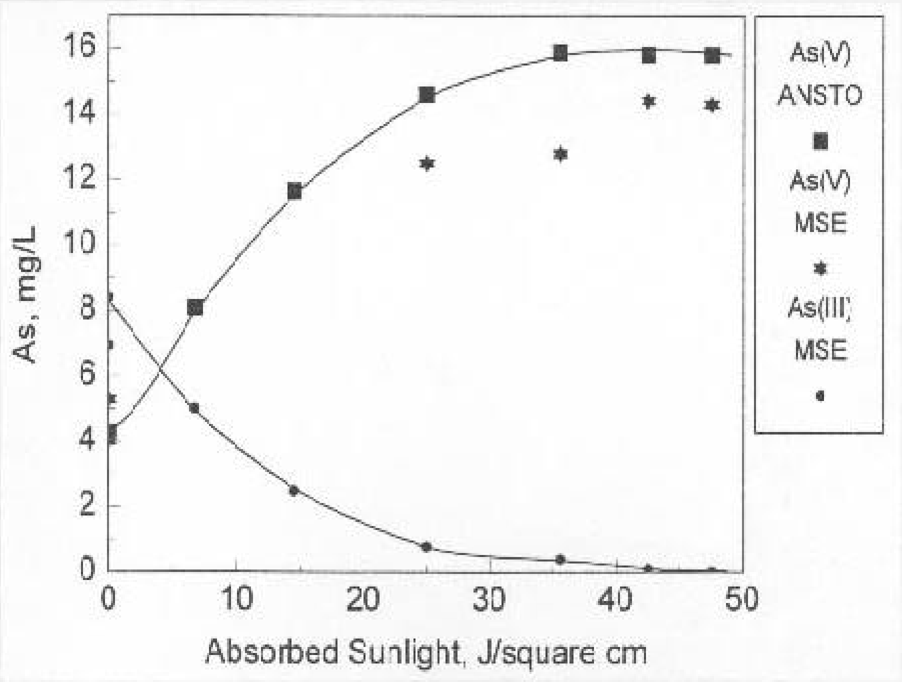

Figure 4-9. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 7.

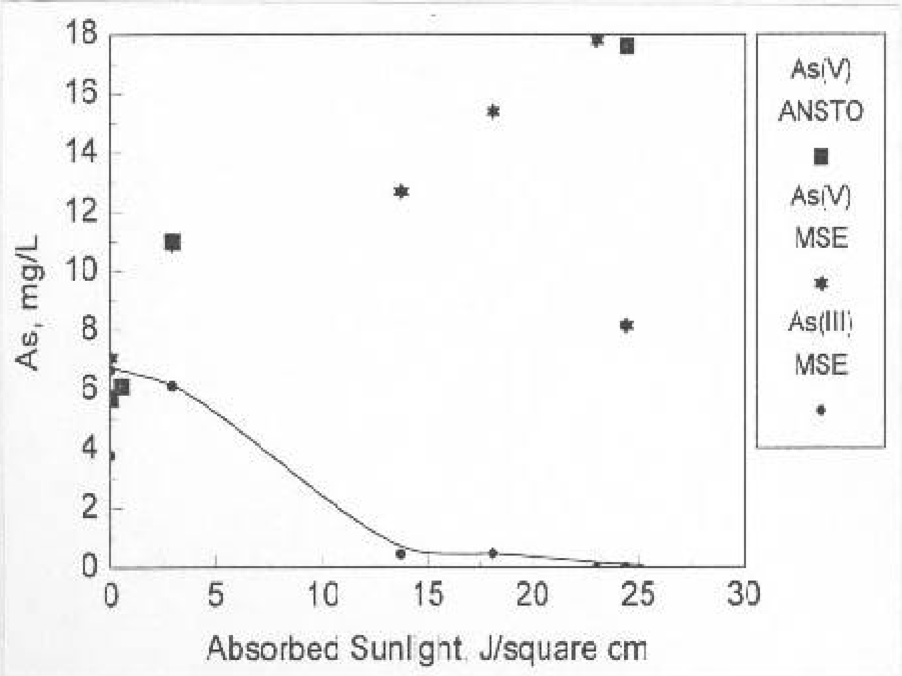

Figure 4-10. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 2.

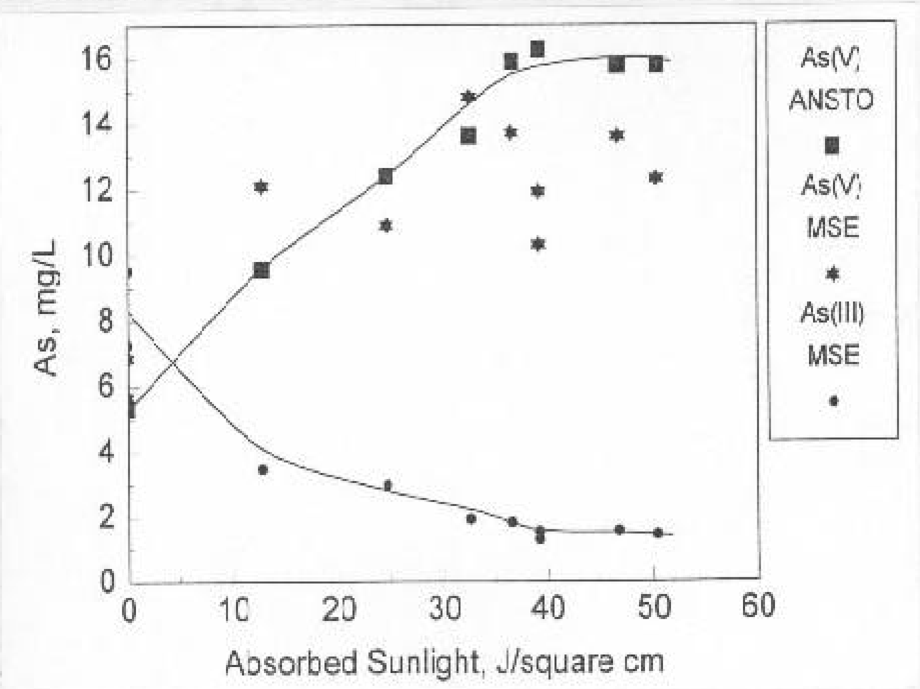

Figure 4-11. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 6.

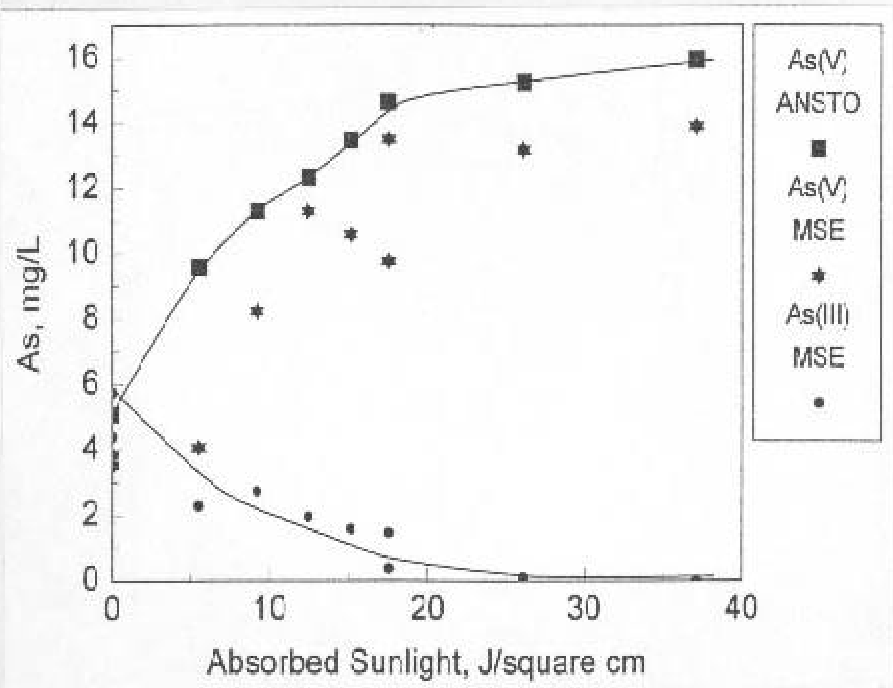

Figure 4-12. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 8.

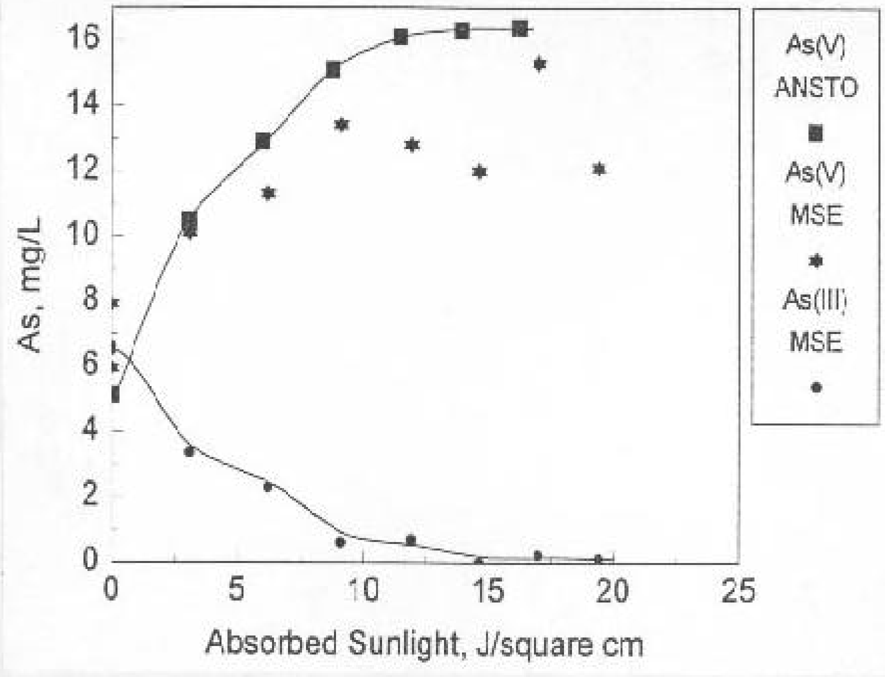

Figure 4-13. As(III) and (V) concentration in the Susie Mine water as a function of cumulative absorbed sunlight UVA energy for solar batch test 4.

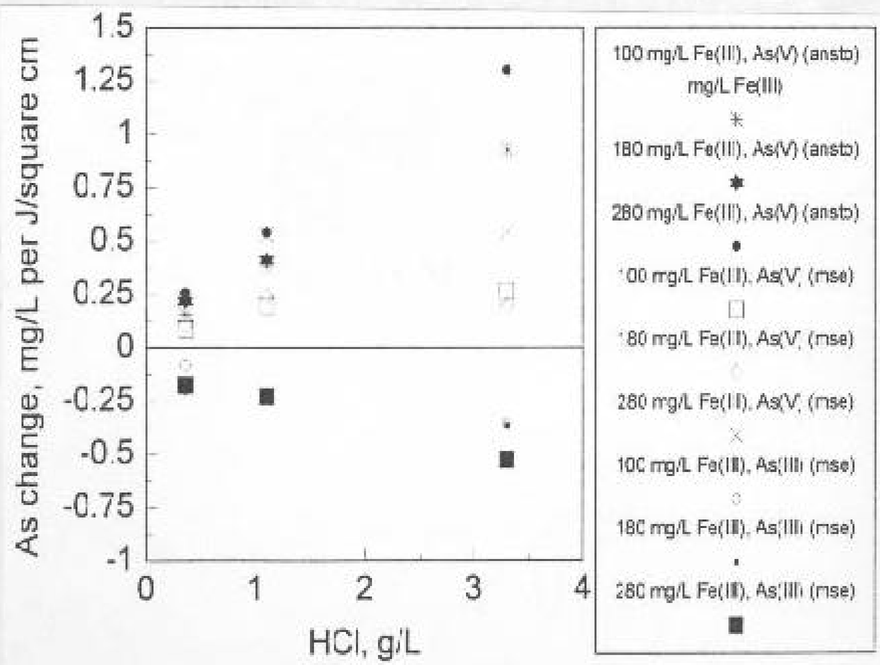

Figure 4-14. Arsenic oxidation rate in the Susie Mine water as a function of acid addition for three different Fe(III) dosages during the nine solar batch tests.

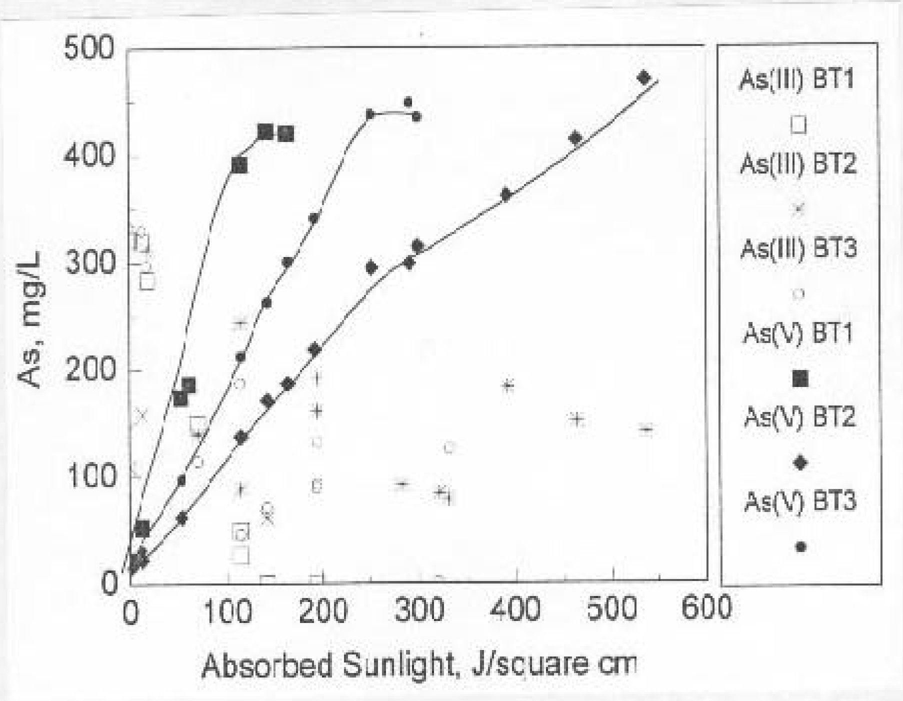

Figure 4-17. As(III) (MSE) and As(V) (ANSTO) concentrations in the flue dust leachate as a function of cumulative absorbed sunlight UVA energy for solar batch tests 1 to 3.

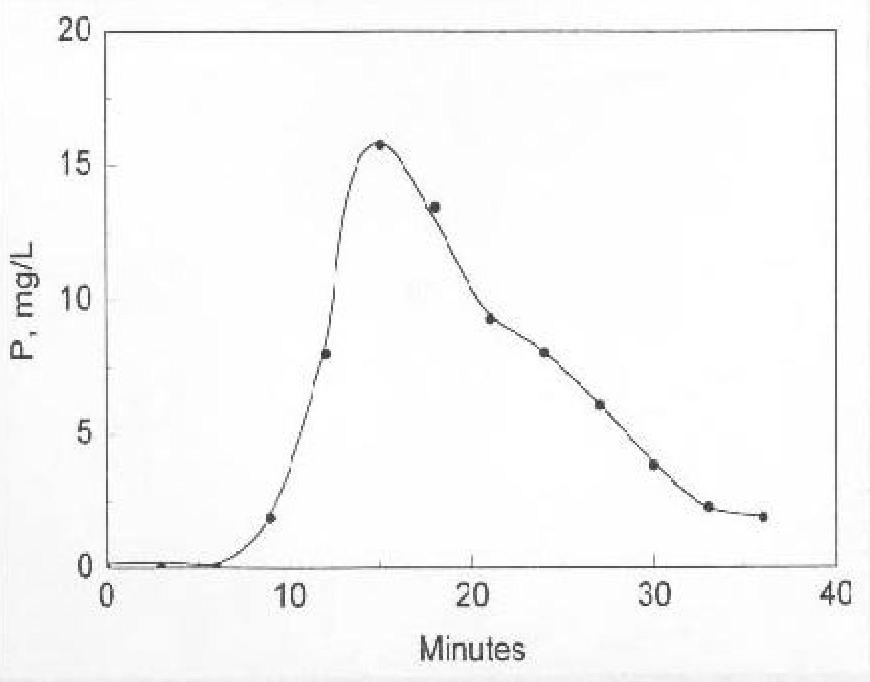

Figure 4-18. Phosphorus concentration as a function of time during a test to characterize the hydraulic behavior of the solar ponds when used as a continuous flow reactor.

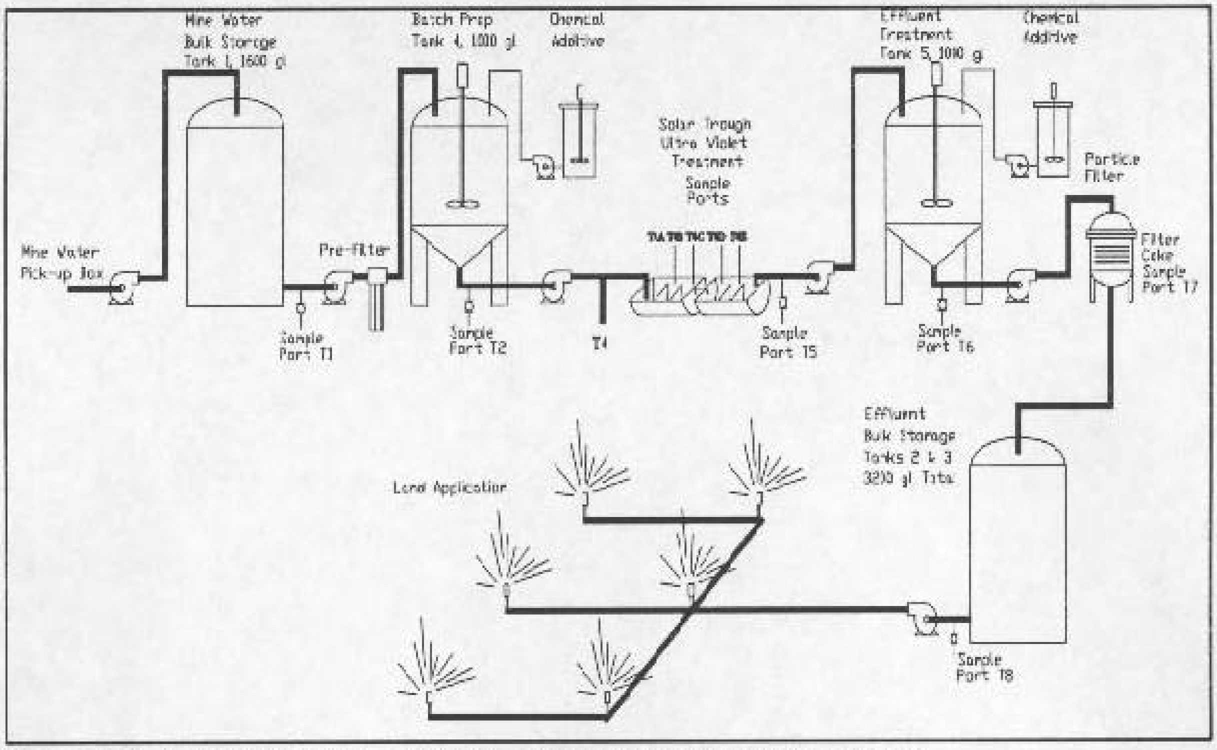

Figure 4-19. Solar trough arsenic oxidation and removal continuous flow method.

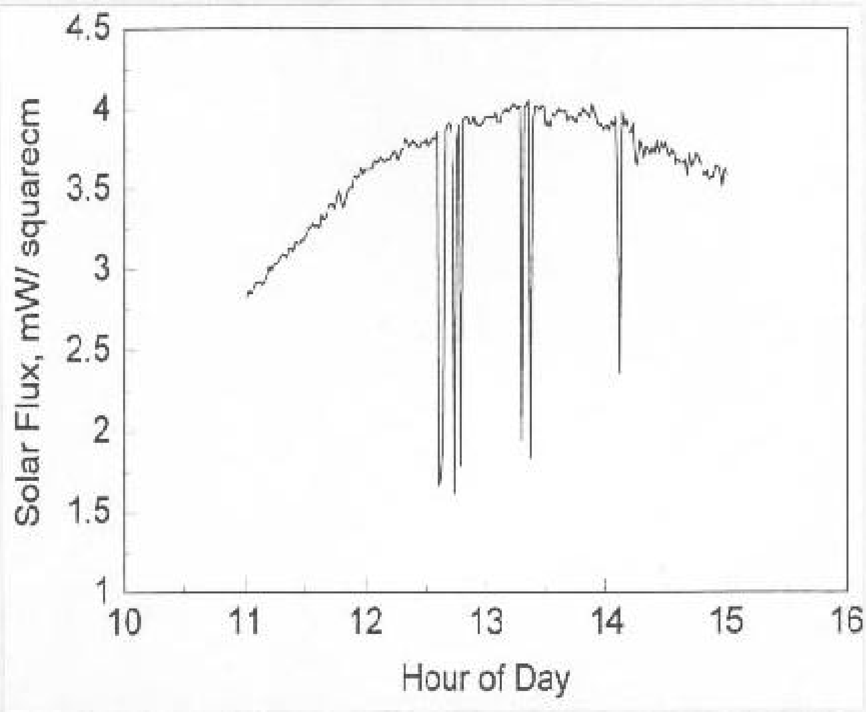

Figure 4-20. UVA solar flux measurements during continuous flow Test 1 using Susie Mine water.

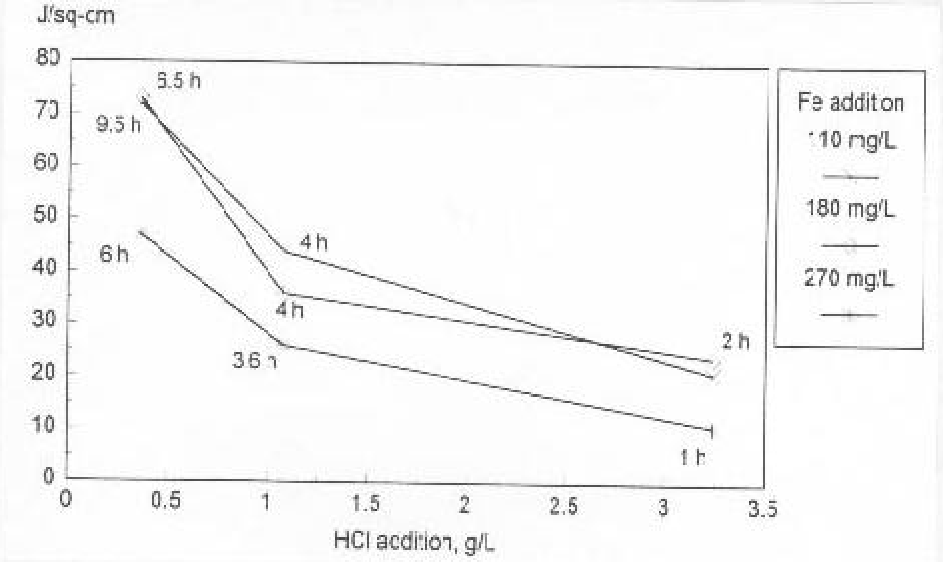

Figure 4-15. UVA solar energy (J/cm^2) and time (hours) required to complete the oxidation process as a function of acid addition for three different additions of iron.

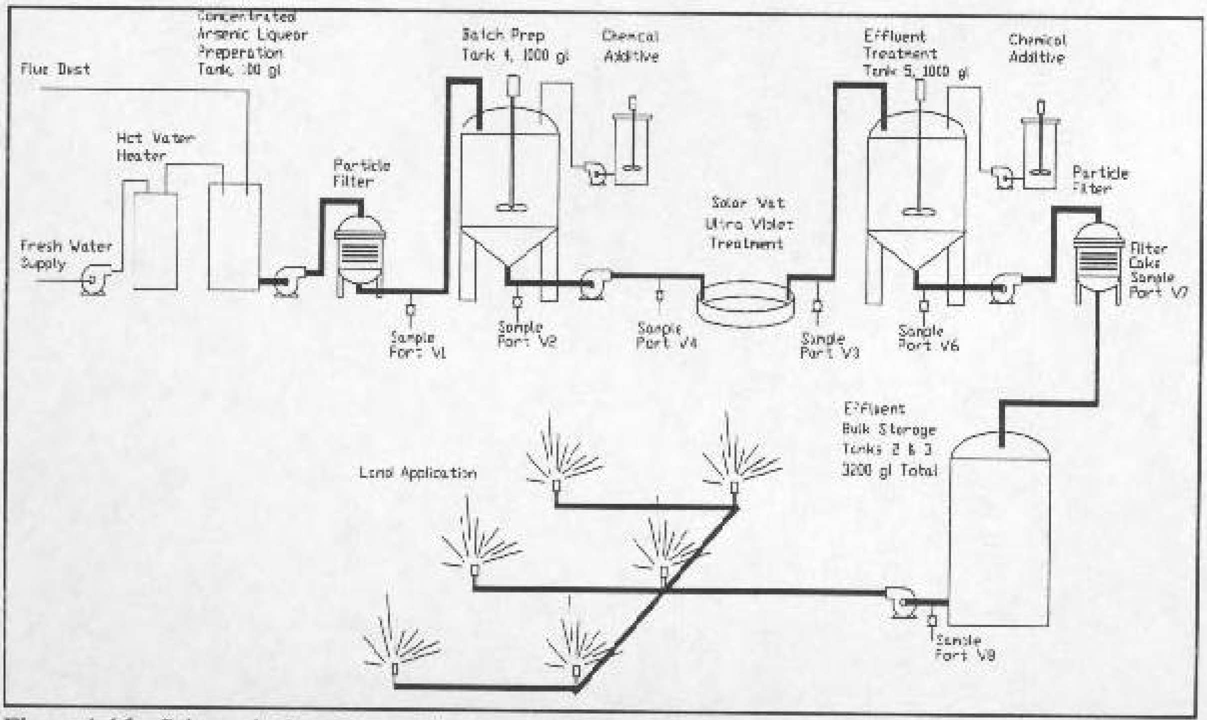

Figure 4-16. Schematic for solar vat flue dust leachate batch tests.

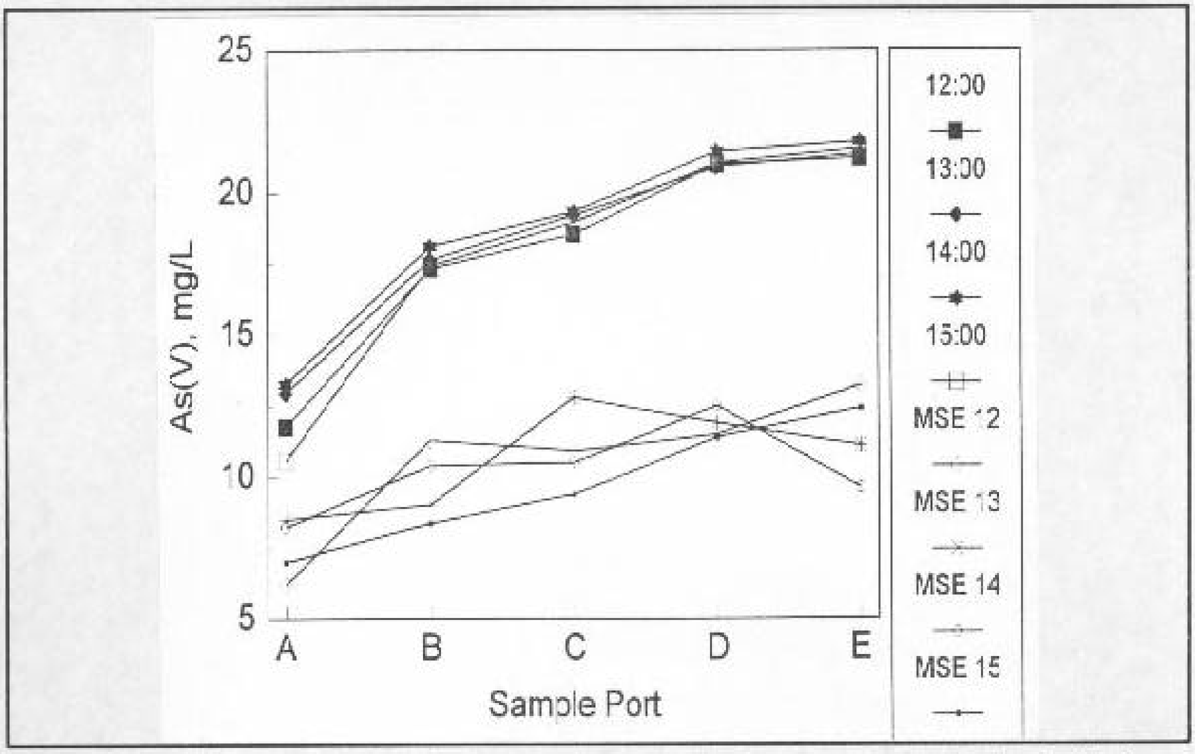

Figure 4-21. As(V) concentrations at the five sample ports during Continuous Flow Test 1 using Susie Mine water.

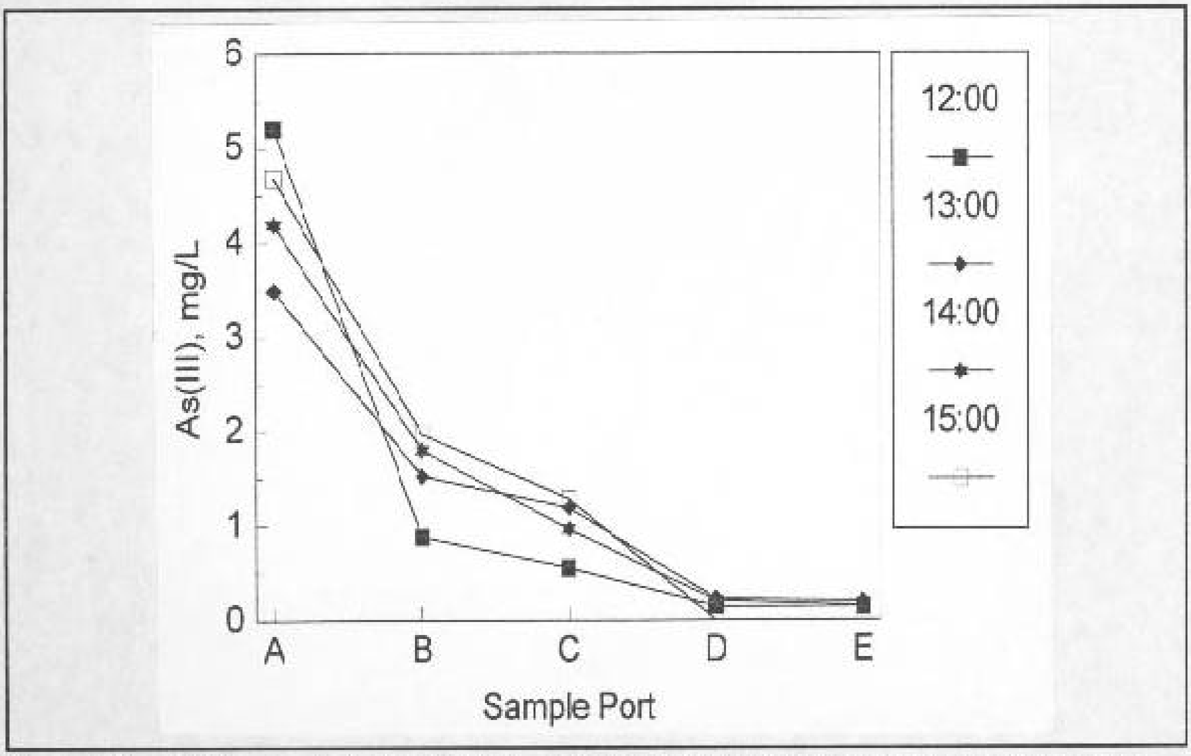

Figure 4-22. As(III) concentrations at the five sample ports during Continuous Flow Test 2 using Susie Mine water.

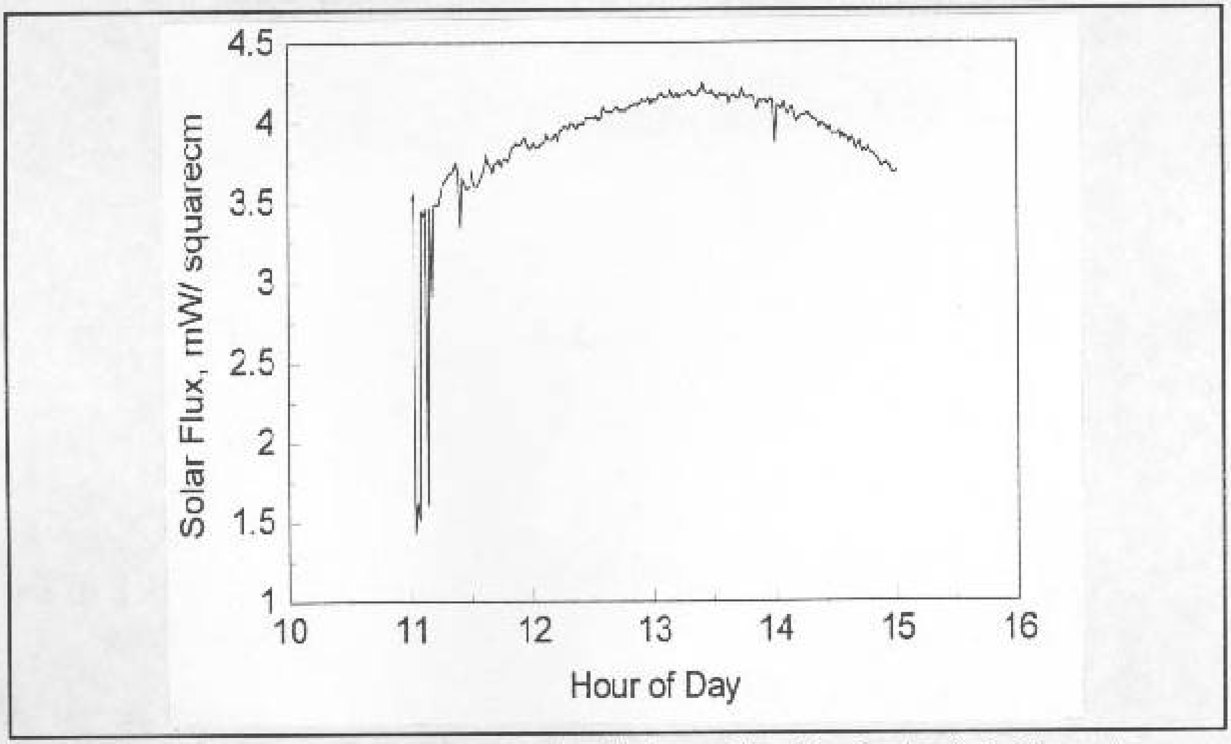

Figure 4-23. UVA solar flux measurements during Continuous Flow Test 2 using Susie Mine water.

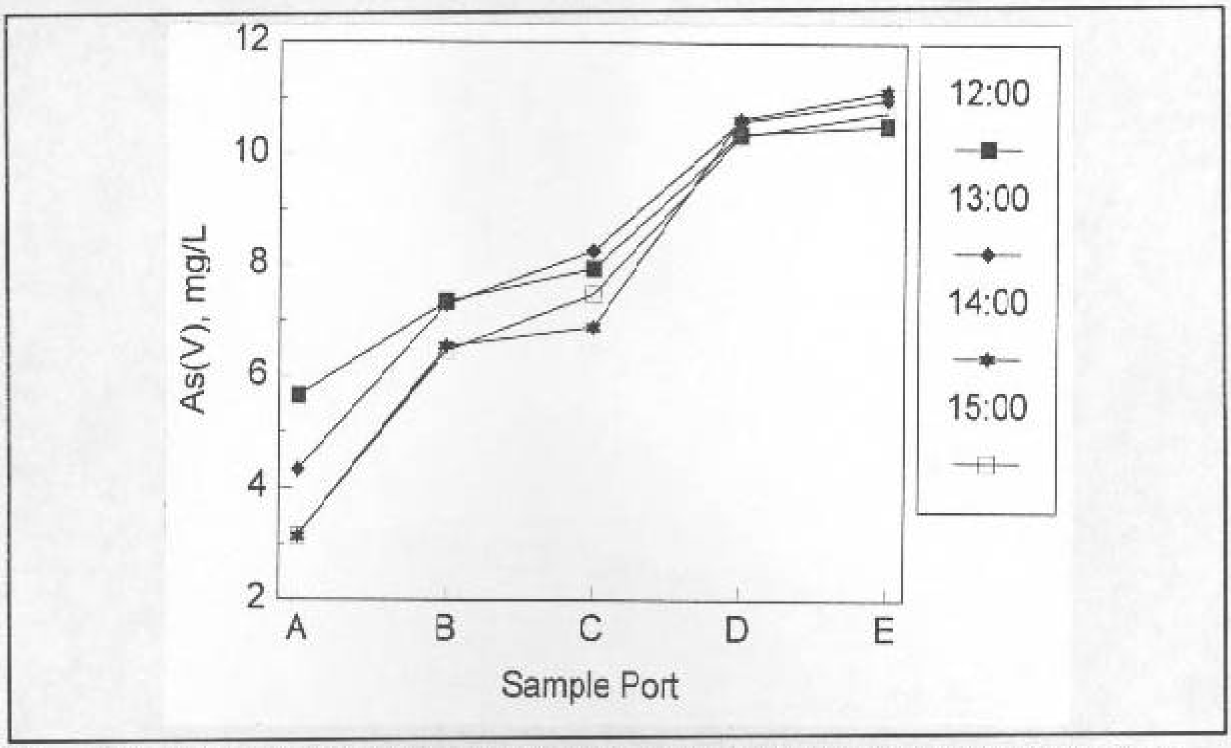

Figure 4-24. As(V) concentrations at the five sample ports during Continuous Flow Test 2 using Susie Mine water.

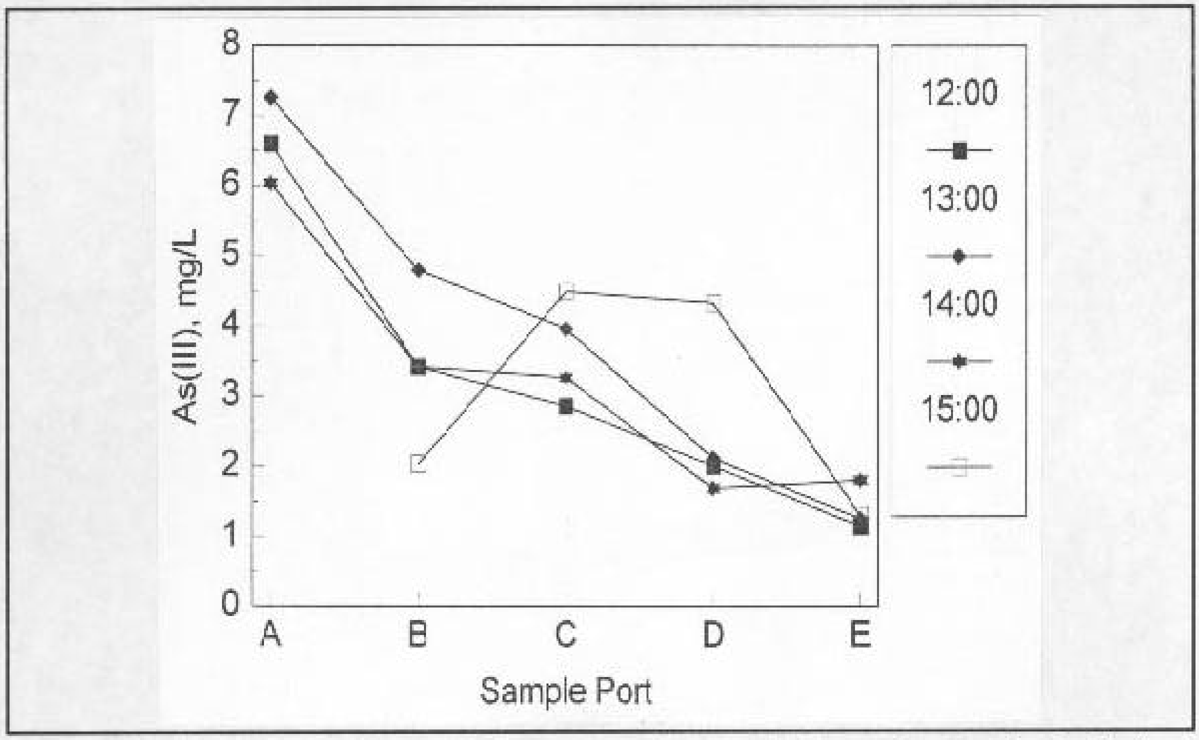

Figure 4-25. As(III) concentrations at the five sample ports during Continuous Flow Test 2 using Susie Mine water.

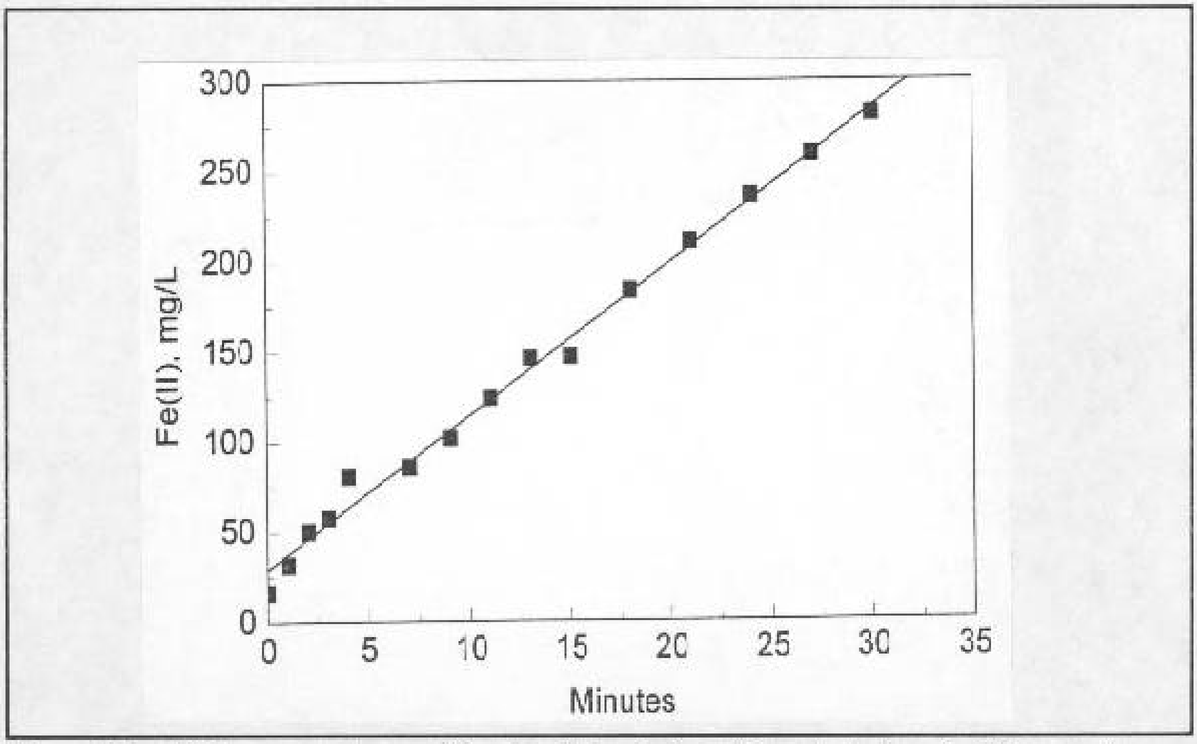

Figure 4-26. Fe(II) concentrations as a function of time during actinometry tests on the Ultrox reactor.

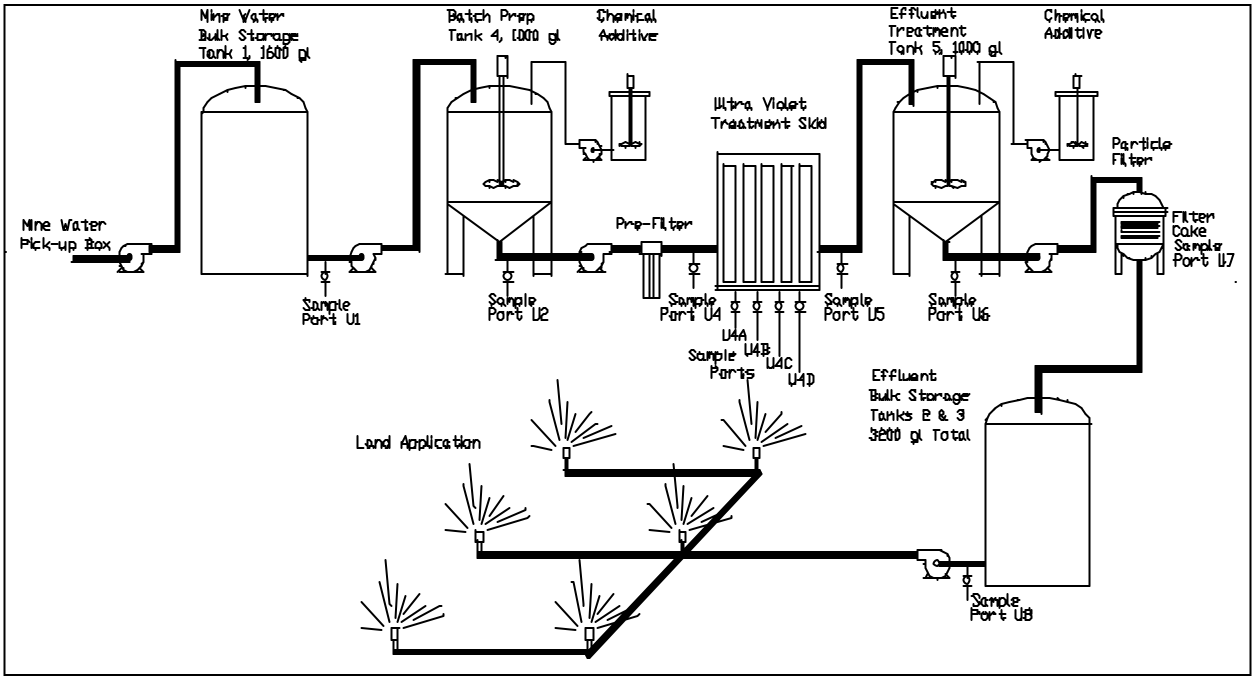

Figure 4-27. Ultrox UV system for arsenic oxidation and removal, batch or continuous flow methods.

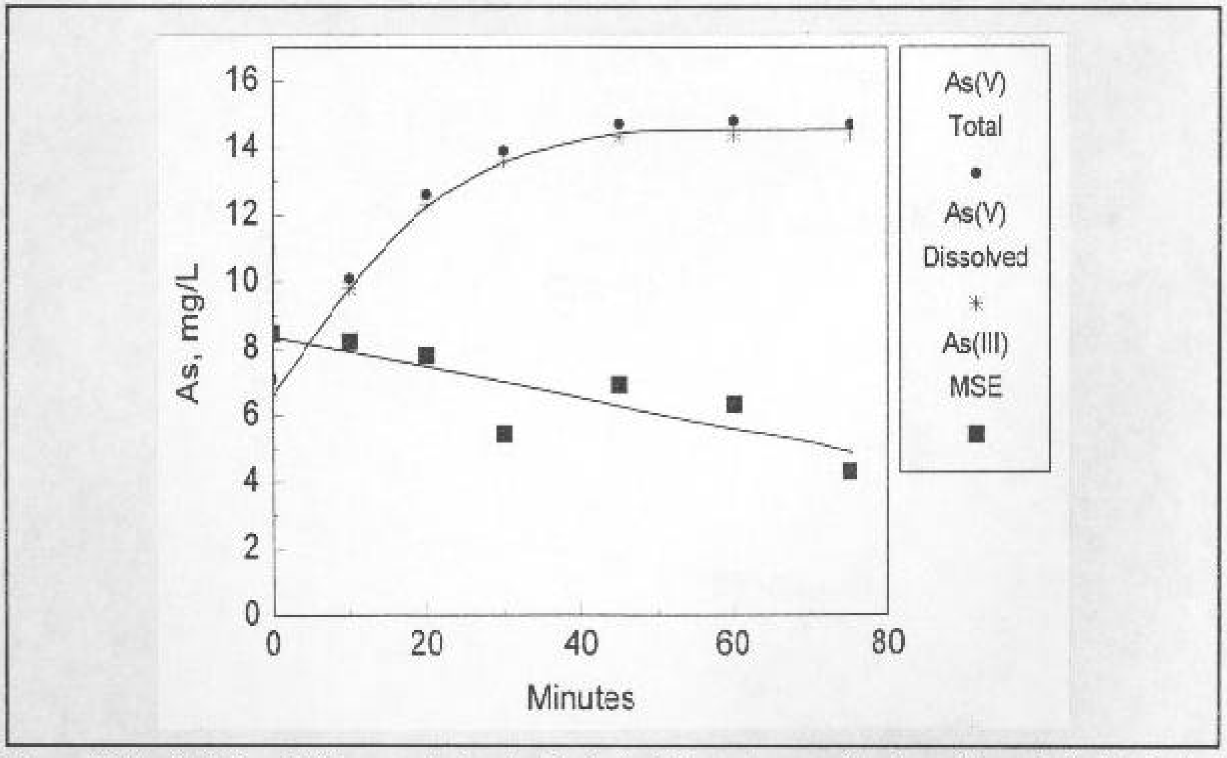

Figure 4-28. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 6 in the Ultrox reactor.

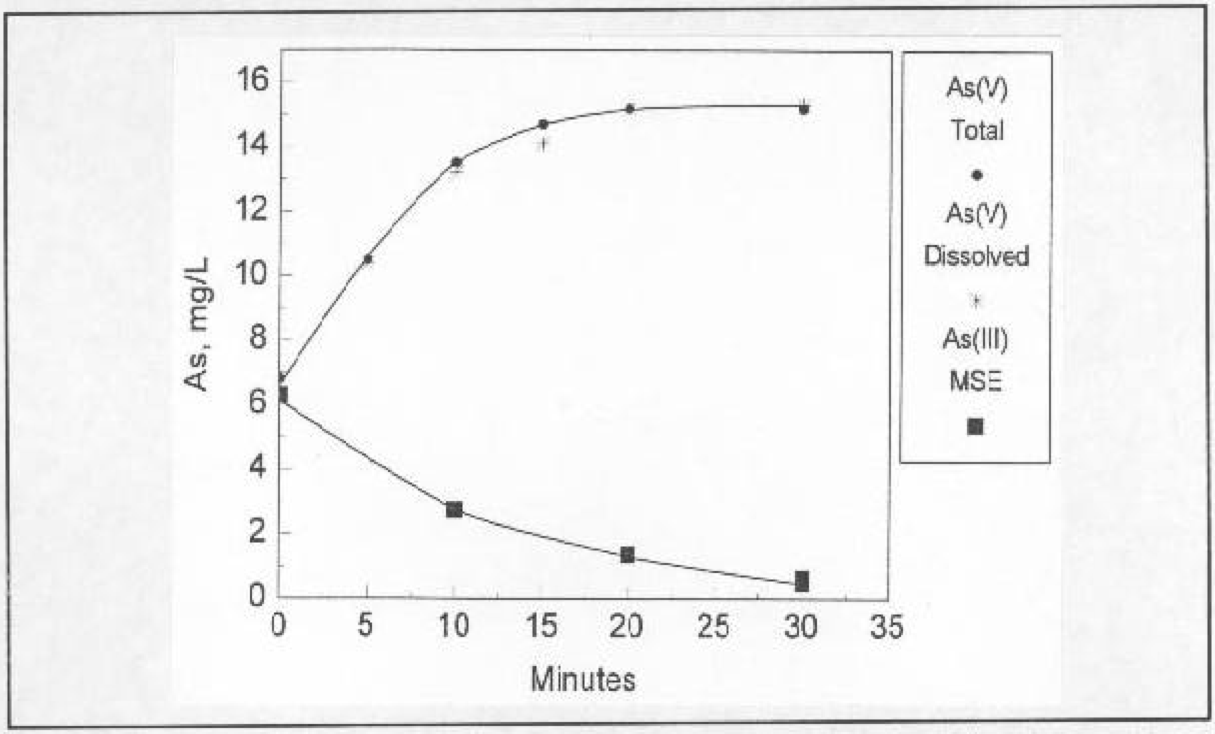

Figure 4-29. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 4 in the Ultrox reactor.

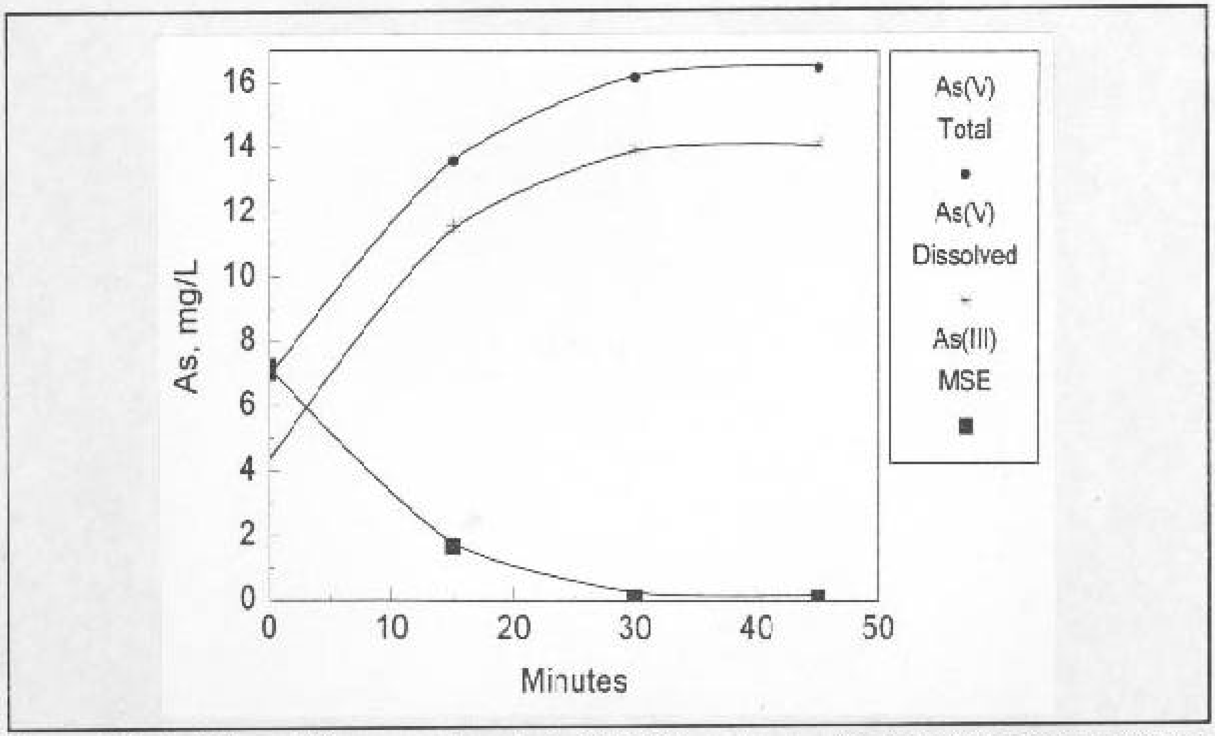

Figure 4-30. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 1 in the Ultrox reactor.

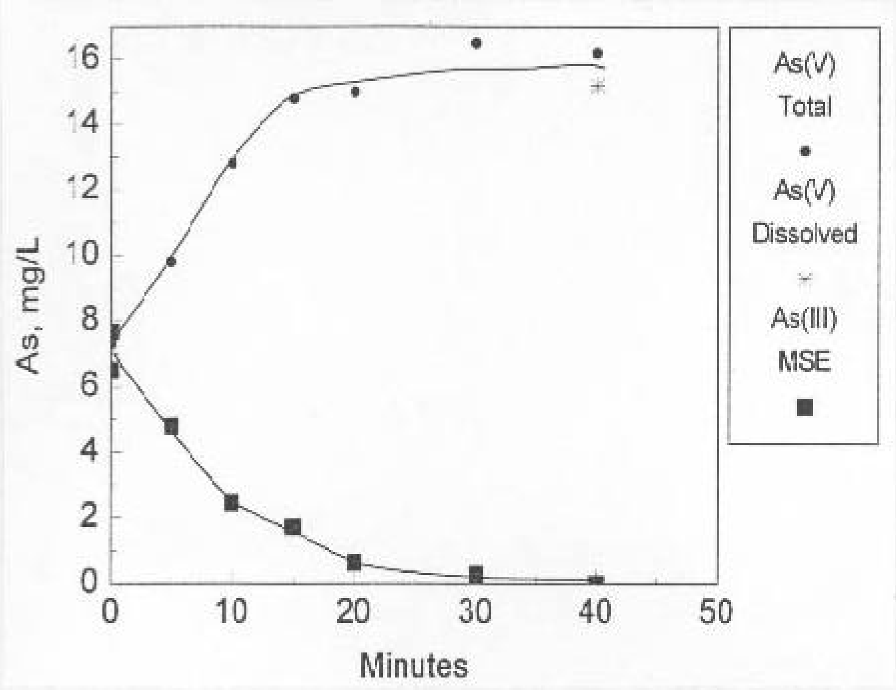

Figure 4-31. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 3 in the Ultrox reactor.

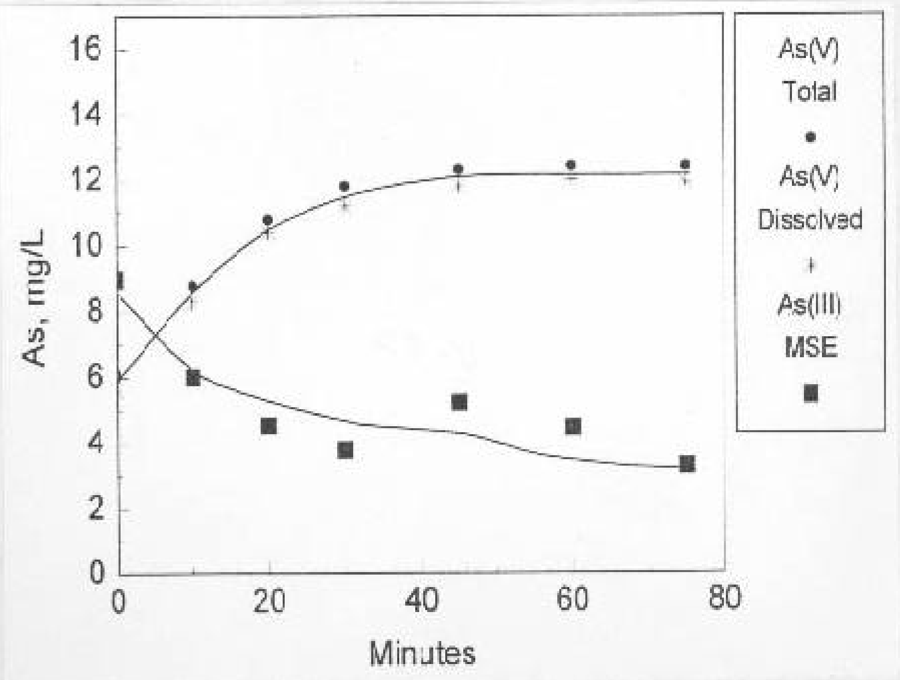

Figure 4-32. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 7 in the Ultrox reactor.

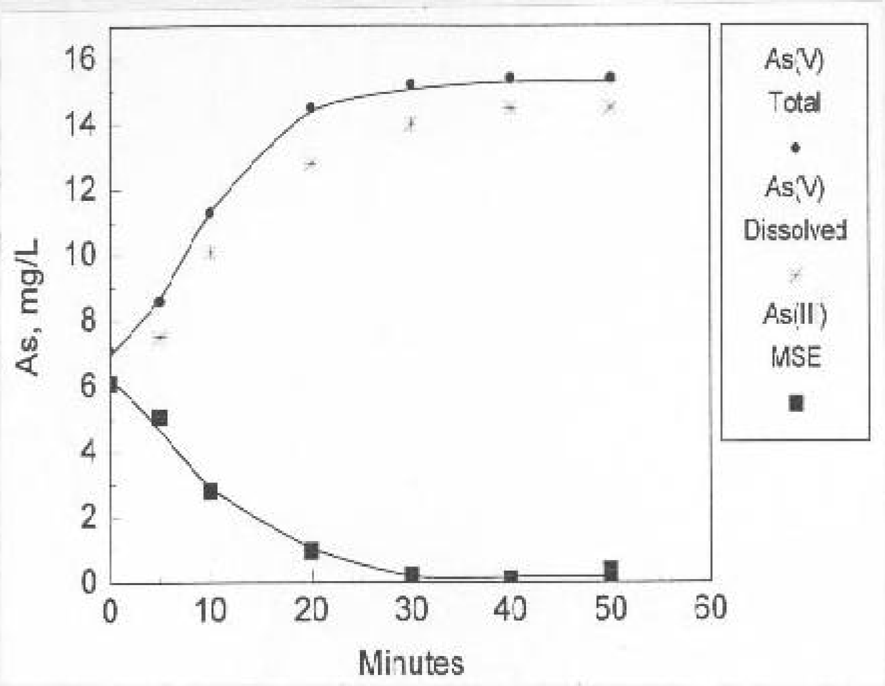

Figure 4-33. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 2 in the Ultrox reactor.

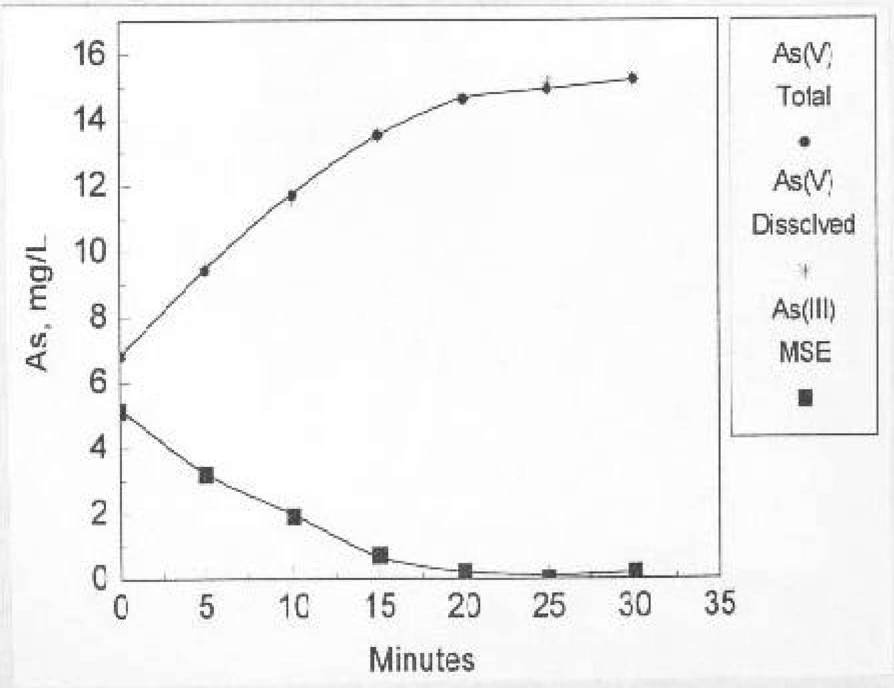

Figure 4-34. As(III) and (V) concentrations in the Susie Mine water as a function of time during batch test 5 in the Ultrox reactor.

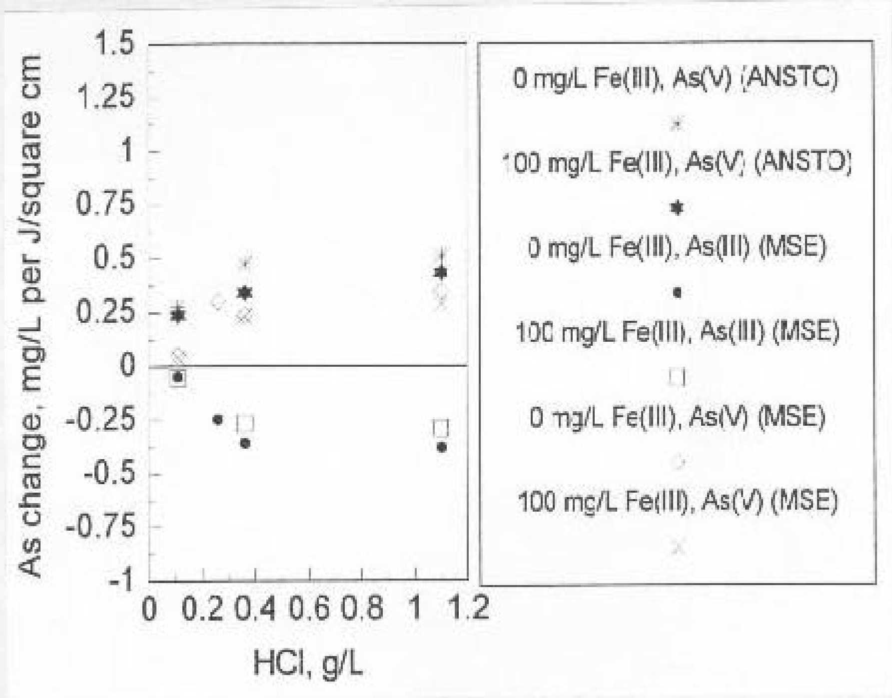

Figure 4-35. Arsenic oxidation rate in the Susie Mine water as a function of acid addition during batch tests using Ultrox reactor.

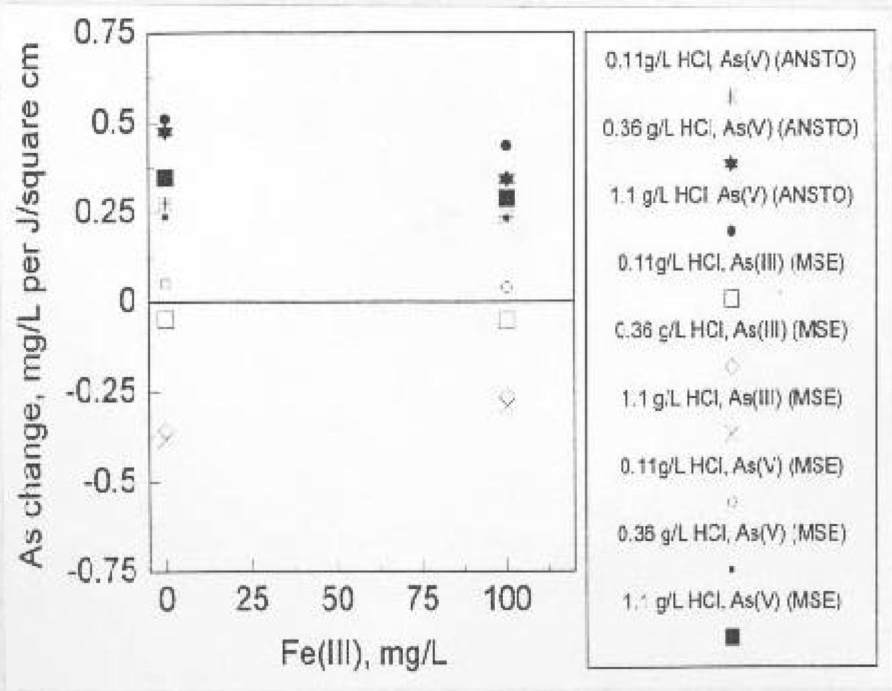

Figure 4-36. Arsenic oxidation rate in the Susie Mine water as a function of ferric chloride addition during batch tests using Ultrox reactor

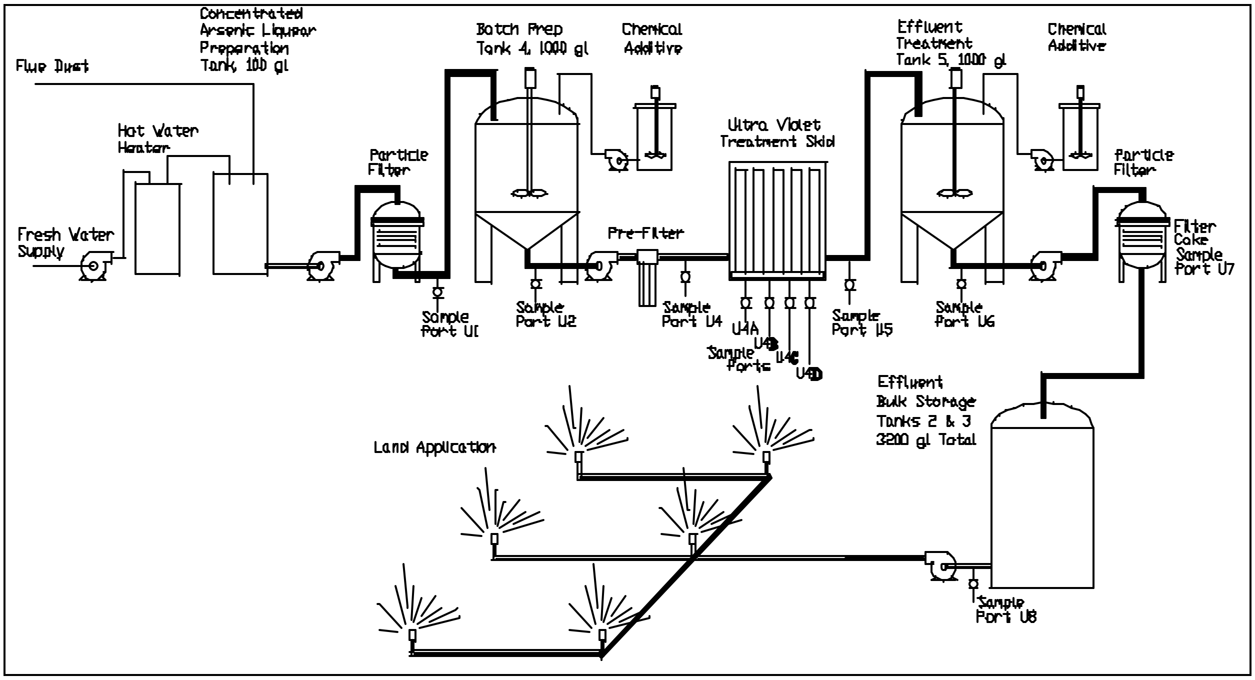

Figure 4-37. Ultrox UV treatment of flue dust leachate concentrated arsenic oxidation and removal, batch method.

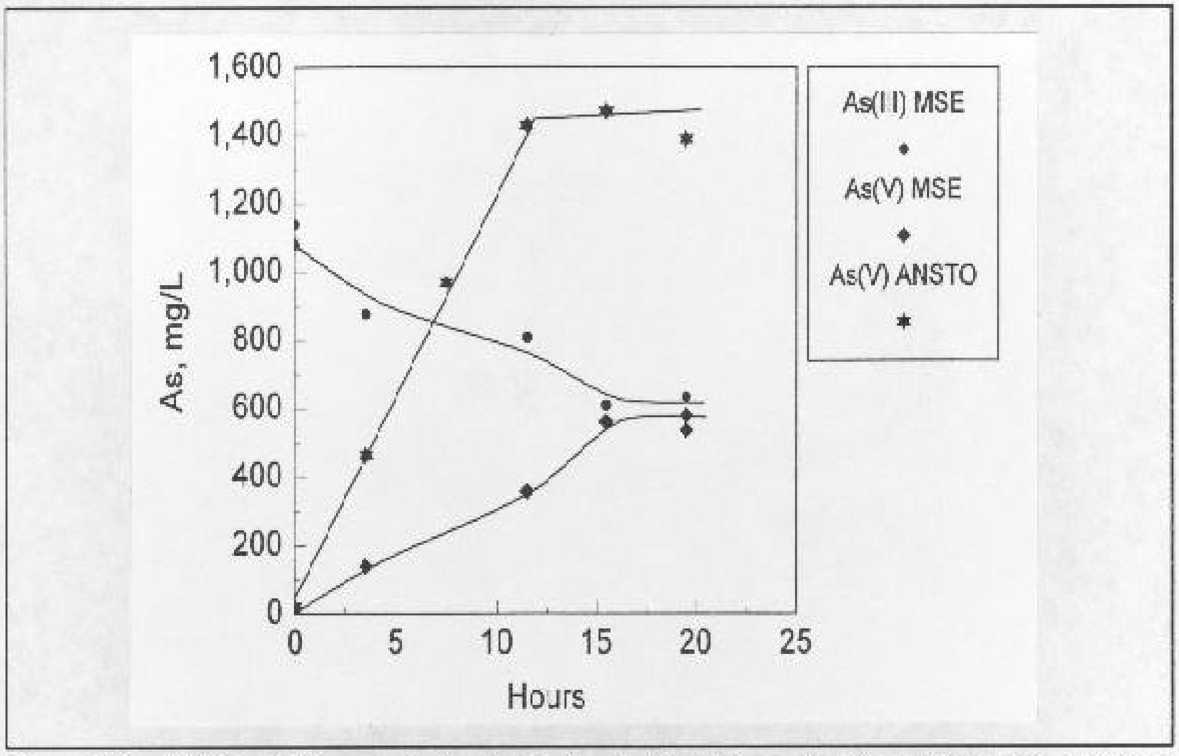

Figure 4-38. As(III) and (V) concentrations in the flue dust leachate as a function of time during batch test 1 in the Ultrox reactor.

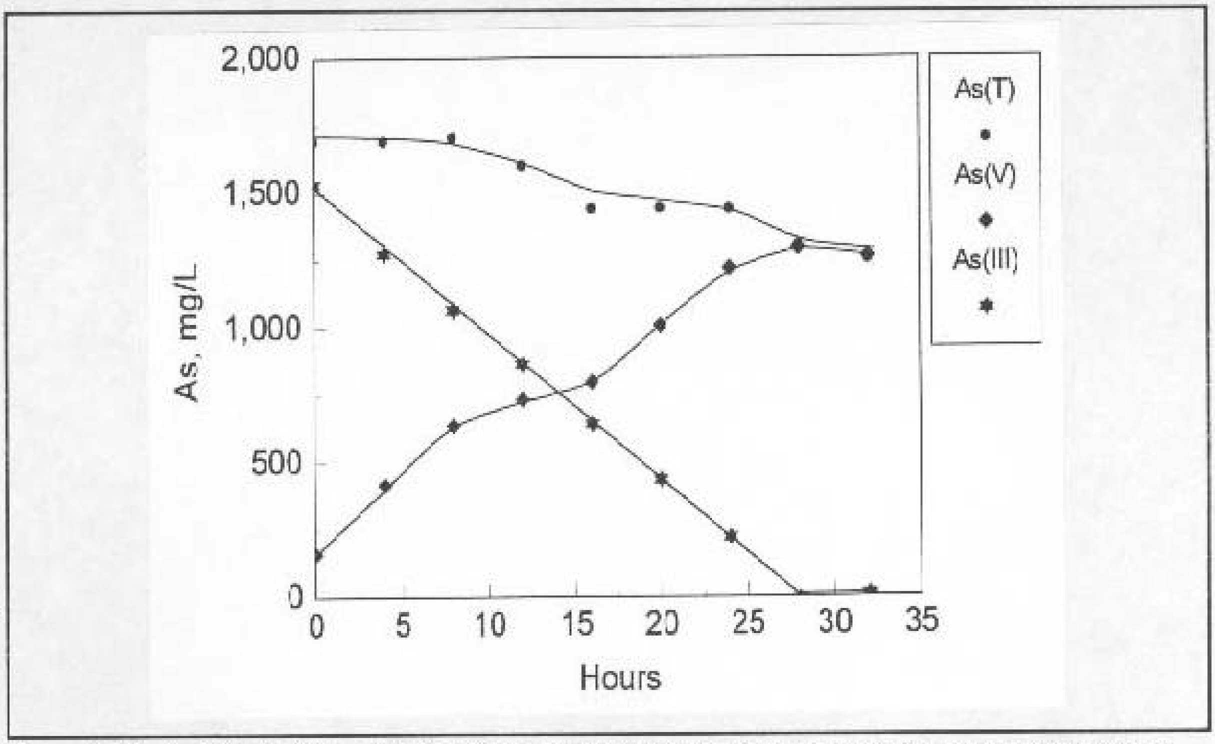

Figure 4-39. As(III), As(V), and As(total) concentrations in the flue dust leachate as a function of time during batch test 2 in the Ultrox reactor.

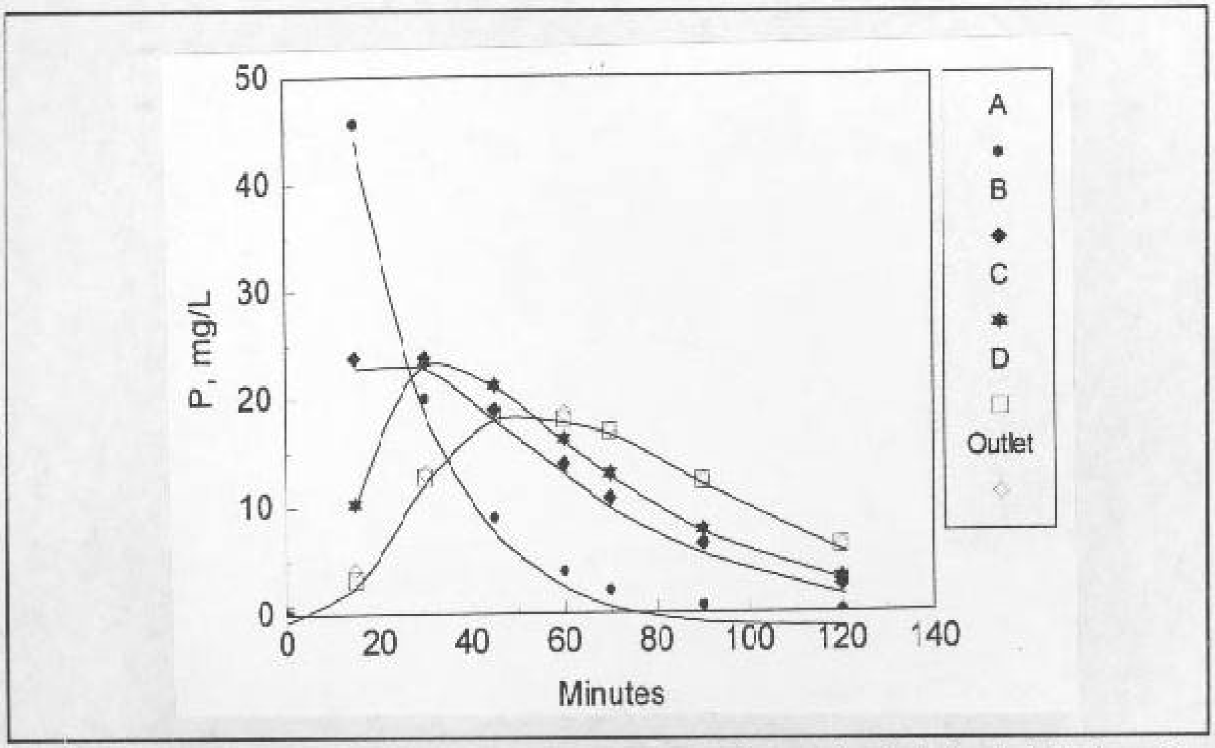

Figure 4-40. Phosphorus concentrations during tracer testing to characterize the hydraulic behavior of the Ultrox reactor before modification. Flow equals 2 gpm.

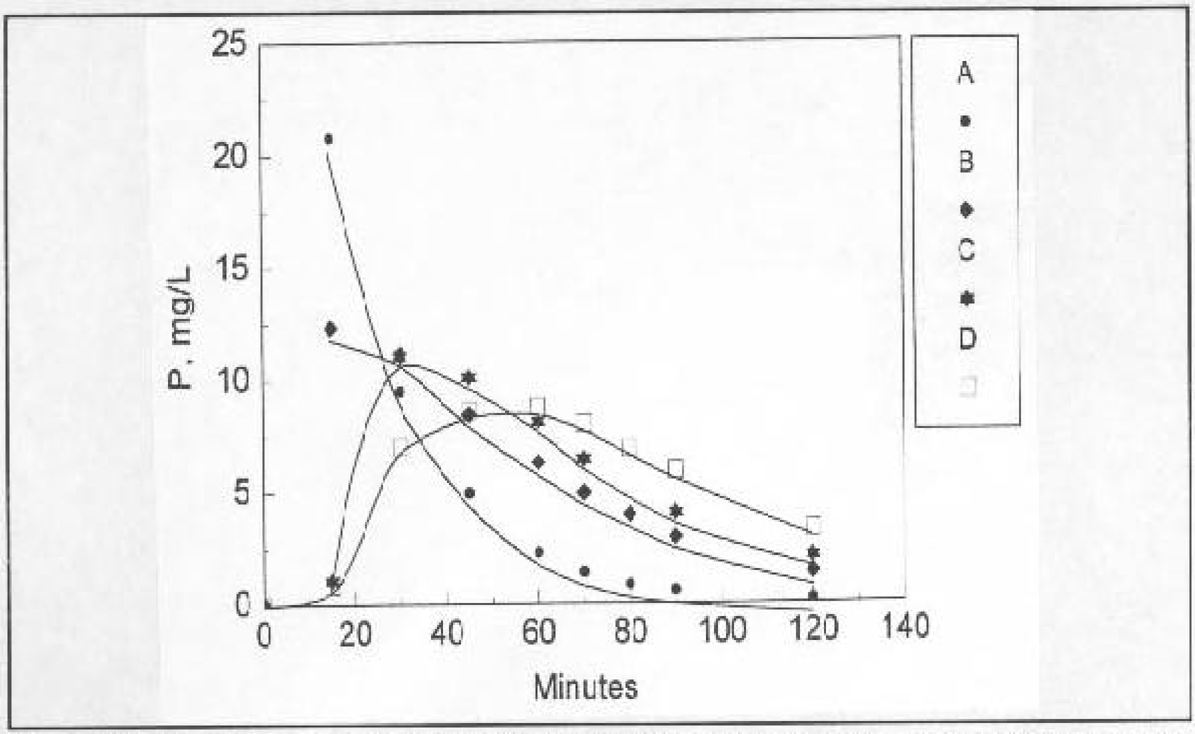

Figure 4-41. Phosphorus concentrations during tracer testing to characterize the hydraulic behavior of the Ultrox reactor after modification. Flow equals 2 gpm.

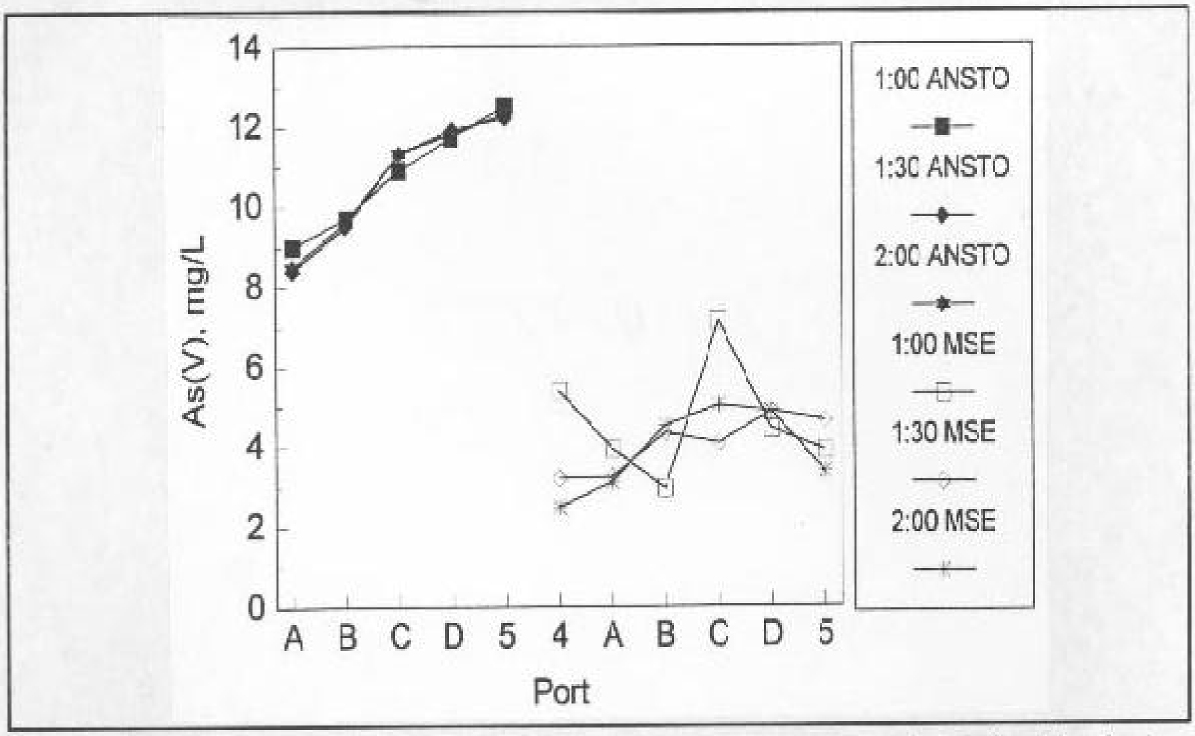

Figure 4-42. As(V) concentrations were taken at six sample ports during the continuous flow Test 1 using the Ultrox reactor. Samples were taken at three different times from: A, B, C, and D equal (reactor sample ports), 4 equals (inlet), and 5 equals (outlet).

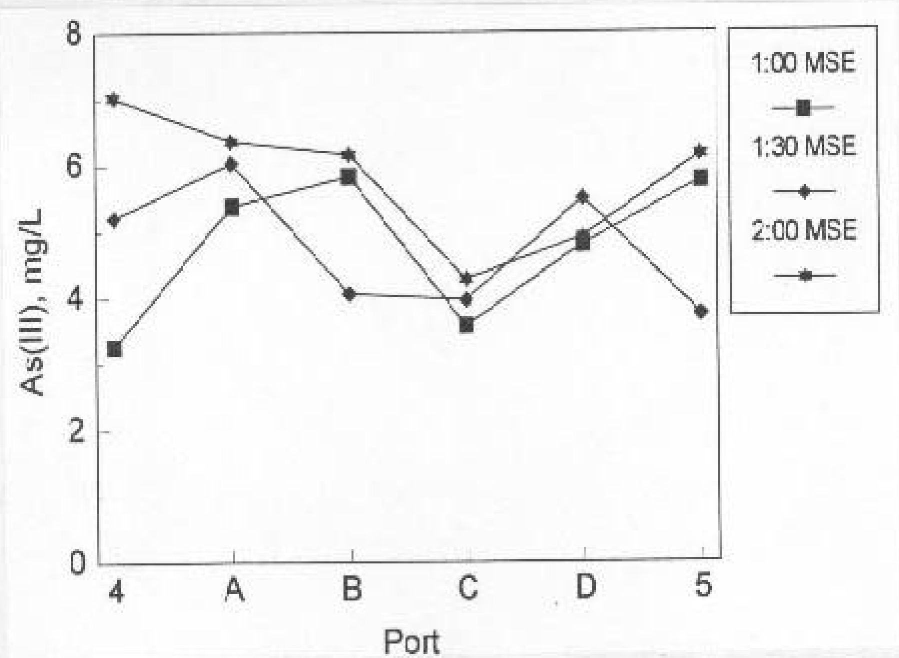

Figure 4-43. As(III) concentrations were taken at six sample ports during the continuous flow Test 1 using Ultrox reactor. Samples were taken at three different times from: A, B, C, and D equal (reactor sample ports), 4 equals (inlet), and 5 equals (outlet).

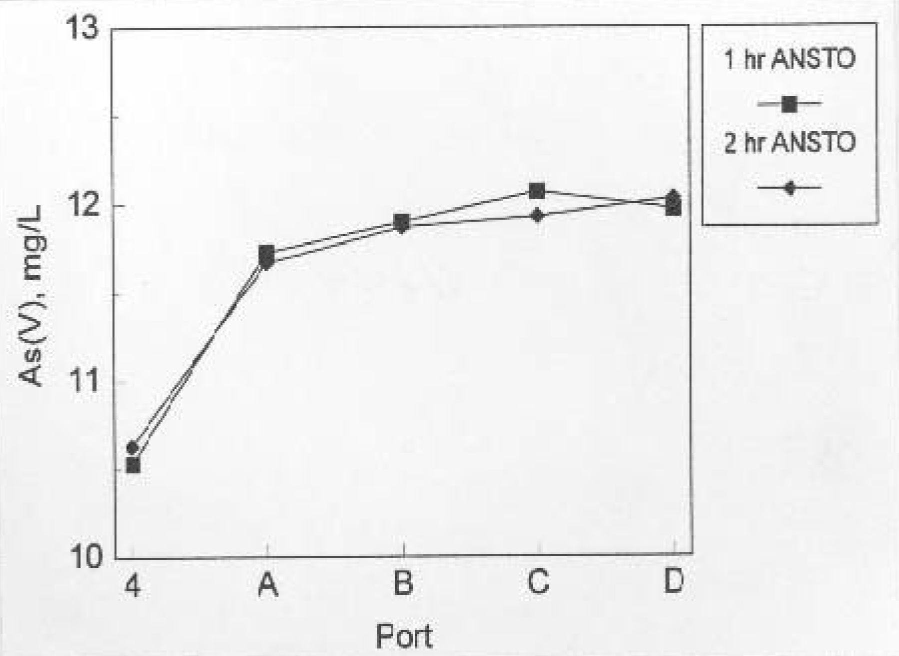

Figure 4-44. As(V) concentrations in the Susie Mine water at the five sample ports during continuous flow Test 2 using Ultrox reactor.

5. Coprecipitation of Oxidized Arsenic with Iron(III)

The oxidized arsenic in the Susie Mine water and flue dust leachate was removed from solution by iron adsorptive-coprecipitation. This was performed by adjusting the pH of the water to approximately pH 7 using lime and aerating the solution to oxidize and precipitate dissolved ferrous to ferric hydroxide. Dissolved As(V) is removed from the solution by the ferric hydroxide precipitate because of the strong bonding existing between the precipitate and As(V) species (Ref. 20).

The residual solutions from each series of the photo-oxidation test runs were mixed, and the composition before the coprecipitation procedure is given in Table 5-1. The concentrations of residual arsenic and other analytes remaining in the filtrate are shown in Table 5-2.

As shown in Table 5-2, the residual dissolved arsenic concentration after filtration using a filter press was found to be 35 to 80 ppb. After a second stage filtration using a filter membrane (0.6 to 0.8 micron), the residual arsenic was found to be 17 to 53 ppb. These values are greater than the revised World Health Organization (WHO) limit (of 10 ppb) for arsenic in drinking water. In contrast, residual arsenic concentrations less than 10 ppb were obtained when the filtration procedure was performed in an analytical laboratory, e.g., the results obtained using Susie Mine water reported in Section 3.3 and those obtained during laboratory-scale tests using synthetic water (Ref. 12) are all less than 10 ppb arsenic. These results highlight the fact that in order to achieve residual arsenic concentrations less than 10 ppb, a proper solid-liquid separation procedure and the elimination of contamination from laboratory hardwares are essential.

The preparation and operation of the four coprecipitation procedures are described in detail below.

Susie Mine Water from Solar Test Runs (August 22, 1997, at Rimini)

The Susie Mine water from the batch and continuous solar experiments was combined after the arsenic was oxidized to give a final volume of 3,230 L. In the case of the continuous flow tests where the oxidation was not completed in the entire volume of the sample, namely in that part of the sample near the inlet, the oxidation was completed in batch mode. HCl was added to the residual solution from batch tests 1 and 11, and the mixture was exposed to sunlight to complete the arsenic oxidation.

The iron/arsenic mole ratio in the bulk solution was 36/1, which is sufficient for the precipitation to be carried out without adding more Fe(III) sulphate. The concentration of the other components of the bulk solution were calculated from the individual analysis and are listed in Table 4-1.

An air sparger was installed in the base of the precipitation tank because the Fe(II) that was present in the original liquor at 200 mg/L reacted rapidly with oxygen at pH values greater than 4 with an equivalent demand of 28 mg/L of oxygen. Lime was added as a concentrated slurry till the pH reached about 7. After 1 hour of additional stirring, the final pH was 6.99. The sparger was removed, and the slurry was left to settle overnight. The next day, 2,850 ml of supernatant liquor was decanted, and the concentrated slurry was subsequently filtered using a filter press.

Flue Dust Leachate from Solar Test Runs (August 30, 1997, at MSE Testing Facility in Butte, Montana)

The three batches of flue dust leachate oxidized during the solar tests were combined to give one lot with a volume of 1,200 L. The composition of this liquor before precipitation was calculated from the analyses of the individual batches and is listed in Table 4-1. Fe(III) sulphate was added to give an iron/arsenic mole ratio of 4/1. Lime was added as a concentrated slurry to give a final pH of 7. All of the liquor was filtered using the filter press.

Susie Mine Water from Ultrox Test Runs (September 9, 1997, at MSE Testing Facility)

The seven batches of Susie Mine water used for the Ultrox tests were combined to give one lot with a volume of 4,000 L. The iron/arsenic mole ratio in the liquor was 22/1 so no more iron was added. The precipitation and filtration was carried out in a similar manner to that used for the water from the solar tests.

Flue Dust Leachate from Ultrox Test Runs (September 16, 1997, at MSE Testing Facility)

Liquor from the two oxidation tests of flue dust leachate in the Ultrox reactor was combined to give a total volume of 1,100 L. Mistakenly, 2.5 kilograms (kg) of lime was added before Fe(III) was added producing a calcium (arsenate+ sulphate) precipitate. This was redissolved by adding 2 L of concentrated sulphuric acid. Fe(III) sulphate was added to give an iron/arsenic mole ratio of 4/1. Lime was then added to complete the precipitation and filtered using the filter press.

Table 5-1. Calculated composition of the test mixtures prior to the precipitation tests.

Bulk Liquor Precipitation date Metals Total	Flue Dust Ultrox Sept 16	Flue Dust Solar Aug 30	Susie Mine Water Ultrox Sept 9	Susie Mine Water Solar Aug 22	Susie/Ultrox 2nd stage Sept 24	Susie/Solar 2nd Stage Sept 24
Al, mg/L	0.165	0.148	3.76	3.45	0.05	0.03
As, mg/L	1250	389	15.1	14.22	0.08	0.06
Cd, mg/L	0.02	0.027	0.55	0.545	0.041	0.036
Cr, mg/L					0.009	
Cu, mg/L					0.021	
Fe, mg/L	179.75	428	250	370	1.31	0.51
Pb, mg/L					0.05	0.05
Mg, mg/L					93.8	
Mn, mg/L					11.9	9.35
Hg, mg/L					0.0002	
Mo, mg/L					0.759	
Ni, mg/L					0.07	
Se, mg/L					0.07	
Ag, mg/L					0.006	
Na, mg/L	1.97	506.37	20.21	21.1	23.7	23.1
Zn, mg/L	1.48	9.25	64.61	64.9	0.755	0.295
Ca, mg/L	24.42	71.38	233	224.1		1800
Chloride, mg/L	2807	3350	470	2300	729	
Sulfate, mg/L	389	403	937	1060	1440	

Table 5-2. Elemental analysis of the filtrates following iron coprecipitation in mg/L unless noted otherwise.

	1st Stage Precipitation				2nd Stage Precipitation		
Feed	Flue Dust	Flue Dust	Susie	Susie	Susie	Susie	
Light Source	Ultrox	Solar	Ultrox	Solar	Ultrox	Solar	Blk
Precipitation date	Sept 16	Aug 30	Sept 9	Aug 22	Sept 24	Sept 24	Sept 24
Sample date	Sept 19	Sept 6	Sept 10	Aug 23	Sept 24	Sept 24	Sept 24
Laboratory ID	W014816	W014628	W014638	W014393	WO14807	W014808	W01480
Metals Total mg/L							
Al	0.98	0.03	<0.05	<0.03			
As	0.035	<0.32	0.08	0.06	**0.033**	**0.053**	**0.017**
Cd	0.03	0.042	0.041	0.036			
Cr	<0.105	0.009	<0.009				
Cu	1.36	0.043	0.021				
Fe	3.92	0.128	1.31	0.51			
Pb	<0.24	<0.04	<0.05	<0.05			
Mg	65.9	86.7	93.8				
Mn	3.37	7.29	11.9	9.35			
Hg	0.0001		<0.0002				
Mo	0.035	<0.015	0.759				
Ni	0.6	0.02	0.07				
Se	<0.35	<0.07	<0.07				
Ag	<0.03	<0.006	<0.006				
Na	27.1	105	23.7	23.1			
Zn	6.05	1.61	0.755	0.295			
Ca				1800			
Total Alkalinity	10	<40.0	28				
Carbonate*	10	10.0	10				
Bicarbonate*	10	<40.0	28				
Hydroxide*	10	10.0	10				
Chloride	5270	1930	729				
Cyanide	0.005	0.007	0.005				
Fluoride	0.5	<2.8	2.6				
Nitrate/Nitrite-N	0.09	0.25	0.05				
pH, SU	4.25	7.44	7.38				
TDS	9740	5380	3250				
TSS	4	23	4				
Sulfate	1020	1410	1440				

* as calcium carbonate

6. Leach Testing of the Iron(III)-Arsenic(V) Coprecipitation Residues

Four types of arsenic-bearing solids were produced from the iron coprecipitation operation as mentioned in the previous section, i.e., from the processing of:

(a) Susie Mine water used during solar test runs.
(b) Susie Mine water used during Ultrox test runs.
(c) Flue dust liquor used during solar test runs.
(d) Flue dust liquor used during Ultrox test runs.

The metal concentrations (mg/kg) in each dried filter cake (MSE analyses) are shown in Table 6-1. ANSTO's analyses of As(III) in the dried filter cakes range from 0.73% to 2.4% of total arsenic indicating that more than 97% of the initial As(III) in the test streams was converted to As(V) during the photo-oxidation test runs.

Apart from the standard EPA TCLP test, the ANSTO leach test of the solids suspended in aerated water for 3 months was also performed. This test was used to verify whether arsenic was present in the residues as a mixture of arsenic-bearing hydrous ferric oxide and calcium arsenate. Calcium arsenate compounds, which are subject to attack by dissolved atmospheric carbon dioxide, may have formed during the lime neutralization operation usually practiced in conjunction with the iron coprecipitation process (Ref. 16).

Two lots of solids, those with the higher arsenic contents, i.e., filter cakes derived from Ultrox test runs using Susie Mine water (abbreviated as Susie/Ultrox) and those from solar tests using flue dust leachate (flue dust/solar), were selected for the 3-month leach testing using aerated water. As required by the demonstration plan, some of the two selected solids were solidified using Portland cement before leach testing was performed. Details of the cement solidification procedure are given in Appendix C.

Previous leach testing work performed at ANSTO showed that some arsenic-bearing wastes that had passed the EPA TCLP test failed when placed in aerated water. For example, Figure 6.1 shows the results of leach testing using aerated water (previous work at ANSTO) of cement-solidified forms containing calcium arsenate or arsenic-bearing hydrous ferric oxide. The water to solid ratio used in these tests was 20/1. Both cement forms had passed the TCLP test. After a week of immersion in aerated water, the arsenic leached from the calcium/arsenate solid (Figure 6-1a) resulting in a dissolved arsenic concentration of >100 mg/L in the test water. Thereafter, it increased to more than 200 mg/L. In contrast, the dissolved arsenic concentration from the cement form containing arsenic-bearing hydrous ferric oxide (Figure 6-1b) remained below 5 mg/L for 6 months. In both cases when carbon dioxide-free air was used, arsenic was not leached into solution.

6.1 TCLP Test of the Dried Filter Cakes and Cement-Solidified Filter Cakes

Samples of the dried filter cakes and the cement-solidified (broken down to 1–9 mm sizes) were used in the TCLP tests. Extraction fluid #1 (pH 4.93) was used for the dried filter cakes, while Extraction fluid #2 (pH 2.88) was used for the cement-solidified filter cakes. Duplicate samples were run on each sample.

TCLP test results for both dried filter cakes (Table 6-2) and cement-solidified solids (Table 6-3) were far below the TCLP limits for all metals. The data in the tables also indicated that the reproducibility of results was achieved for all duplicate samples.

The main reasons for this difference are the pH of the final TCLP leachate of the two cement-solidified samples and the difference in the Fe/As mole ratio of the initial dried filter cakes: the iron/arsenic mole ratio in the flue dust/solar filter cake was 3.9, and the pH of the final TCLP leachate was about 7.7 (the corresponding arsenic concentrations in the leachate were 2.9 and 3.3 mg/L). In comparison, the pH of the final leachate of flue dust/Ultrox cement was about 6.6, and the iron/arsenic mole ratio in flue dust/Ultrox filter cake was 5.6. Because of the lower pH and the higher iron/arsenic mole ratio, the arsenic concentrations in the latter leachate were lower, i.e., 0.22 and 0.15 mg/L. These results were in agreement with literature values for chemical adsorption of arsenic on hydrous ferric oxide particles (Ref. 11), (Figure 6-2). This indicates that the arsenic leachability from the filter cakes was controlled by an adsorption mechanism on the surface of hydrous ferric oxide particles (Ref. 11).

6.2 Leach Tests using Aerated Water

Leach tests using aerated water for the Susie/Ultrox and flue dust/solar dried filter cakes and the corresponding cement-solidified solids were conducted for about 3 months. Three samples from each type of solid were tested concurrently: two samples immersed in aerated water (duplicate samples) and one in water sparged with carbon dioxide-free air (control sample). Periodic measurements of the leachate pH, dissolved As, and Ca concentrations are shown in Figures 6-3 to 6-6. Other metal concentrations as well as the procedure for the leach test are shown in Appendix C.

At the commencement of the leach test with the Susie/Ultrox sample, the pH of the aerated water and the *control* solution (with no carbon dioxide in the air) increased from 5.9 (deionized water) to about pH 8 (Figure 6-3b). The concentrations of As in the leachates were very low (<0.015 ppm) for all samples (Figure 6-3a) because the Fe/As mole ratio in the filter cakes was high (about 31).

For the flue dust/solar sample, the pH of the leachates for all samples (both control and aerated samples) stabilized at about 6–6.5 (Figure 6-4b). Because of the lower pH (compared to the Susie/Ultrox sample), the concentrations of arsenic in the leachate were still low (0.25–0.4 mg/L) in spite of the lower Fe/As mole ratio (3.9) in the filter cakes (Figure 6-4a). Dissolved Ca concentrations in the leachate were high in all samples (Figure 6-4c) because more lime was needed to neutralize the higher concentration of ferric chloride used during the photo-oxidation processing of the flue dust leachate. Arsenic removal from 300 mg/L As(V) solution with six different levels of iron/arsenic mole ratios is shown in Figure 6-2 (Ref. 11).

The concentrations of other metals in the leachates were shown in Tables C.1 to C.9 in Appendix C. All metals passed the limits (using TCLP limits). Silver and lead were lower than the detection limits of the analytical instrument (<0.001 ppm). Barium, chromium, cadmium, mercury, and selenium concentrations were also very low (Ba <0.021 ppm, Cr <0.06 ppm, Cd <0.011 ppm, Hg <0.004 ppm, and selenium (Se) <0.028 ppm).

For the two cement-solidified samples, periodic measurements of pH, dissolved As and Ca are shown in Figures 6-5 and 6-6. Other metal concentrations are given in Appendix C.

Because of the presence of excess lime in the samples, the pH of the leaching solutions rapidly increased from 5.9 to greater than 11 (Susie/Ultrox/cement) and 10 (flue dust/solar/cement). After one week, the leachate pH of the cement-solidified samples decreased to about 8 for flue dust/solar/cement and to about 10 for Susie/Ultrox/cement. The dissolved calcium concentration increased significantly for all samples (Figures 6-5 and 6-6). It appeared that although $Ca(OH)_2$ in the solution reacted with carbon dioxide from air to form calcium carbonate, other calcium compounds (especially $CaCl_2/CaSO_4$) released calcium into solution. As noted in the previous section, the flue dust/solar filter cakes contained more $CaCl_2/CaSO_4$ because of the extra lime used in the neutralization of Fe(III) added for photo-absorber. Dissolved arsenic concentrations in the leachates were always less than 5 mg/L.

It should be noted that the pH of the *control* leach solution stayed at pH of about 11 or greater. This confirms that carbon dioxide was effectively removed from the sparging air for the *control* run. Furthermore, it was evident that no calcium carbonate was formed as the control solutions remained clear throughout the experiment. (Figures 6-5b and 6-6b).

The concentrations of other metals in the test leachate are shown in Appendix C. All metals passed the TCLP limits. Silver and lead were lower than detection limits (<0.001 ppm). Barium, chromium, cadmium, mercury, and selenium concentrations were also very low (Ba <0.021 ppm, Cr <0.08 ppm, Cd <0.011 ppm, Hg <0.004 ppm, and Se <0.03 ppm). Generally, the concentrations of dissolved metals in the leachate were constant throughout the experiment.

Table 6-1. Metal concentrations in the dried filter cakes from processing photo-oxidized Susie Mine water and flue dust leachate (milligrams/kilograms unless stated otherwise).

Element	Susie/Solar	Susie/Ultrox	Flue Dust/Solar	Flue Dust/Ultrox
As	8830	13300	102000	34300
As(III) (% of total)	(0.88%)	(0.73%)	(2.3%)	(0.81%)
Ag	<1.073	<1.135	<1.180	<1.157
Ba	123	78.3	71.6	32.5
Cd	366	611	28.0	17.6
Cr	59.3	317	7.80	66.9
Hg	0.103	0.112	0.156	0.071
Pb	54.4	794	63.4	48.2
Se	<12.64	<13.37	24.0	<13.63

Table 6-2. TCLP test results (mg/L) for the dried filter cakes from the Susie Mine water and flue dust leachate.

Element	TCLP Limit	Susie/Solar		Susie/Ultrox		Flue Dust/Solar		Flue Dust/Ultrox	
As	5.0	0.007	0.0076	0.0051	0.0054	0.658	0.547	0.272	0.238
Ag	5.0	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ba	100.0	0.0582	0.0619	0.0516	0.0542	0.0401	0.0427	0.0921	0.0891
Cd	1.0	0.1153	0.1297	0.1306	0.1289	0.0056	0.0063	0.0027	0.0025
Cr	5.0	0.0126	0.0271	0.0783	0.0778	0.0153	0.0144	0.0154	0.015
Hg	0.2	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	5.0	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Se	1.0	0.0038	0.0043	0.0047	0.0056	0.0328	0.0335	0.1021	0.1088

Table 6-3. TCLP test results (mg/L) for the cement-solidified samples (after 7 days cement curing time) from the Susie Mine water and flue dust leachate.

Element	TCLP Limit	Susie/Solar		Susie/Ultrox		Flue Dust/Solar		Flue Dust/Ultrox	
As	5.0	0.021	0.016	0.032	0.018	2.9	3.3	0.15	0.22
Ag	5.0	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Ba	100.0	0.392	0.368	0.381	0.295	0.236	0.21	0.304	0.218
Cd	1.0	0.067	0.077	0.098	0.087	0.0003	0.0001	0.0006	0.0003
Cr	5.0	0.0045	0.0055	0.0505	0.0484	0.0025	0.0019	0.0147	0.0171
Hg	0.2	0.0018	0.0017	0.0016	0.0018	0.0022	0.0026	0.0016	0.0016
Pb	5.0	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Se	1.0	0.0104	0.0108	0.0106	0.0115	0.0352	0.0327	0.0421	0.0438

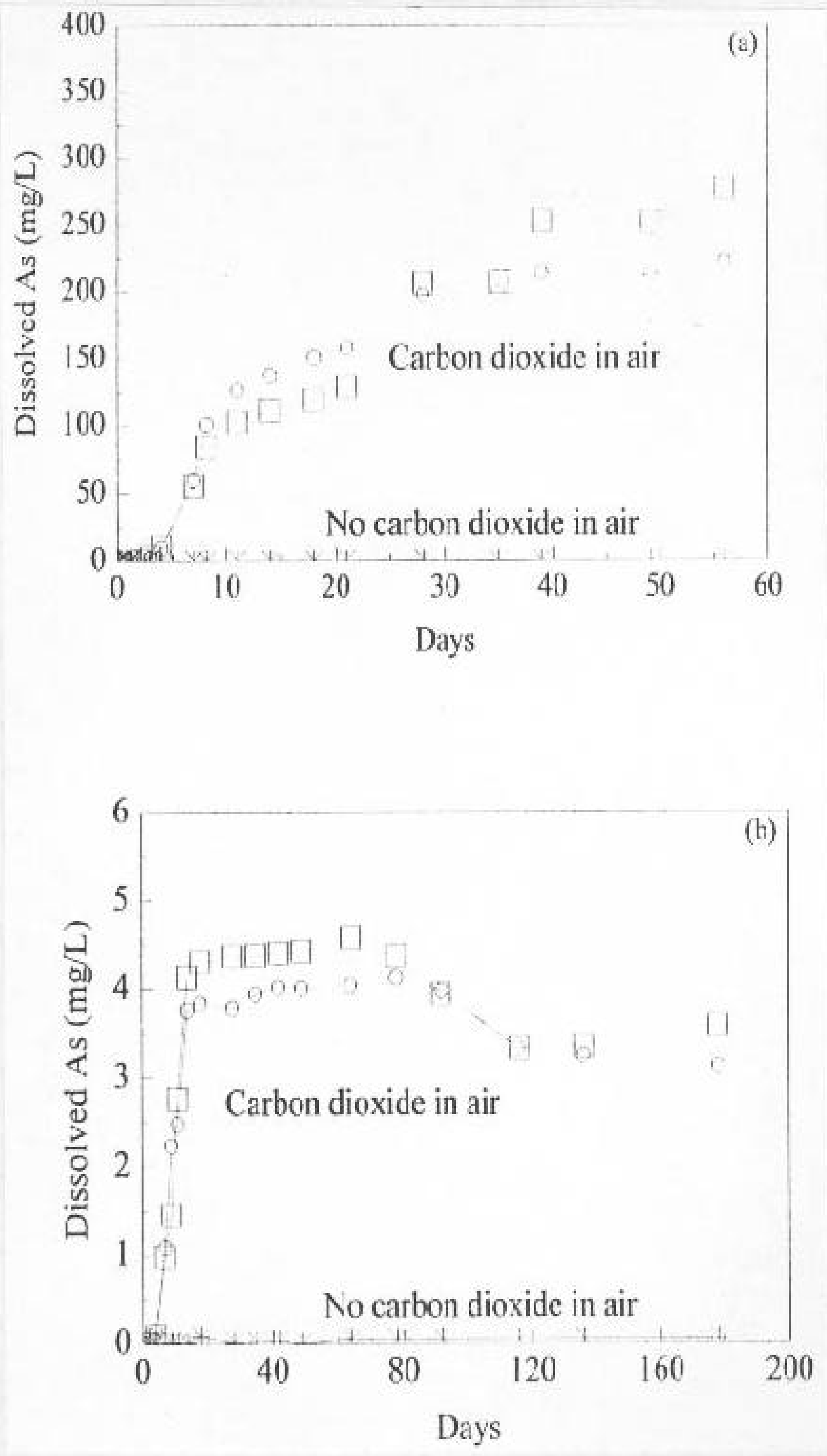

Figure 6-1. Leach testing using water sparged with air and carbon dioxide-free: (a) cement-solidified calcium arsenate solids, and (b) arsenic-bearing hydrous ferric oxide in cement (Fe/As mole ratio 2/1).

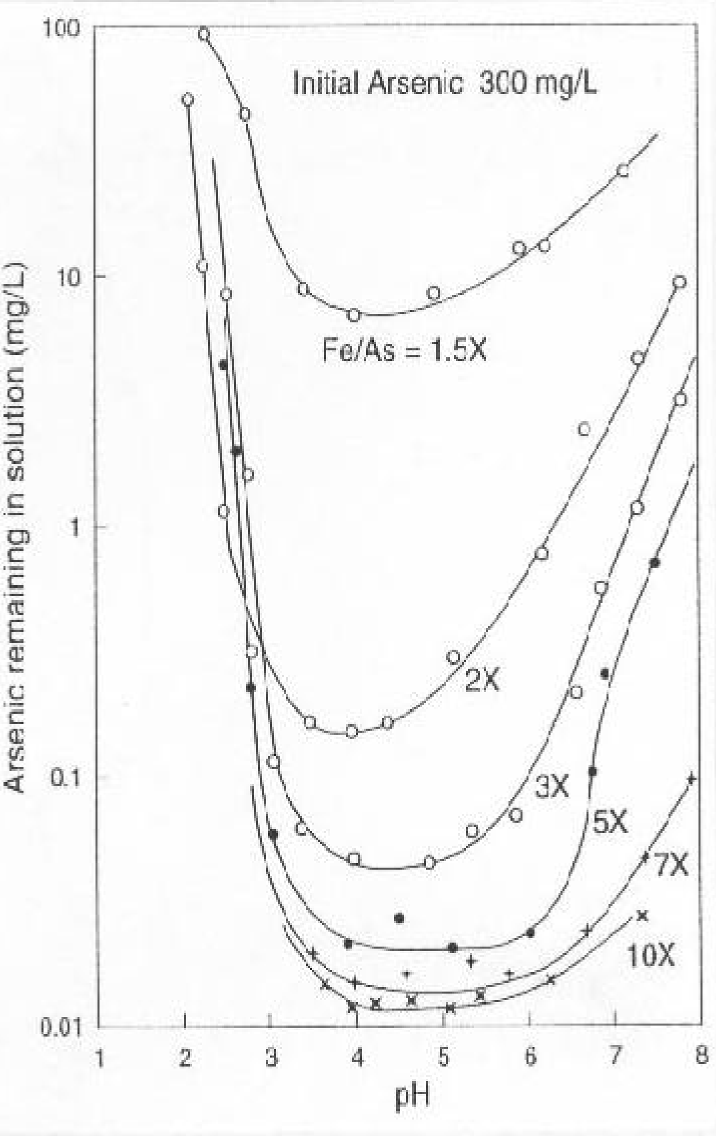

Figure 6-2. Arsenic removal from 300 mg/L As(V) solution with six different levels of iron/arsenic mole ratios (Ref. 11).

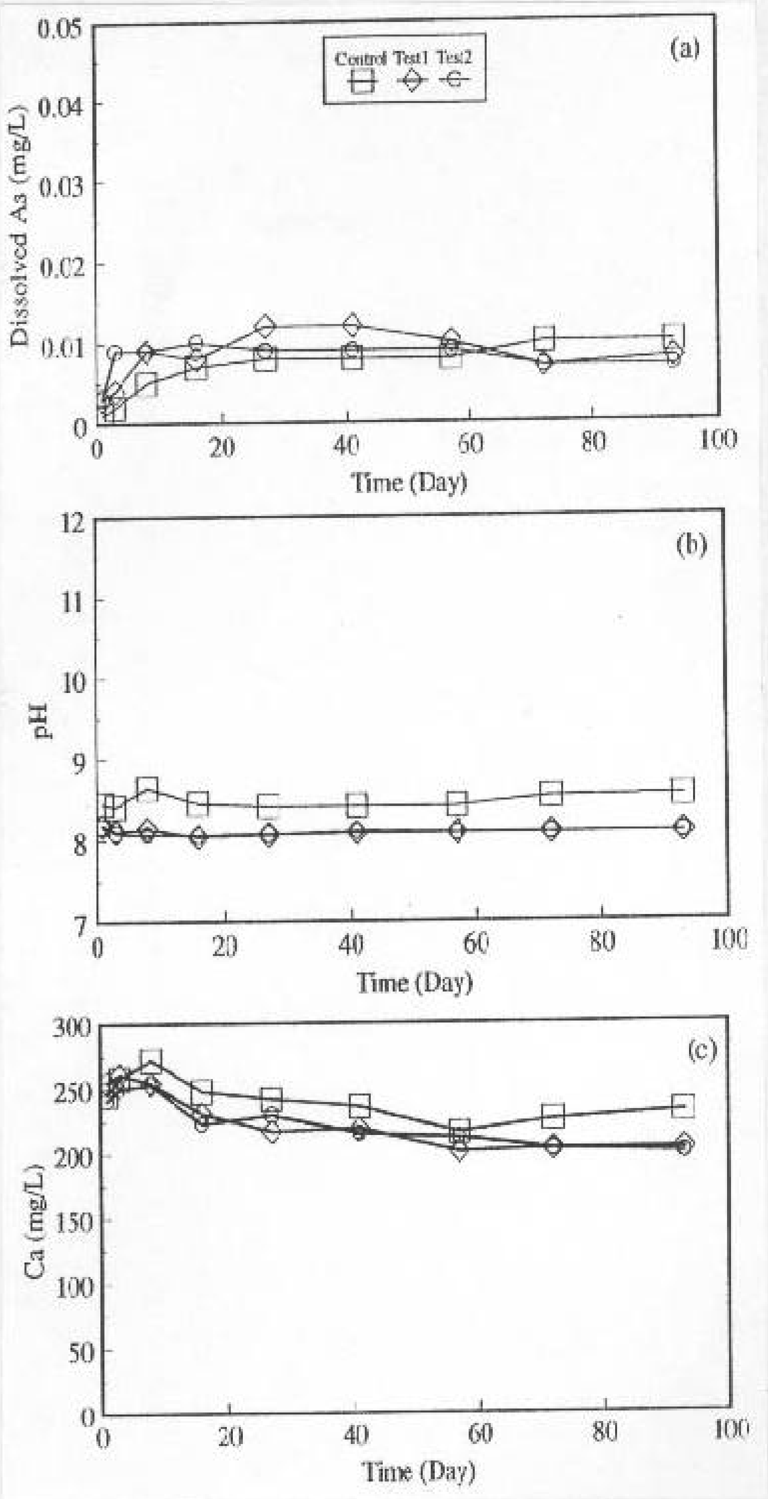

Figure 6-3. (a) Dissolved arsenic, (b) pH, and (c) calcium concentrations in the leachates as a function of time when residues from Susie/Ultrox test runs were immersed in aerated water. Control: carbon dioxide-free air used for sparging. Tests 1 and 2: tests with aerated water.

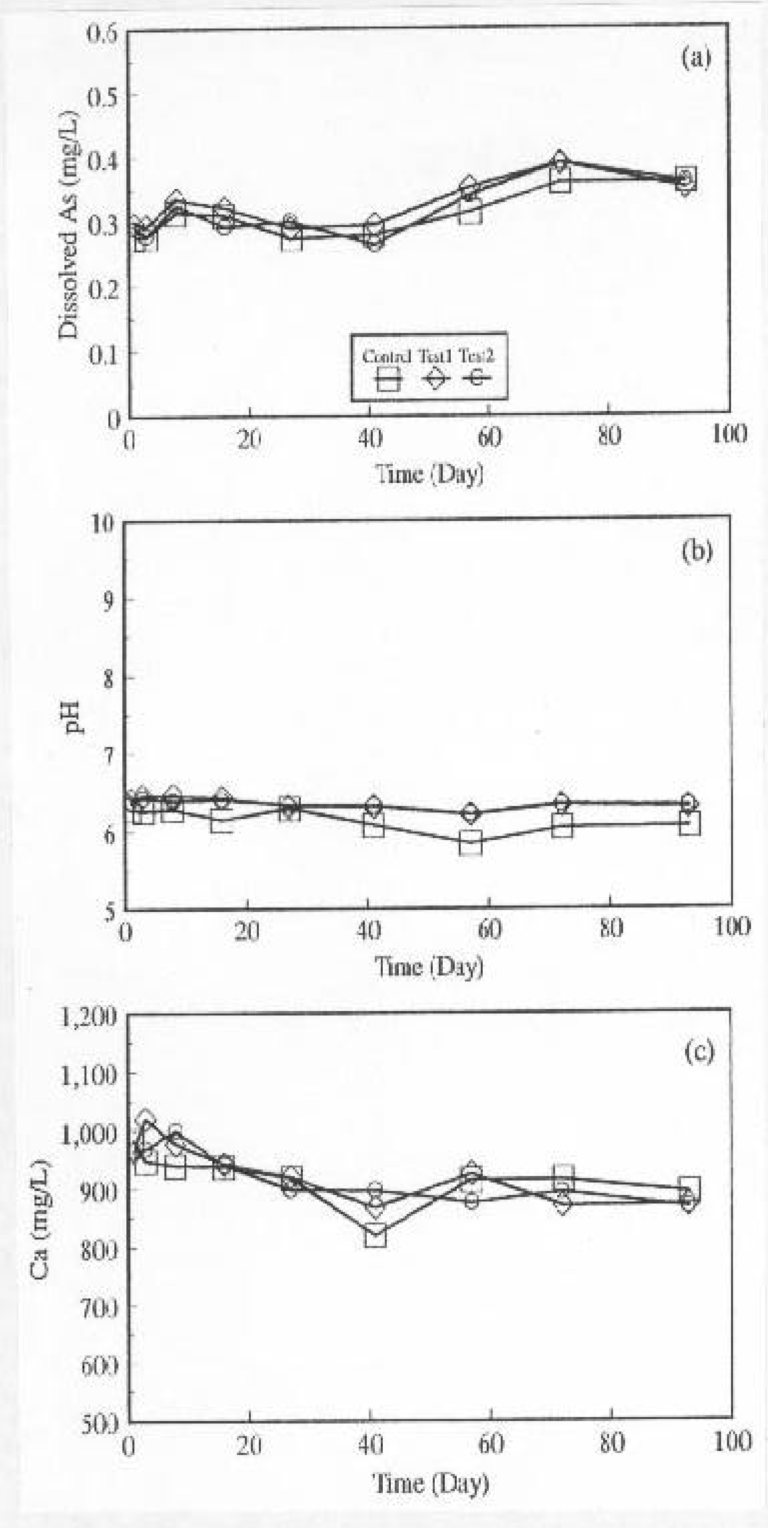

Figure 6-4. (a) Dissolved arsenic, pH, and (c) calcium concentrations in the leachates as a function of time when residues from flue dust/solar test runs were immersed in aerated water. Control: carbon dioxide-free air used for sparging. Tests 1 and 2: tests with aerated water.

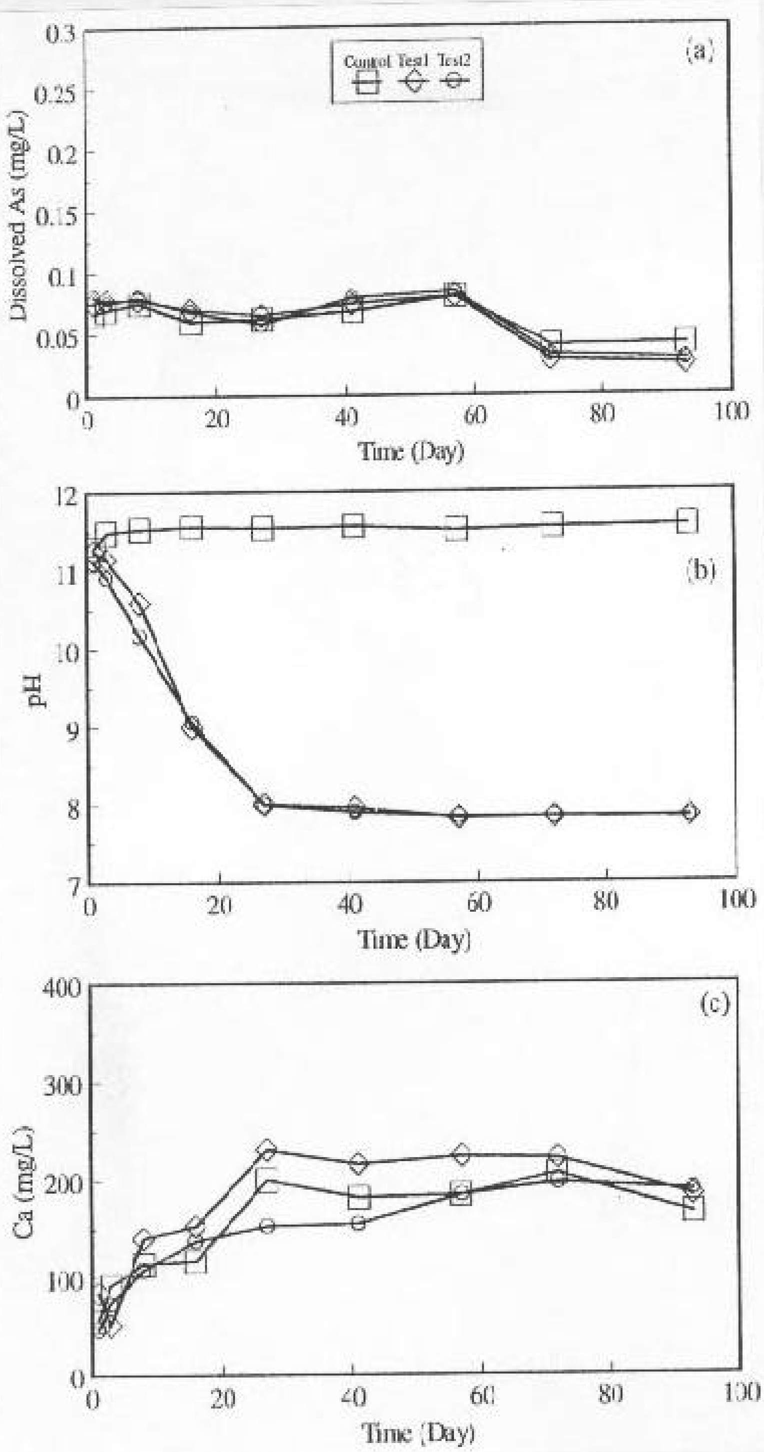

Figure 6-5. (a) Dissolved arsenic, (b) pH, and (c) calcium concentrations in the leachates as a function of time when cement-solidified residues from Susie/Ultrox test runs were immersed in aerated water. Control: carbon dioxide-free air used for sparging. Tests 1 and 2: tests with aerated water.

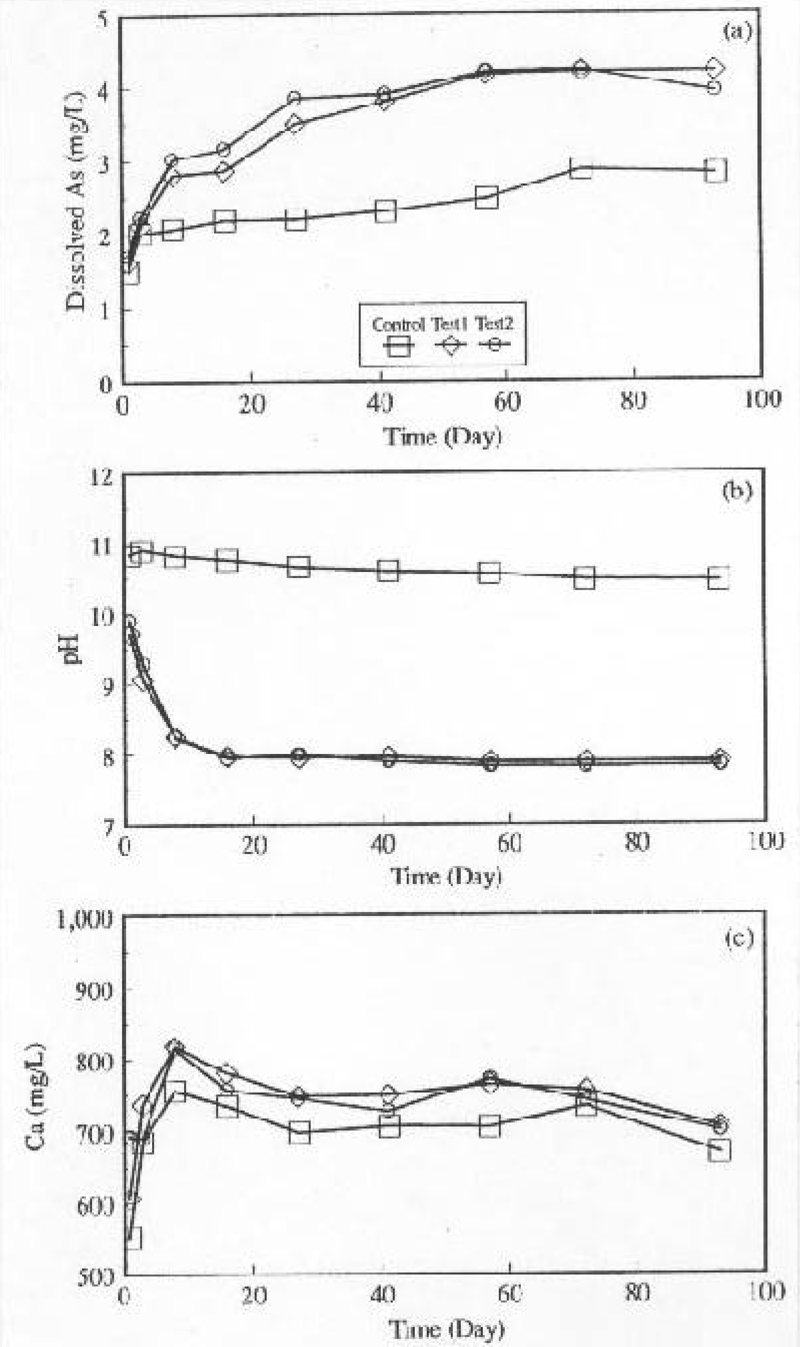

Figure 6-6. (a) Dissolved arsenic, (b) pH, and (c) calcium concentrations in the leachates as a function of time when cement solidified residues from flue dust/solar test runs were immersed in aerated water. Control: carbon dioxide-free air used for sparging. Tests 1 and 2: tests with aerated water.

7. Technology Applications Analysis

Test results given in Sections 3 to 6 demonstrate that the light-assisted oxidation process effectively oxidize dissolved As(III). Although there are limits to conclusions that can be drawn from a single field demonstration, this section evaluates the economics of the process and the comparison with conventional chemical oxidants.

7.1 Economic Analysis

Both the Ultrox reactor and solar ponds can be used in a batch or continuous mode depending on effluent treatment requirements. However, as noted in Section 4, the continuous flow tests could not be performed properly because of a problem in the reactor design that caused short-circuiting within the Ultrox reactor, and the time constraint during the solar test work in Rimini that prevented the operation of an optimized continuous test run. Consequently, the process economics was calculated based on the results of batch tests only.

It should be noted that the cost data presented here are order-of-magnitude estimates and several factors affecting the process economics are highly site-specific, e.g., the composition of the effluent to be treated, reagent and electric power costs, local climate, and the value of land occupied by solar ponds. The reactor, which was built for treating of dissolved organics using ozone, H_2O_2, and UV light, was purchased without any design modifications (apart from material of construction). The solar ponds were designed to treat acid mine water of a different composition to that of Susie Mine water.

7.1.1 Photo-Oxidation using Ultrox Reactor Susie Mine Water

The results of batch tests using Ultrox reactor are reproduced from part of Table 4.12 in Table 7.1 below. Since arsenic analysis performed by MSE and ANSTO personnel are used in this report, the oxidation rates obtained from both sources are given in Table 7.1. The rates using ANSTO results were calculated based on the total As(V) and dissolved As(V) analyses. Since the two sets of figures are very similar, the average values were used for the cost calculation.

As discussed in Sections 3.2 and 4.2, mainly because some of the ferrous ions in the sample were oxidized to ferric before the test runs, the addition of Fe(III) did not increase the rate of arsenic oxidation using low-pressure mercury lamps as used in the Ultrox reactor. In fact as shown in Table 7.1, the addition of Fe(III) apparently resulted in slightly lower rates. All test results were used, but the cost of adding iron was not included in the cost calculation as shown in Table 7.2. It was observed during bench-scale tests that 20 mg/L of Fe(III) was sufficient to promote and sustain the photo-oxidation process. In fact Fe(III) was generated during the test runs using low-pressure mercury lamps (Tables 3.2 and 4.13).

In the absence of chemical price data for remote areas in Montana, the cost of adding acid (and other chemicals) was calculated based on the price of $78 per ton (2,000 pounds) of 31% w/w HCl (22 degree Baume) in railroad tanks obtained from Chemical Marketing Reporter, April 1997 (the bulk price of chemical oxidants such as calcium hypochlorite, H_2O_2, and potassium permanganate were, for comparison purposes in Section 7.2, also a source from the same publication).

Electricity cost was calculated based on $0.075 per kilowatt hour (kWh) and the oxidation times were estimated from the slope of the curves depicted in Figures 4.28 to 4.34 and multiplied by a factor of 1.2, i.e., assuming that 20% excess time is needed (equivalent to 20% excess dosage for conventional chemical oxidants). The calculated results are summarized in Table 7.2, details are given in Appendix C.

The cost of electric power used to oxidize arsenic in 1,000 gallons of Susie Mine water as a function of acid additions is shown in Figure 7.1. It indicates that there is a distinct point where the acid addition was optimized, i.e., where a minimum of electricity used was observed. The complex influence of HCl addition on the rate of arsenic oxidation can be explained by the fact that the rate is largely determined by the concentration of dissolved Fe(III) and the proportion of dissolved-free iron and the hydroxide- and chloride-complexes. The latter species are more effective in initiating the photochemical processes.

According to MSE results, the optimum test was batch test 6 where the total cost of acid and electricity was $0.521 per 1,000 gallons. In contrast, based on ANSTO results the minimum total cost of $0.603 per 1,000 gallons for acid and electricity was achieved in batch test 4.

Capital Cost

The Ultrox unit for the present demonstration was purchased for $100,000 because special material (Inconel) was used for its construction to allow use over a wide range of conditions including low pH with high chloride concentrations. Based on the operating conditions used for treating acid mine water, a normal stainless steel reactor would be sufficient. The cost of a standard 325-gallon capacity Ultrox F-325 reactor with 36 lamps without ozone generator/destructor and air compressor was reported to be $30,000 (Ref. 21). Since the completion of arsenic oxidation using Susie Mine water was achieved in about 20 minute, the F-325 would have a capacity of approximately 15 gpm. Assuming the life of the reactor is 10 years, the average annualized cost of the reactor would be $3,000 per year. Annual lamp replacement costs = (lamp cost) x (number of lamps) x (hours per year) divided by lamp life (13,000 hours) = $98 x 36 x 8760/13000 = $2,377 per year.

Labor cost [assumed to be half the labor cost for operating a small calcium hypochlorite (which involves dissolution of solids) disinfection plant 365 hours per year at $10/hour (Ref. 22)] at 0.5 hours per day @ $10/hour = $1,825 per year.

Total capital and operating cost = $7,202 per year.

Or in terms of gallons of water treated, the operation and maintenance cost: $7,202/(15 x 60 x 24 x 365) = $0.91 per 1,000 gallons. It might be possible to reduce this cost by optimizing the use of construction materials or using a modified UV lamp water disinfection unit.

The estimated total cost of arsenic oxidation per 1,000 gallons of Susie Mine water using Ultrox UV lamp reactor = $0.62 + $0.91 = <u>$1.53</u>.

Flue Dust Liquor

Since the objective of flue dust treatment is to immobilize its arsenic trioxide content, the cost calculation was done on the basis of gram or kilogram of As(III) oxidized.

Batch Test 1

150 gallons of flue dust leachate of 971 mg/L of As(III) was oxidized in 7.5 hours.

The electric power consumption for operating the UV lamps and pump = 1.75 kilowatt (kW).

HCl added to acidify the leachate to pH 1 = 3.6 g/L.

Cost per 150 gallons (570 L).

Acid = 3.6 g/L x 570 L @ $0.286/kg of HCl = $0.586.

Electricity cost = 7.5 x 1.75 kWh = 13.125 kWh @ $0.075/kWh = $0.984.

Total cost to oxidize 0.971 g/L of As(III) in 570 L [or 553.5 g of As(III)] is $0.586 + $0.984) = $1.57; or $2.84 per kg of As(III).

Batch Test 2

920 mg/L of As(III) in 570 L of leachate was oxidized in 16 hours: 524.4 g of As(III).

Electricity cost = 16 hours x 1.75 kW = 28 kWh @ $0.075 = $2.10 or $2.10/0.5244 = $4.00 per kg of As.

Acid cost = 0.36 g/L x 570 L @ $0.286/kg HCl = $0.059 or $0.106 per kg of As.

Total cost = $4.00 + $0.11 = $4.11 per kg of As.

Alternative Oxidant

H_2O_2 can be used in this case because hot water was used to leach the flue dust (the kinetic of an arsenic oxidation reaction using H_2O_2 is too slow at a temperature <80 °C).

In an acid solution, the oxidation reaction involving H_2O_2 is as follows:

$$H_2O_2 + 2H^{+} + As^{3+} \rightarrow As^{5+} + 2H_2O \tag{7-1}$$

Hence, 1 mole of As^{3+} requires 1 mole of H_2O_2 or 1 gram of As^{3+} requires 0.453 g of H_2O_2. Because H_2O_2 decomposes rapidly at 80 °C, 75%, excess reagent is needed (from past work at ANSTO). To oxidize 1 kg of As(III) with 75% excess oxidant, H_2O_2 required = 1.75 x 0.453 kg = 0.815 kg of H_2O_2; or at $1.54/kg ($0.70/pound) = $1.22. (From Chemical Marketing Reporter, April 1997: $0.245/pound of H_2O_2 of 35% solution.)

It is, therefore, economically more attractive to use H_2O_2 than the photochemical process.

7.1.2 Photo-Oxidation Using Solar Ponds Susie Mine Water

The cost of reagents used in the batch tests and the required UVA solar energy were calculated based on the data given in Figure 4.15 and Table 4.3. Ferric chloride cost was obtained from Chemical Marketing Reporter, i.e., technical grade, 100% basis tanks FOB works $190 per ton (2,000 pounds) or $0.209 per kg (100%). The calculated cost figures are given in Table 7.3.

The UVA solar energy required to complete the oxidation reaction is shown in Figure 7.2 as a function of acid additions for the three different iron additions. There was no difference between the results when 110 or 180 mg/L of ferric chloride additions were used. Thus, from the available data, the cheapest cost of reagent additions (39¢ for acid and 22.9¢ for iron chloride) gave a completion time of about 6.5 hours. This time is actually shorter (and the absorbed UVA energy was slightly smaller) than the corresponding batch test run with a larger iron dose of 180 mg/L.

The solar test runs were planned with completion times of approximately 1 day of sunshine in late summer (6–9 hours). If there had been no time constraint, more runs with less iron dosages, i.e., <110 mg/L, could have been done to confirm that less iron dosage can be used (20 mg/L of iron was sufficient during the test runs using Ultrox reactor). Assuming that 39¢ of acid cost per thousand gallons of mine water is the minimum because less acid would give a solution pH of >2, which results in the precipitation of Fe(III) hydroxide, the total reagent cost per 1,000 gallons is 62¢.

Considering that a plastic-lined pond (including site preparation) can be built for $1 per square foot, and aeration can be achieved using agricultural *leaky pipes*, the capital cost of the solar ponds is small relative to other costs (it is assumed that the land value in remote areas is minimal). Consequently, it is considered that the operating and maintenance cost for the ponds consist of labor and the cost of electricity for operating the air blower and pump.

It is assumed that a 5 kW air blower is required for the aeration of a set of shallow ponds (1-foot deep) with a total surface area of 80 by 40 feet. These ponds would hold 22,000 gallons of water. The cost of electricity for 7 hours per day = 5 x 7 x $0.075 = $2.63.

If it takes 7 hours to oxidize the arsenic, cost per 1,000 gallons = $2.63/22 = $0.12.

Labor cost at 0.5 hours per day @ $10/hour (same as in Ultrox case) $5/22 = $0.23.
The total cost to oxidize arsenic per 1,000 gallons of Susie Mine water using solar ponds = $0.12 + $0.23 + $0.619 = <u>$0.97 per 1,000 gallons</u>.

Flue Dust Liquor
The cost of reagents used in the batch tests and the completion time were obtained based on the data given in Figure 4.17 and Table 4.6. Ferric chloride and HCl costs were as used in the previous section. Sodium chloride cost was taken from an EPA report (Ref. 22): $85 to $105 per ton depending on the size of the plant. The calculated cost figures are given in Table 7.4.

The cheapest reagent cost (batch test 2) corresponds to 7.8¢ per 176 grams of arsenic oxidized in 400 L of leachate (48 hours to oxidize 430 mg/L of arsenic). This is equivalent to $0.45 per kg of arsenic for the reagent cost.

The next cheapest is batch test 3, where sodium chloride was used (24-hour completion time):
the reagent cost = $1.59 per kg.

From batch test 1, the reagent cost = $2.55 per kg of arsenic oxidized.

As in the previous section, it is assumed that electric motors with a total power of 5 kW are required for the aeration (and occasional pumping) of a set of shallow ponds (1-foot deep) with a total surface area of 80 by 40 feet. These ponds would hold 22,000 gallons of water. The cost of electricity for 48 hours to complete of oxidation = 48 x $0.075 = $3.60.

For a concentration of arsenic of 430 mg/L, the set of ponds would hold 35.8 kg of arsenic. Thus, the electricity cost = 10.05¢ per kg. Labor cost at 0.5 hours per day @ $10/hour (same as in Ultrox case) $10/35.8 kg = 27.9¢ per kg.

Total cost per kg of arsenic using batch test 2 data = $0.45 + $0.10 + $0.28 = <u>$0.83</u> per kg of arsenic oxidized.

Using batch test 3 data = $1.59 + $0.05 + $0.14 = $<u>1.78</u>.

Using batch test 1 data = $2.55 + $0.02 + $0.14 = <u>$2.71</u>.

In comparison, the equivalent cost for H_2O_2 as calculated in the Section 7.1.1 is $1.22 per kg.

Although, the cheapest option is about 30% cheaper than the cost for using H_2O_2, it is a rather slow rate, i.e., 48 hours to oxidize 430 mg/L of As(III). Arsenic trioxide from the flue dust material can be dissolved to give a liquor with more than 10 grams of As(III) per L. Hence, it is concluded that there is no great incentive in using the photochemical process to oxidize As(III) in flue dust leachate.

7.2 Technology Applications Analysis

This section is intended to provide data for evaluating the photo-oxidation process as applied to the treating acid mine water and its comparison with conventional chemical oxidants.

Innovative Features of the Technology

The oxidation of arsenic by dissolved oxygen occurs at an extremely slow rate. Consequently, chemical oxidants such as H_2O_2, chlorine compound, or ozone are used in conventional treatment plants. Even strong oxidants such as H_2O_2 or sodium chlorate have kinetic limitations when used in ambient conditions. The ANSTO photo-oxidation process has the following innovative features:

- In the presence of dissolved iron, the oxidation of As(III) to As(V) by air can be accelerated 10,000 fold when the mixture is illuminated with sunlight or an artificial UV light source. Therefore, air can be used as a substitute for conventional chemical oxidants.

- Selectively oxidize arsenic in the presence of dissolved ferrous ions that represent an extra demand of chemical oxidant in conventional processes. In acid mine water, the concentration of dissolved ferrous can be more than a dozen times greater than arsenic. For example, dissolved Fe(II)-to-As(III) mole ratio in the Susie Mine water used in this project was 22/1. The Fe(II)-to-As(III) ratios in other acid mine waters under consideration by MSE in 1994–96 were in some cases larger than 22/1 (Table 7.5). In fact, the ratio in the

Susie Mine water sampled previously was 39/1.

- The synergistic use of iron as both a photoabsorber and coprecipitant for the removal of arsenic.

- The absence of halogenated organics as a by-product of the oxidation process. The production of chlorinated organics such as chloroform has precluded the use of some chlorine-based compounds as an oxidant in drinking water treatment.

Dissolved Chloride Concentration
For the present photochemical process to function effectively, the pH of the reaction mixture needs to be kept below the precipitation pH of Fe(III)-hydroxide (pH 2 to 3). The precipitation pH depends on the amount of Fe(III) dosage [if no Fe(III) is present], which is dependent on the initial concentration of As(III). If the initial concentration of As(III) is 1 mg/L (the concentration at Crystal Mine or Londonderry, see Table 7.5) instead of 12 mg/L as in the present case, the amounts of Fe(III) and HCl dosages will be significantly less than those reported here. This will result in much smaller reagent costs and added chloride concentration.

Alternative Oxidants
Since the cost of using a chemical oxidant is more attractive than the photochemical process in the case of flue dust liquor (see previous section), only acid mine water is considered here. For comparison purposes, the cost of arsenic oxidation per 1,000 gallons of Susie Mine water using conventional chemical oxidants was calculated based on the following:

- H_2O_2 is not considered because the kinetics of the oxidation reaction is too slow at less than 80 °C or solution pH of less than 11.

- Chlorine gas is too hazardous for applications in remote mine sites.

- Calcium hypochlorite is used in excess (20%) of the oxidant demand imposed by the 12 mg/L of As(III) and 200 mg/L of Fe(II) in Susie Mine water.

- Potassium permanganate is applied without excess addition (otherwise, a pink solution would result from the excess, residual permanganate ions).

The oxidation reaction between calcium hypochlorite and dissolved As(III) and Fe(II) can be represented as follows:

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2 \tag{7-2}$$

$$H^{+} + HOCl + As^{3+} \rightarrow As^{5+} + Cl^{-} + H_2O \tag{7-3}$$

$$H^{+} + HOCl + 2Fe^{2+} \rightarrow 2Fe^{3+} + Cl^{-} + H_2O \tag{7-4}$$

at pH greater than 2 when Fe^{3+} hydrolyzes to give $Fe(OH)_3$:

$$HOCl + 5H_2O + 2Fe^{2+} \rightarrow 2Fe(OH)_3 + Cl^{-} + 5H^{+} \tag{7-5}$$

Thus, the oxidation of 1 mole of As^{3+} to As^{5+} requires 0.5 mole of $Ca(OCl)_2$ and the oxidation of 1 mole of Fe^{2+} to Fe^{3+} requires 0.25 mole of $Ca(OCl)_2$.

Because of the usual presence of Fe(II) in acid mine water, it is not possible to calculate a generalized cost for oxidizing arsenic in the water, i.e., the cost calculation is highly site specific because it depends on the ratio of Fe(II)/As(III) in the water.

For Susie Mine water in which Fe(II) was present at 200 mg/L and As(III) 12 mg/L (mole ratio of 22/1), the $Ca(OCl)_2$ required to treat 1,000 gallons of Susie Mine water would be $1.17. Had the mole ratio in the Susie Mine water been 39/1 (as in the Susie Mine water sampled before the commencement of this project), the cost for $Ca(OCl)_2$ required would have been $1.97 (Appendix D).

The operating and maintenance cost for a 15 gpm plant calculated from published data (Ref. 22) = $0.56.

Total cost per 1,000 gallons = $0.56 + $1.17 = <u>$1.73</u>.

If permanganate is used instead, and it is reduced to solid, filterable MnO_2, the following oxidation reaction would take place:

$$2MnO_4^- + 8H^+ + 3As^{3+} \rightarrow 3As^{3+} + 2MnO_2 + 4H_2O \tag{7-6}$$

$$MnO_4^- + 4H^+ + 3Fe^{2+} \rightarrow 3Fe^{3+} + MnO_2 + 2H_2O \tag{7-7}$$

If the same calculation procedure, as carried out with calcium hypochlorite, is applied (but with no excess reagent), the permanganate cost for 1,000 gallons of Susie Mine water would be $2.33 + $0.56 (the operating and maintenance cost is assumed to be the same as that of $Ca(OCl)_2$) = <u>$2.89 per 1,000 gallons</u>.

Table 7.6 summarizes the cost of arsenic oxidation per 1,000 gallons of Susie Mine water:

Table 7-1. Reagents added during Ultrox batch tests using Susie Mine water. The rate of arsenic oxidation calculated using MSE and ANSTO analyses are shown in milligrams of arsenic oxidized per liter per minute.

Batch Test	HCl added g/L	Fe(III) added mg/L	Rate (MSE) mg/L/min	Rate (ANSTO) mg/L/min	
1	0.36	0	-0.24[1]	0.44	0.48
2	0.36	100	0.23	0.38	0.34
3	1.08	0	0.35	0.51	ND
4	0.27	0	0.30	0.67	0.67
5	1.08	100	0.29	0.45	0.44
6	0.11	0	0.52	0.27	0.28
7	0.11	100	0.40	0.24	0.24

[1] Not included in cost calculations.

Table 7-2. Calculated cost of acid additions and electricity (cents) required to oxidize arsenic in 1,000 gallons of Susie Mine water using Ultrox reactor.

Batch Test	Addition Cost of Acid	Electricity Cost based on results of	
		MSE	ANSTO
1	38.9		45.5
2	38.9	89.8	58.1
3	116.7	60.2	41.0
4	29.1	69.5	**31.2**
5	116.7	72.4	47.5
6	11.9	**40.2**	74.7
7	11.9	52.3	87.2

Table 7-3. Reagent additions and costs (per 1,000 gallons) for solar batch tests using Susie Mine water.

Batch Test	Iron Addition		Acid Addition		UVA Solar Energy Required to Complete Oxidation J/cm^2
	mg/L Fe	cost ($)	g HCl/L	Cost ($)	
3	98	$0.23	0.36	0.39	70
9	110	0.253	1.08	1.17	45
10	110	0.253	3.24	3.52	25
5	180	0.412	0.36	0.39	70
7	180	0.412	1.08	1.17	35
2	180	0.412	3.24	3.52	14 (based on As(III) readings)
6	270	0.62	0.36	0.39	36
8	270	0.62	1.08	1.17	35
4	270	0.62	3.24	3.52	13

Table 7-4. Solar batch tests for the oxidation of 430 mg/L of As(III) in flue dust leachate. The cost of reagent was calculated on the basis of 400 L of leachate.

Batch Test	Completion Time	Iron		HCl		NaCl		Total Cost
	Hours	mg/L	Cents	mg/L	Cents	mg/L	Cents	Cents
1	10	440	3.7	3600	41.2	0		44.9
2	48	440	3.7	360	4.1	0		7.8
3	24	440	3.7	360	4.1	4425	20.2	28.0

Table 7-5. As(III) concentration and Fe(II)/As(III) mole ratio in acid mine waters sampled in 1994–96.

Mine Site	As(III) ppb	Fe(II)/As(III) mole ratio
Bullion Mine	410	506
Crystal Mine	930	36
Londonderry	1090	12
Susie Mine	11420	39
Washington #1	540	13
Washington #2	150	219

Table 7-6. Comparison of oxidation cost per 1,000 gallons of Susie Mine water. For small plants of 15 gpm or 22,000 gallons per day capacity.

	Photo-oxidation		Calcium Hypochlorite	Potassium Permanganate
	UV lamps	Solar		
Reagent cost	$0.291 (acid)	$0.39 (acid)	$1.17	$2.33
		$0.229 (iron)		
Electricity	$0.312	$0.12		
Capital and O&M	$0.91	$0.23	$0.56	$0.56
Total cost	$1.53	$0.97	$1.73	$2.89

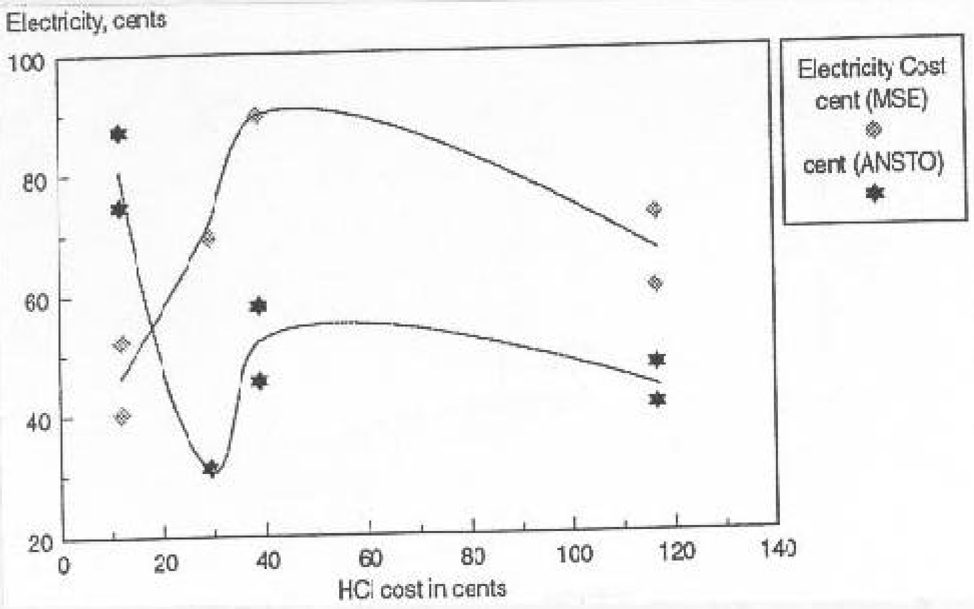

Figure 7-1. Electricity cost required to oxidize As(III) per thousand gallons of Susie Mine water as a function of acid addition.

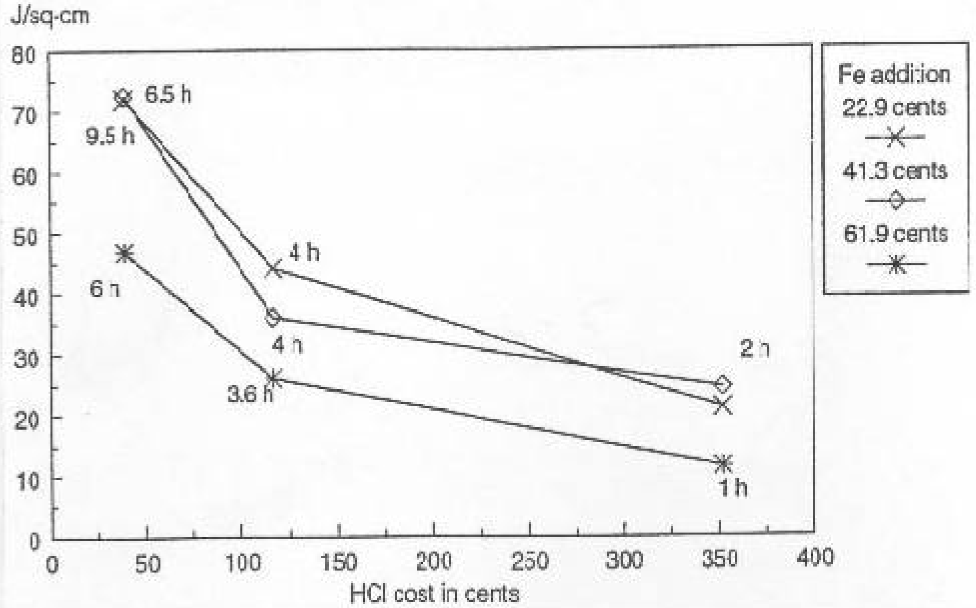

Figure 7-2. UVA solar energy (J/cm^2) and time (hours) required to complete the oxidation process as a function of acid addition for three different additions of iron. The cost of reagent additions are calculated in cents per thousand gallons of Susie Mine water.

8. Conclusions

The following conclusions are drawn from the results of the demonstration project. They are listed according to the specific objectives of the project that are essentially the claims for the technology.

Objective 1. To demonstrate that the photo-assisted oxidation process can oxidize at least 90% of the initial dissolved As(III) in the test streams.

- The project was successful in demonstrating the effectiveness of the photochemical process to oxidize dissolved As(III). Both sunlight and artificial light from UV lamps can be used to initiate and sustain the photochemical process. The completion of the oxidation process was confirmed by the analyses of arsenic in the residues produced during the demonstration: at least 97% of the arsenic was As(V).

- As previously determined at ANSTO, ferric chloride was the most effective iron compound to add to the reaction mixture to initiate the photochemical reaction. As a photo-absorber, it undergoes photolysis to produce reactive radicals with high oxidative potentials. HCl is required to acidify the reaction mixture to pH less than 2 to 3 in order to keep the photo-absorber, Fe(III) compounds, in solution. Sulfuric acid can be used, but the rate of oxidation will be adversely affected.

- During photo-oxidation tests using acid mine water collected from the abandoned Susie Mine site, As(III) was preferentially oxidized in the presence of a large excess of dissolved Fe(II) (22/1 mole ratio). In conventional treatment plants, dissolved Fe(II) represents an extra chemical oxidant demand that has to be satisfied during the oxidation of As(III).

- Although it has been reported that there are hundreds of acid mine drainage waters containing arsenic in the Western United States, only seven sets of data complete with arsenic and iron speciation analyses were available before this project commenced. The As(III) concentrations range from 150 to 11,420 ppb, while the Fe(II)/As(III) mole ratios range from 12 to 506. Of the seven sets of data, the highest As(III) concentration was that of Susie Mine water with an Fe(II)/As(III) mole ratio of 39/1.

- For acid mine waters with smaller concentrations of As(III) than that of Susie Mine water, smaller dosages of Fe(III) chloride and HCl will be required.

- Characterization of the hydraulic flow behavior of the UV lamp reactor used in the demonstration project (commercially manufactured in the United States) revealed a problem in the reactor design that caused short-circuiting within the reactor. Consequently, only the batch test results were used to calculate process economics.

- Analytical results produced by the MSE-HKM Laboratory and ANSTO personnel (in situ analysis in the field) were both used for compilation of this report. It was noted, however, that the method for separating As(III) from As(V) using ion-exchange resins as used by the MSE-HKM Laboratory is adversely affected when As(V) in the sample is present at high concentrations or as iron arsenate colloidal particles. The method is designed primarily for trace amounts of arsenic in ground water.

Objective 2. To reduce the concentration of dissolved arsenic in the test water to a level under the drinking water limit for arsenic established by the World Health Organization of 10 ppb.

- The oxidized As(V) can be removed from the test stream to residual levels of less than 10 ppb using the iron coprecipitation process if a proper filtration procedure in a clean working environment is followed. Three iron coprecipitation procedures using oxidized Susie Mine water performed at the pilot plant building gave residual arsenic concentrations in the filtrate of 17, 35, and 53 ppb. However, the same procedure performed five times in an analytical laboratory gave results ranging from 1 to 5 ppb.

- The coprecipitation process can be optimized to remove both arsenic and heavy metals. The concentrations of chloride and sulfate in the treated water, however, may be greater than the statutory discharge limits.

Objective 3. To render the arsenic-bearing precipitate generated by the flue dust and mine water tests environmentally stable.

- The arsenic-bearing solids produced by the iron coprecipitation process (with and without cement solidification) met the requirements of both the EPA TCLP and a leach test using aerated water for 3 months. The second test is used to verify whether arsenic is present in the residues as iron/arsenate material. Calcium arsenate compounds, which are subject to attack by dissolved atmospheric carbon dioxide, may form during the lime neutralization operation usually practiced in conjunction with the iron coprecipitation process.

- Although there are limits to conclusions that can be drawn from a single field demonstration, process economics on the application of the photochemical process to the treatment of acid mine water was calculated based on test results using Susie Mine water. It should be noted, however, that the cost data are approximate figures, and several factors affecting the process economics are highly site-specific, e.g., the composition of the effluent to be treated, reagent and electric power costs, local climate, and the value of land occupied by the solar ponds.

- The total cost for arsenic oxidation per thousand gallons of water of Susie Mine water is \$1.50 using a UV lamp reactor or \$1.00 using solar ponds. Both the reagent and operating cost would be less for acid mine waters with smaller concentrations of As(III).

- For comparison, the equivalent cost using calcium hypochlorite is \$1.75 or using potassium permanganate is \$2.90 (H_2O_2, which is a cheaper oxidant, is too slow to react with As(III) at room temperature). All the cost data were calculated based on the bulk price of reagents without consideration of transportation costs to remote mine sites. The operation and maintenance as well as the capital cost are based on a small plant of 15 gpm or a set of solar ponds of 22,000 gallons in total capacity. For a given As(III) concentration, the cost of required chemical oxidant would increase with an increase in the Fe(II)/As(III) ratios.

- Compared to the cost of alternative chemical oxidants such as calcium hypochlorite or H_2O_2, the photochemical process is less attractive when used to oxidize As(III) in the hot flue dust leachate.

Despite the need for more survey data on the composition of acid mine waters in order to assess the more general application of the oxidation technology, the main conclusion that can be drawn from this project is that the photo-oxidation/iron coprecipitation process was successfully demonstrated to treat arsenical acid mine water and that the process economics appears to be very promising.

Due to the successful demonstration of this technology, more research is warranted to employ the use of photocatalyses for the oxidation and/or removal of other target metals associated with industrial wastes, such as selenium.

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APPENDIX A

Analytical Methods

APPENDIX A

ANALYTICAL METHODS

Arsenic speciation

MSE-HKM laboratory used ion-exchange resin to separate the two arsenic species followed by the determination of the separated amounts of arsenic using graphite furnace. This method was designed for the separation of trace amount of arsenic(III) and arsenic(V) in ground water (Ficklin, 1983).

Arsenic(V) was determined in the field by ANSTO personnel using a spectrophotometric method published by Johnson and Pilson(1972). The reagents used for colour development are the same as those endorsed by the American Wastewater Association (APHA. 1992) for Phosphorus(V) determination (Method 4500-P E). A Hach DR2000 spectrophotometer was used to measure all the absorbances. The cuvette of this instrument had a path length of 2 cm and it was used for all standards and samples. No significant concentrations of phosphate were measured in the test streams.

Ammonium molybdate and potassium antimonyl tartrate react in acid medium with arsenic(V) to form a heteropoly acid-arsenomolybdic acid- that is reduced to intensely coloured molybdenum blue by ascorbic acid. The intensity of this colour is then read as the solution's absorbance at 865 nm. Arsenic(III) does not react or produce any blue colour making the method suitable for distinguishing As(V) from other inorganic arsenic species.

Total Arsenic

Where it was desired to determine the sum of the concentrations of all the arsenic species then a preoxidation step was added to ensure that all the arsenic was present as As(V). It consisted of adding 0.01M potassium permanganate drop wise to the sample until the pink end point was reached. The colour was then discharged by the addition of 0.01M Iron(II) chloride. If it was desired to determine As(III) then both As(V) and the total arsenic were analysed in the solution and the As(III) calculated from the difference.

If the sample is not filtered then the sulphuric acid in the colouring reagent dissolves any solid present allowing all the As(V) to be measured regardless of whether it was originally present in solution or with the solids. Dissolved As(V) was distinguished from the total arsenic concentration by filtration of the sample before analysis.

Sampling Procedure

The objective of the project was to demonstrate that arsenic(III) is oxidised to arsenic(V) in the presence of iron, air and light. The analytical program was therefore required to accurately record the changing As(III) and As(V) concentrations. Whether the arsenic was present in solution or formed part of a precipitate was irrelevant to this objective. Consequently, unless stated otherwise the ANSTO analyses were determined on unfiltered samples.

It was crucial that the oxidation reactions cease at the time the sample was taken otherwise a positive error would result. As the reactions only run in the presence of light all the samples were stored and analysed in the dark, apart from less than 10 minutes during dilution and addition of the colour development reagents.

A 30 mL sample bottle was filled with process liquor and labelled with

1. Feed liquor, Flue Dust Leachate or Susie water
2. Test type. Batch or Continuous
3. Test number
4. Time sample was taken.

As all of the samples collected during the solar experiments were analysed and discarded before the Ultrox experiments commenced the type of light was not recorded on the bottles.

Quality control checks of the arsenic analyses performed by ANSTO personnel

The following checks were performed and the results are tabulated in **Tables A1** to **A4** below:

- A field blank was prepared for every set of analysis from the deionised water used for analytical dilutions. In the attached tables this is expressed as the equivalent concentration of As(V) in the cuvette.
- A 2 mg/L spike of the field blank was used to confirm the validity of the calibration curve for each set of analysis.
- Where one feed solution was used for a series of tests the total arsenic in the feed solution was repetatively determined to measure the consistency of results between analytical batches. In the case of flue dust batch tests the total arsenic in the reaction mixture was determined several times. The standard deviation for each set of analyses was determined and has been expressed as an absolute amount and as a percentage of the average arsenic concentration.

These results indicate that the colorimetric method is capable of precisely determining arsenic at the concentrations found in the samples as the percentage error did not exceed 5 %.

TABLE A1

Quality control checks for the solar batch tests with water from the Susie mine

Batch	Field Blank mg/L As(V)	Field Std 2 mg/L As(V)	Reference mg/L As(T)
1	0.017	2.08	17.5
2	0.024	2.00	16.9
3	0.017	2.04	16.3
4	0.137	2.14	16.4
5	0.103	2.06	17.0
6	0.017	1.96	17.0
7	0.051	2.16	15.9
8	0.017	2.21	15.9
9	0.024	2.00	15.4
10	0.021	1.96	15.1
11	0.014	2.12	15.1
Average	0.040	2.06	16.2
Std dev			0.8
% error			5.1

TABLE A2

Quality control checks for the batch tests with water from the Susie mine and the Ultrox reactor

Batch	Field Blank	Field Std 2 mg/L As(V)	Reference mg/L As(T)
1	0.012	2.06	16.5
2	0.052	2.16	15.4
3	0.021	2.08	15.2
4	0.1	2.14	15.2
5	0.018	2.2	15.2
6	0.016	1.96	14.7
7	0.015	2.04	*
Average	0.033	2.09	15.4
Std dev			0.6
% error			3.8

*The precipitate formed during this test settled reducing the true arsenic concentration during the test

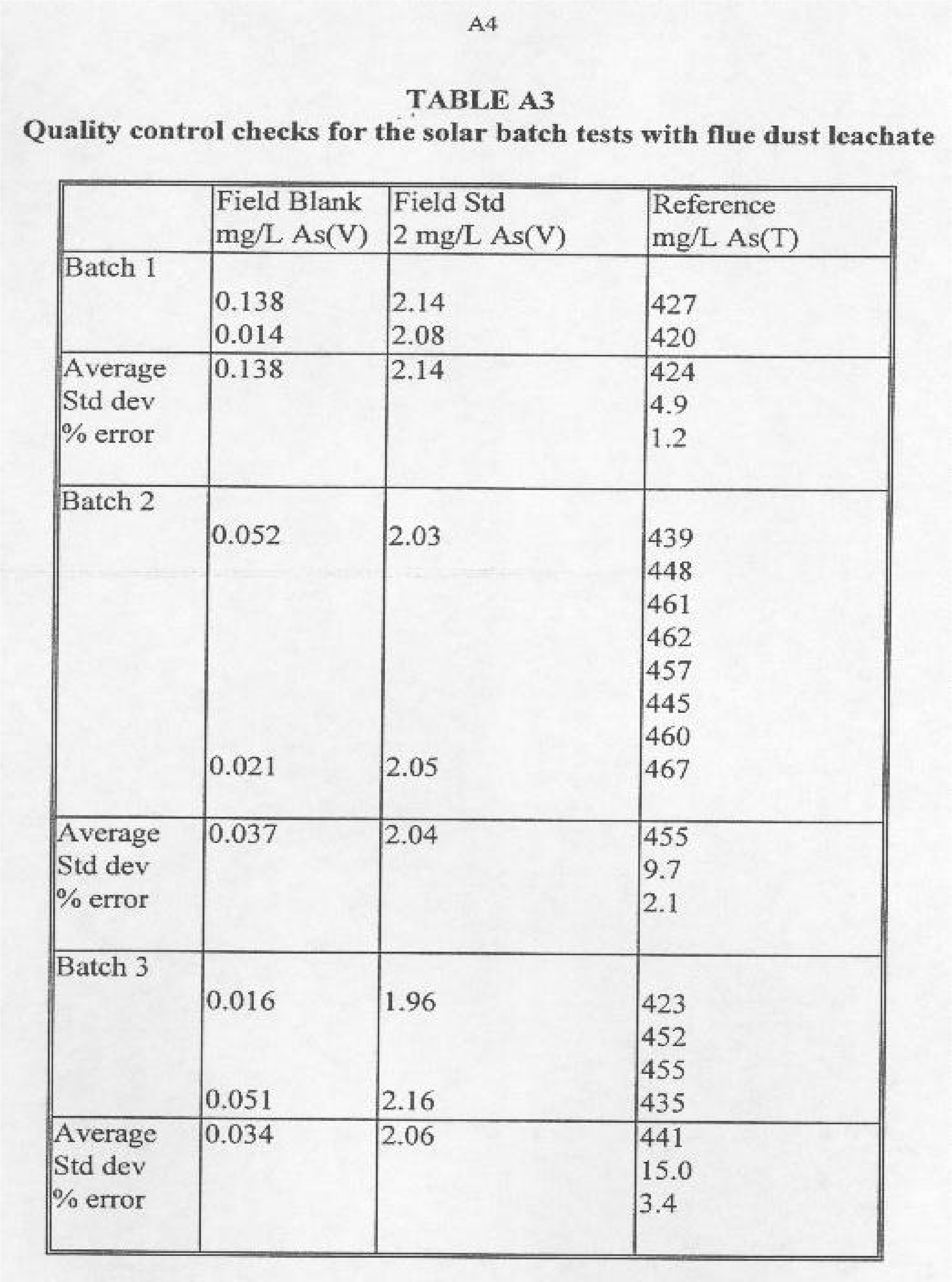

TABLE A3
Quality control checks for the solar batch tests with flue dust leachate

	Field Blank mg/L As(V)	Field Std 2 mg/L As(V)	Reference mg/L As(T)
Batch 1			
	0.138	2.14	427
	0.014	2.08	420
Average	0.138	2.14	424
Std dev			4.9
% error			1.2
Batch 2			
	0.052	2.03	439
			448
			461
			462
			457
			445
			460
	0.021	2.05	467
Average	0.037	2.04	455
Std dev			9.7
% error			2.1
Batch 3			
	0.016	1.96	423
			452
			455
	0.051	2.16	435
Average	0.034	2.06	441
Std dev			15.0
% error			3.4

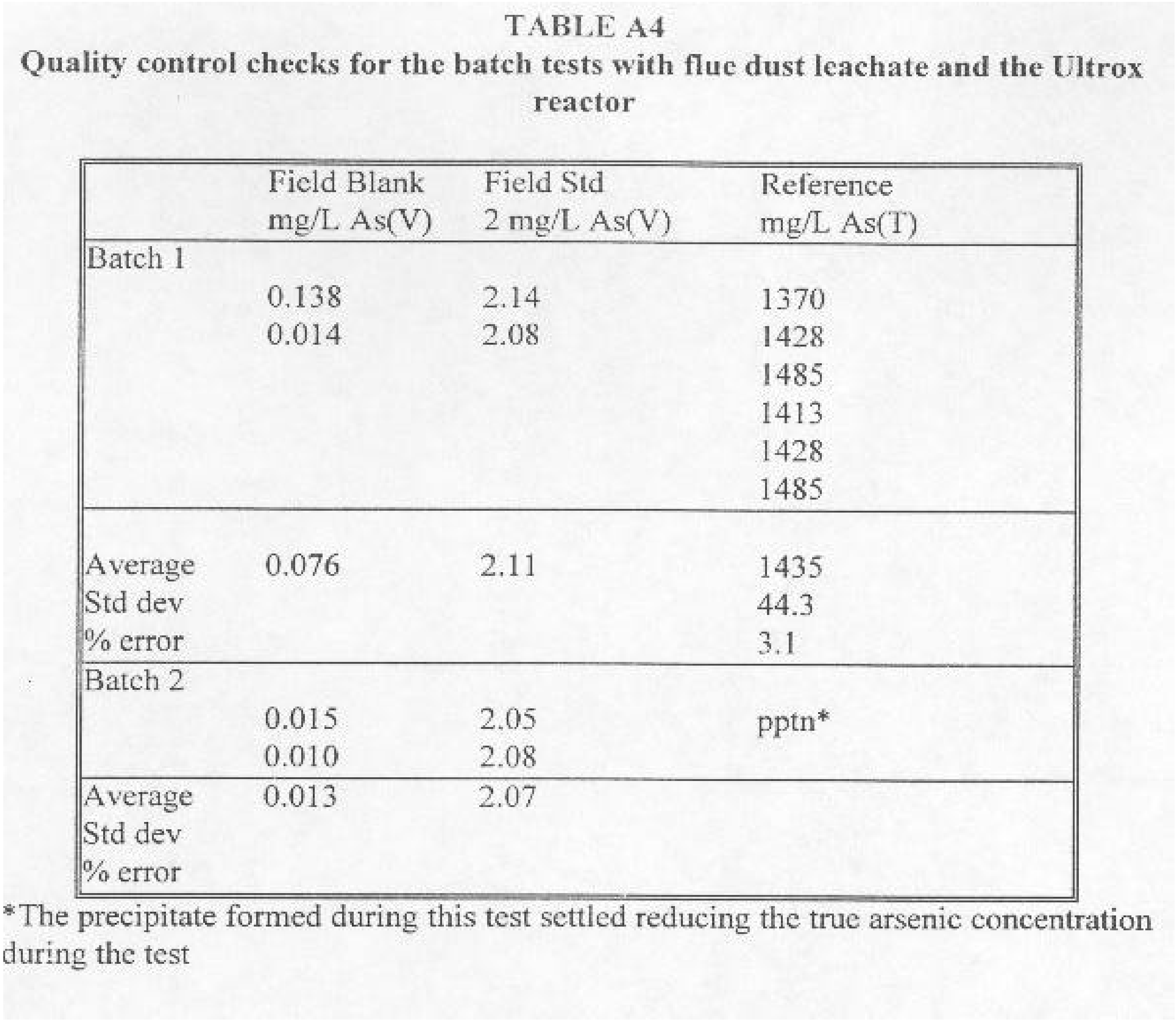

TABLE A4
Quality control checks for the batch tests with flue dust leachate and the Ultrox reactor

	Field Blank mg/L As(V)	Field Std 2 mg/L As(V)	Reference mg/L As(T)
Batch 1			
	0.138	2.14	1370
	0.014	2.08	1428
			1485
			1413
			1428
			1485
Average	0.076	2.11	1435
Std dev			44.3
% error			3.1
Batch 2			
	0.015	2.05	pptn*
	0.010	2.08	
Average	0.013	2.07	
Std dev			
% error			

*The precipitate formed during this test settled reducing the true arsenic concentration during the test

A6

OTHER ANALYTICAL METHODS

Actinometry

The radiation flux generated by the lamps are measured by solution actinometer i.e. the potassium ferrioxalate actinometer (Hatchard and Parker, 1956). Solution actinometers possess many advantages over instrumental systems because they are simple and require no specialized equipment. They are less prone to systematic error and give reproducible results. The efficiency of conversion of electrical power to utilisable photons in a photoreactor can be calculated from the actinometry results and the electrical wattage input of the lamp

Hydraulic Flow Testing of UV Photo-reactor

The physical mixing characteristics and mean residence time of the Ultrox reactor and solar ponds will be determined by monitoring the time taken for distribution of a concentrated sodium hydrogen phosphate spike. Phosphate was chosen because it can be easily analysed with the same reagents as dissolved arsenate and is non toxic.

Iron(II)

A spectrophotometric method for the determination of iron(II) using Ferrozine reagent (Stookey, 1970)

Power Input Measurements

The electrical power input to the low-pressure mercury lamps, the ballast and the pump motor within the Ultrox reactor will be measured using a power meter.

Solar Flux

During solar experiments, the UV radiation flux on a horizontal plane is monitored, in a non-tracking fashion, using a UVA light intensity meter (Solar Light Co. Model 3D V2.0)..

APPENDIX B

Tables of Analytical Results Produced by the MSE-HKM Laboratory for Arsenic and Iron Speciation and Elemental Analyses for TCLP Leachate

TABLE B1

Arsenic speciation during solar batch tests using Susie Mine water

Day	Time	Hours	Energy J/cm^2	As (µg/L)	As(III) (ug/L)	As(V) (ug/L)	Recovery
Batch 1							
11	12:10	0:00	0.0	12,100	8,360	6,410	123
11	13:00	0:50	8.1	9,940	7,240	2,790	101
11	14:55	2:45	22.5	8,830	7,040	2,640	110
11	15:27	3:17	27.0	9,120	7,110	2,870	109
11	17:00	4:50	31.9	8,160	7,050	3,120	125
12	13:30	8:50	73.0	8,930	4,820	5,490	115
				<20			
				slope	**-44**	**9**	
Batch 2							
11	13:05	0:00	0.0	15,000	6,660	7,070	91.5
11	13:05	0:00	0.0	8,940	3,780	5,630	105
11	14:00	0:55	2.9	16,300	6,120	10,900	104
11	14:55	1:50	13.7	13,300	444	12,700	99.8
11	15:27	2:22	18.1	14,900	469	15,400	106
11	17:00	3:55	23.0	15,000	<20	17,800	119
11	18.00	4:55	24.4	7,370	<20	8,160	111
				<20			
				slope	**-368**	**432**	
Batch 3							
12	11:30	0:00	0.0	13,800	6,170	5,990	88.1
12	11:30	0:00	0.0	14,200	6,730	7,520	100
12	12:30	1:00	12.3	14,600	4,900	9,030	95.0
12	13:30	2:00	26.3	13,500	4,000	9,210	97.8
12	14:30	3:00	39.9	15,300	3,100	13,000	105
12	15:30	4:00	51.9	13,600	2,230	11,100	98.0
12	16:30	5:00	61.8	15,000	1,180	12,000	87.8
12	17:50	6:20	71.2	14,700	542	13,000	94.4
				<20			
				slope	**-82**	**89**	
Batch 4							
12	14:35	0:00	0.0	11,700	6,640	5,960	108
12	14:35	0:00	0.0	13,400	6,490	7,930	108
12	14:50	0:15	3.1	15,400	3,350	10,100	87.2
12	15:05	0:30	6.2	12,800	2,280	11,300	106
12	15:20	0:45	9.1	14,800	617	13,400	94.4
12	15:35	1:00	11.9	13,200	692	12,800	102
12	15:50	1:15	14.6	14,400	<20	12,000	83.7
12	16:05	1:30	17.0	15,100	239	15,300	103
12	16:20	1:45	19.4	11,400	133	12,100	107
				<20			
				slope	**-528**	**545**	

TABLE B1 CONT.

Arsenic speciation during solar batch tests using Susie Mine water

Day	Time	Hours	Energy J/cm^2	As (μg/L)	As(III) (ug/L)	As(V) (ug/L)	Recovery
Batch 5							
13	11:30	0:00	0.0	13,000	8,290	6,130	111
13	11:30	0:00	0.0	15,000	11,500	6,250	118
13	12:30	1:00	12.8	15,900	5,130	12,400	110
13	13:30	2:00	24.6	13,300	3,380	9,800	99.1
13	14:30	3:00	32.6	15,000	2,510	11,300	92.1
13	15:30	4:00	36.6	13,100	2,440	11,300	105
13	16:30	5:00	39.2	12,000	1,820	10,400	101
14	9:30	5:00	39.2	15,100	2,070	12,900	99.1
14	10:30	6:00	46.7	15,400	1,680	13,100	96.1
14	11:30	7:00	53.6	14,800	1,210	13,000	96.0
14	12:30	8:00	60.3	10,800	623	9,770	96.4
14	14:00	9:30	72.5	13,400	692	14,800	115
				<20			
				slope	**-203**	**109**	
Batch 6							
13	11:30	0:00	0.0	14,800	9,530	5,680	103
13	11:30	0:00	0.0	12,800	7,260	6,870	110
13	12:30	1:00	12.8	14,300	3,460	12,100	109
13	13:30	2:00	24.6	13,000	2,950	10,900	107
13	14:30	3:00	32.6	17,300	1,900	14,800	96.8
13	15:30	4:00	36.6	14,600	1,800	13,700	106
13	16:30	5:00	39.2	13,300	1,290	10,300	87.4
14	9:30	5:00	39.2	13,700	1,520	11,900	97.8
14	10:30	6:00	46.7	12,600	1,550	13,600	120
14	11:00	6:30	50.4	14,300	1,430	12,300	95.8
				<20			
				slope	**-175**	**157**	
Batch 7							
14	11:30	0:00	0.0	10,800	6,940	4,030	102
14	11:30	0:00	0.0	13,100	8,400	5,290	104
14	12.30	1:00	6.7	13,100	5,010	8,110	101
14	13:30	2:00	14.5	14,000	2,480	11,600	101
14	14:30	3:00	25.0	13,700	770	12,500	96.8
14	15:30	4:00	35.6	13,700	387	12,800	96.3
14	16:30	5:00	42.5	13,600	79.5	14,400	106
14	17:30	6:00	47.5	14,900	<20	14,300	96.0
				<20			
				slope	**-218**	**242**	

TABLE B1 CONT.
Arsenic speciation during solar batch tests using Susie Mine water

Day	Time	Hours	Energy J/cm²	As (μg/L)	As(III) (ug/L)	As(V) (ug/L)	Recovery
Batch 8							
14	15:00	0:00	0.0	10.100	5,740	3,830	94.8
14	15:00	0:00	0.0	7,810	4,390	3,520	101
14	15:30	0:30	5.5	7,610	2,290	4,060	83.4
14	16:00	1:00	9.2	11,400	2,730	8,240	96.2
14	16:30	1:30	12.4	13,200	1,960	11,300	100
14	17:00	2:00	15.1	11,600	1,590	10,600	106
14	17:30	2:30	17.5	11,800	1,460	9,790	95.6
15	10:00	2:30	17.5	12,800	376	13,500	108
15	11:00	3:30	26.1	12,300	99.0	13,200	108
15	12:00	4:30	37.1	12,100	<20	13,900	115
				<20			
				slope	**-228**	**530**	
Batch 9							
15	10:30	0:00	0.0	12,600	7,620	4,950	99.8
15	10:30	0:00	0.0	12.900	5,380	7,530	101
15	0:00	13:30	4.5	14,300	6,760	7,060	96.8
15	11:30	1:00	9.8	11,800	3,020	8,520	97.8
15	12:00	1:30	15.5	12,300	2,270	10,100	101
15	12:30	2:00	20.3	11,700	836	9,770	90.7
15	13:30	3:00	32.0	13,900	471	12,700	95.1
15	14:30	4:00	43.9	10,900	89.0	11,000	102
				<20			
				slope	**-220**	**198**	
Batch 10							
15	14:30	0:00	0.0	12,100	3,870	7,950	97.7
15	14:30	0:00	0.0	14,200	8,270	5,830	99.1
15	15:00	0:30	2.9	12,900	4,820	8,060	100
15	15:30	1:00	10.0	12,800	<20	11,500	89.8
15	16:00	1:30	16.1	12,800	285	10,500	84.3
15	16:30	2:00	21.1	11,700	<20	11,900	102
15	17.00	2:30	25.3	14,700	<20	14,000	95.2
				<20			
				slope	**-357**	**267**	
Batch 11							
15	21:00	0:00	0.0	13,200	7,680	4,870	95.1
15	22:00	1:00	0.0	13,500	7.500	3,960	84.9
15	23:00	2:00	0.0	12,300	6.880	4,030	88.7

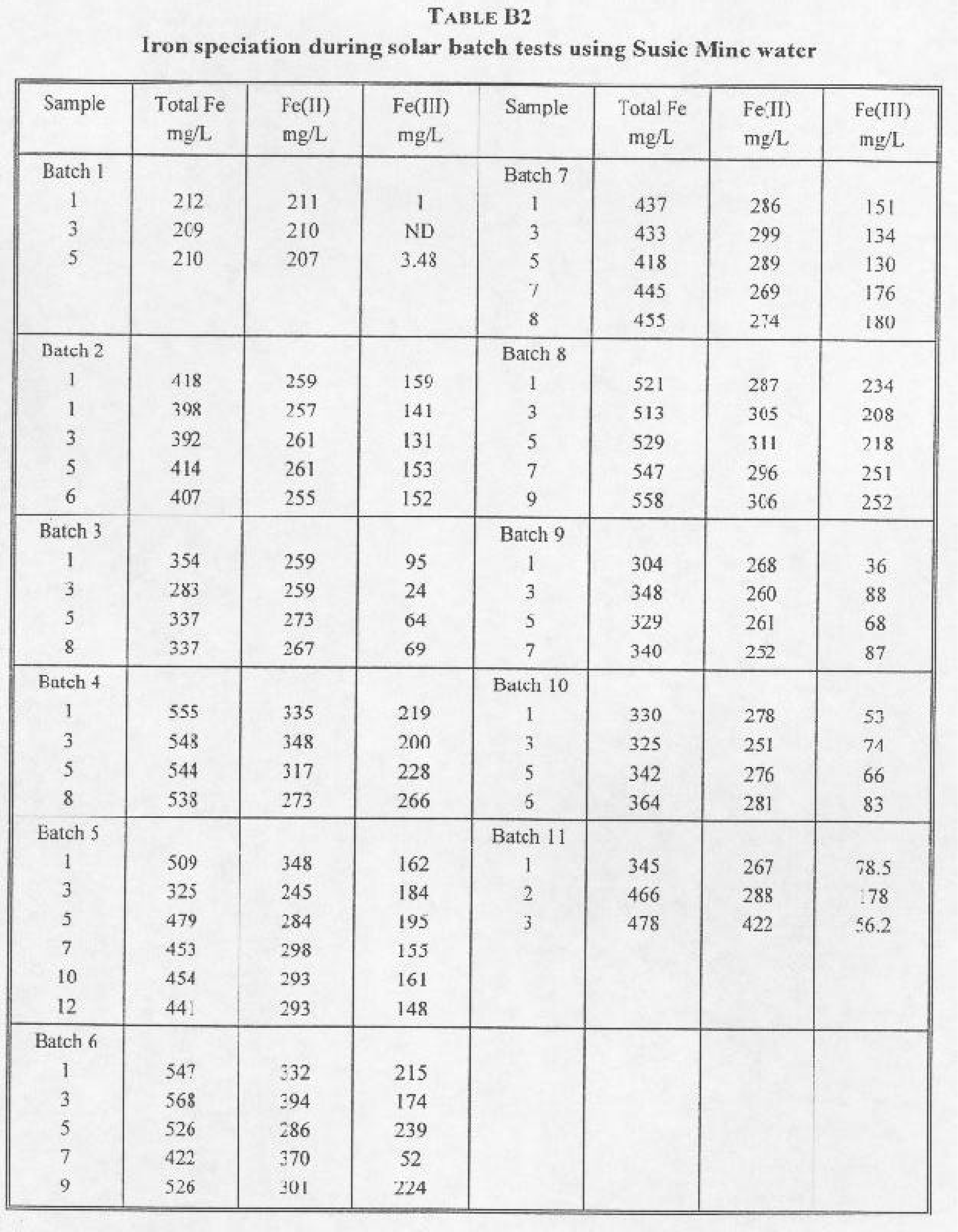

TABLE B2

Iron speciation during solar batch tests using Susic Mine water

Sample	Total Fe mg/L	Fe(II) mg/L	Fe(III) mg/L	Sample	Total Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1				Batch 7			
1	212	211	1	1	437	286	151
3	209	210	ND	3	433	299	134
5	210	207	3.48	5	418	289	130
				7	445	269	176
				8	455	274	180
Batch 2				Batch 8			
1	418	259	159	1	521	287	234
1	398	257	141	3	513	305	208
3	392	261	131	5	529	311	218
5	414	261	153	7	547	296	251
6	407	255	152	9	558	306	252
Batch 3				Batch 9			
1	354	259	95	1	304	268	36
3	283	259	24	3	348	260	88
5	337	273	64	5	329	261	68
8	337	267	69	7	340	252	87
Batch 4				Batch 10			
1	555	335	219	1	330	278	53
3	548	348	200	3	325	251	74
5	544	317	228	5	342	276	66
8	538	273	266	6	364	281	83
Batch 5				Batch 11			
1	509	348	162	1	345	267	78.5
3	325	245	184	2	466	288	178
5	479	284	195	3	478	422	56.2
7	453	298	155				
10	454	293	161				
12	441	293	148				
Batch 6							
1	547	332	215				
3	568	394	174				
5	526	286	239				
7	422	370	52				
9	526	301	224				

TABLE B3
Arsenic speciation during solar batch tests using flue dust leachate

Day	Time	Hours	Energy J/cm^2	As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	Recovery %
Batch 1							
9	16:30	0:00	0	315,000	322,000	14,500	107
9	18:00	1:30	13.11	313,000	320,000	16,000	107
10	10:30	2:00	18.0137	342,000	284,000	68,800	103
10	14:00	5:30	70.4	347,000	149,000	223,000	107
10	17:30	9:00	114.8	328,000	49,100	285,000	102
11	10:15	9:00	114.8	339,000	26,500	330,000	105
11	14:00	12:45	142	299,000	<20	339,000	114
11	18:00	16:45	193.6	348,000	<20	357,000	103
Blk				62.5	30.0	38.1	109
Batch 2							
9	16:30	0:00	0	114,000	109,000	11,200	106
9	18:00	1:30	13.11	194,000	158,000	30,700	97.0
10	10:30	2:00	18.0137	309,000	312,000	27,000	110
10	14:00	5:30	70.4	179,000	139,000	36,400	98
10	17:30	9:00	114.8	320,000	244,000	110,000	111
11	10:15	9:00	114.8	172,000	88,500	44,300	77.0
11	14:00	12:45	142	128,000	61,400	57,900	93.1
11	18:00	16:45	193.6	358,000	219,000	174,000	110
12	9:45	16:45	193.6	348,000	192,000	168,000	103
12	9:45	16:45	193.6	362,000	161,000	164,000	89.8
12	17:50	24:50:00	281.5	389,000	91,500	305,000	102
13	14:00	28:50:00	320.9	358,000	84,100	309,000	110
13	16:00	30:50:00	329.8	307,000	78,700	234,000	102
14	17:30	38:50:00	391.7	372,000	183,000	146,000	88.4
15	17:00	45:50:00	465	371,000	151,000	208,000	96.8
16	16:30	51:50:00	536	427,000	141,000	28,900	99.5
Blk				56.8	30.3	43.3	130
Batch 3							
9	16:30	0:00	0	321,000	332,000	17,900	109
9	18:00	1:30	13.11	335,000	330,000	17,200	104
10	10:30	2:00	18.0137	338,000	297,000	42,700	100
10	14:00	5:30	70.4	195,000	114,000	61,300	89.8
10	17:30	9:00	114.8	316,000	187,000	147,000	106
11	10:15	9:00	114.8	94,300	45,800	55,500	107
11	14:00	12:45	142	187,000	71,000	123,000	104
11	18:00	16:45	193.6	368,000	132,000	252,000	104
12	9:45	16:45	193.6	339,000	89,200	271,000	106
12	9:45	16:45	193.6	348,000	92,600	255,000	99.9
13	14:00	28.50.00	320	385,000	1,110	385,000	100
13	16:30	31:20:00	331	311,000	125,000	177,000	96.8
13	16:30	31:20:00	331	299,000	<20	308,000	103
Blk				63.8	29.9	40.9	111

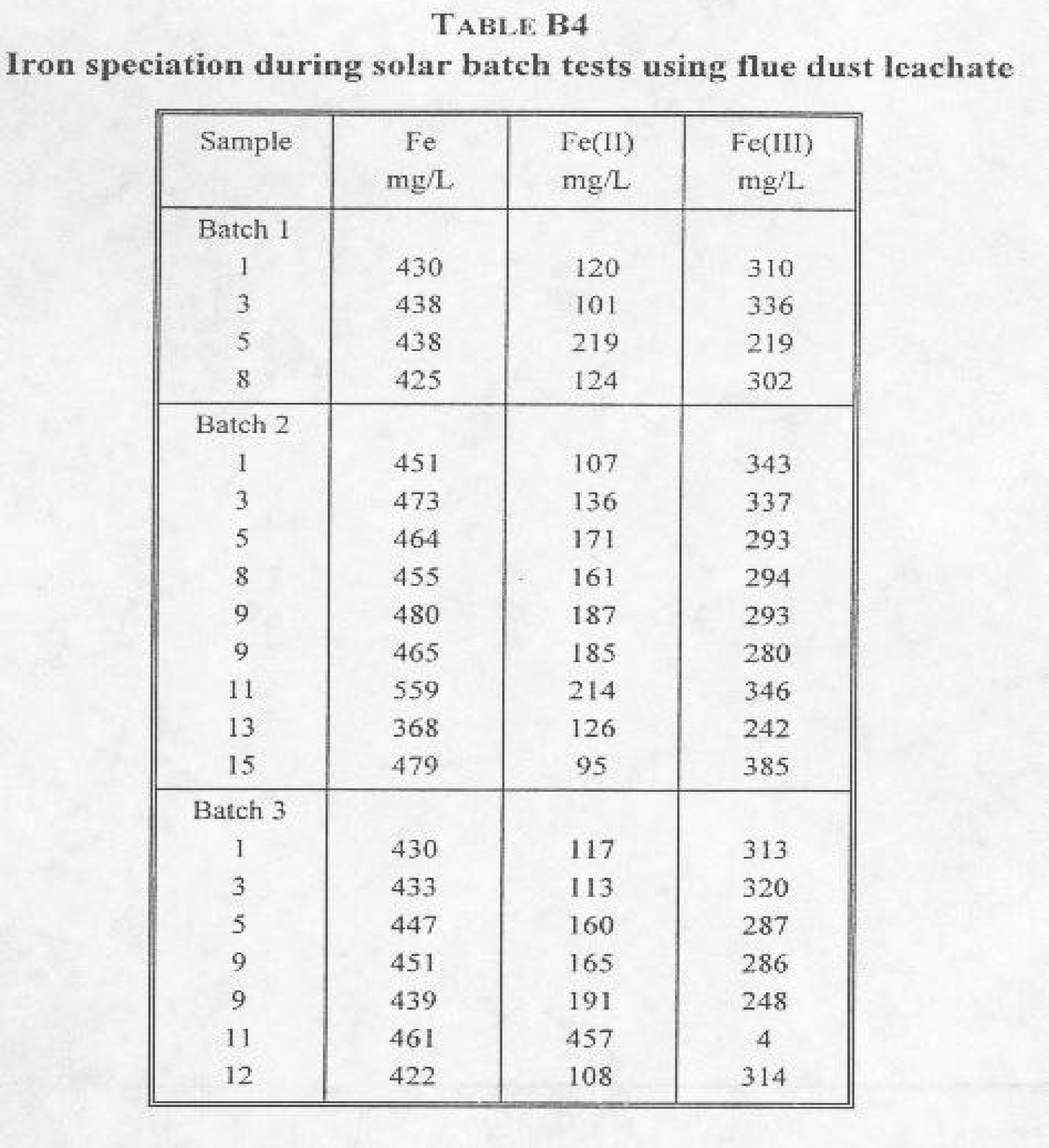

TABLE B4

Iron speciation during solar batch tests using flue dust leachate

Sample	Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1			
1	430	120	310
3	438	101	336
5	438	219	219
8	425	124	302
Batch 2			
1	451	107	343
3	473	136	337
5	464	171	293
8	455	161	294
9	480	187	293
9	465	185	280
11	559	214	346
13	368	126	242
15	479	95	385
Batch 3			
1	430	117	313
3	433	113	320
5	447	160	287
9	451	165	286
9	439	191	248
11	461	457	4
12	422	108	314

TABLE B5
Arsenic speciation during solar continuous tests using Susie Mine water

Time	Port	Total As (ug/L)	As(III) (ug/L)	As(V) (ug/L)	Recovery
	Test 1				
12:00	A	15,200	5,100	7,610	83.6
12:00	A	11,600	5,200	6,220	98.4
12:00	B	13,200	878	11,300	92.3
12:00	C	11,200	555	10,900	102
12:00	D	11,500	146	11,500	101
13:00	E	13,600	141	13,200	98.1
13:00	A	13,400	3,490	8,510	89.6
13:00	B	11,400	1,520	9,020	92.5
13:00	C	13,500	1,190	12,800	104
13:00	D	12,800	228	11,900	94.8
13:00	E	11,800	200	11,100	95.8
14:00	A	12,500	4,190	8,240	99.4
14:00	B	13,400	1,800	10,400	91.0
14:00	C	11,900	965	10,500	96.3
14:00	D	12,500	206	12,500	102
14:00	E	11,000	154	9,620	88.9
15:00	A	11,600	4,680	7,010	101
15:00	B	11,100	1,970	8,380	93.2
15:00	C	12,000	1,280	9,380	88.8
15:00	D	11,800	<20	11,400	96.6
15:00	E	12,100	<20	12,400	102
15:00	Blk	<20			
	Test 2				
12:00	A	12,300	6,380	4,910	91.8
12:00	A	12,600	6,600	5,160	93.3
12:00	B	12,500	3,420	8,580	96.0
12:00	C	12,000	2,850	8,940	98.3
12:00	D	11,400	2,010	9,060	97.1
12:00	E	12,400	1,150	11,500	102
13:00	A	10,900	7,260	3,900	102
13:00	B	12,200	4,800	8,390	108
13:00	C	13,700	3,960	10,300	104
13:00	D	14,700	2,120	13,000	103
13:00	E	11,500	1,260	10,100	98.8
15:00	A				
15:00	B	13,400	2,040	12,800	111
15:00	C	13,600	4,490	8,590	96.2
15:00	D	11,600	4,330	9,260	118
15:00	E	12,000	1,310	10,600	99.3
14:00	A	10,000	6,040	3,560	96.0
14:00	B	11,600	3,420	7,710	96.0
14:00	C	11,700	3,260	8,440	100
14:00	D	12,500		10,200	95.1
14:00	E	13,000		11,300	101
15:00	Blk	<20			

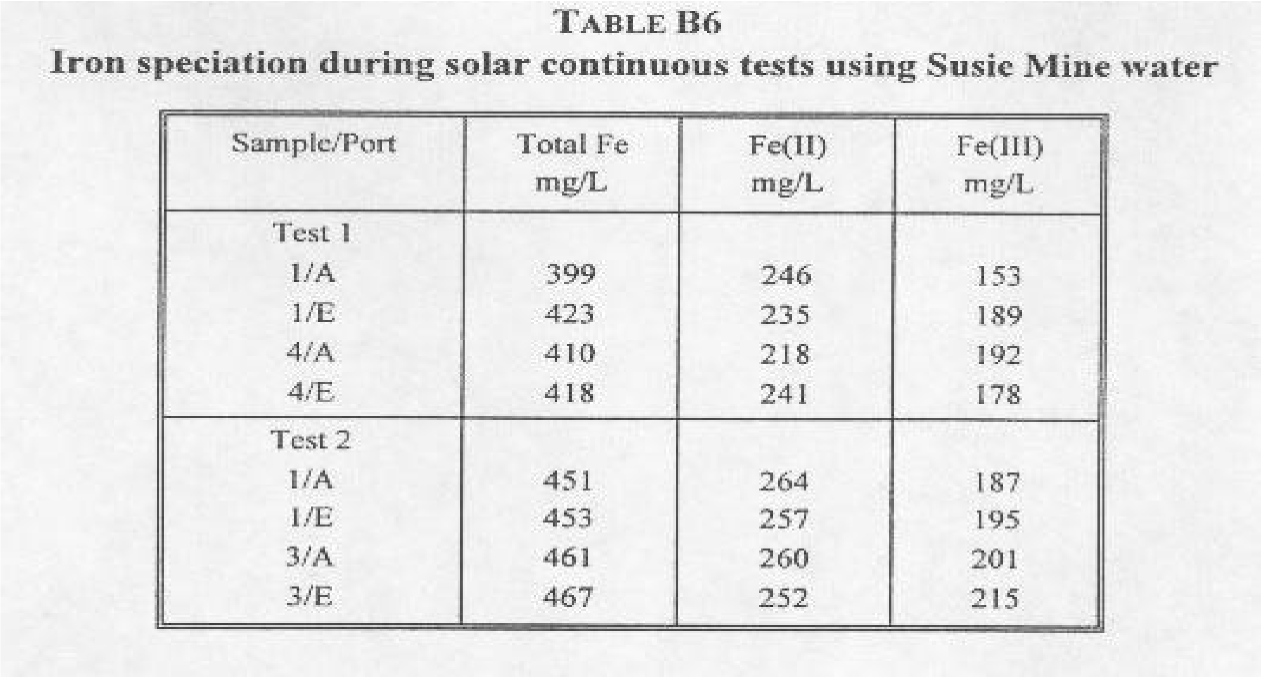

TABLE B6

Iron speciation during solar continuous tests using Susie Mine water

Sample/Port	Total Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
Test 1			
1/A	399	246	153
1/E	423	235	189
4/A	410	218	192
4/E	418	241	178
Test 2			
1/A	451	264	187
1/E	453	257	195
3/A	461	260	201
3/E	467	252	215

TABLE B7

Arsenic speciation during Ultrox batch tests using Susie Mine water

Sample	Time minutes	As ppb	As(III) ppb	As(V) ppb	Recovery
Batch 1					
1	0	12,600	7,230	4,330	91.8
1	0	12,200	7,040	7,130	116.0
2	15	12,000	1,680	10,700	103.0
3	30	12,800	106	12,400	97.7
4	45	12,600	91.6	12,100	96.8
5	60	12,700	90.4	11,400	90.5
6	75	13,200	224	12,100	93.4
7	90	12,300	178	12,600	104.0
blk		<20			
	slope		357	(238)	
Batch 2					
1	0	10,400	6,100	6,610	81.8
2	5	10,300	5,060	6,570	113.0
3	10	10,700	2,790	9,620	116.0
4	20	12,000	970	10,800	98.1
5	30	11,800	209	11,500	99.2
6	40	11,900	102	11,700	99.2
7	50	11,300	236	12,900	116.0
7	50	12,500	368	14,500	119.0
blk		<20			
	slope		(265)	233	
Batch 3					
1	0	13,700	7,670	6,450	103.0
1	0	12,000	6,490	5,450	100.0
2	5	12,300	4,810	7,290	98.4
3	10	12,600	2,450	9,710	96.5
4	15	13,000	1,710	11,000	97.8
5	20	13,000	636	12,000	97.2
6	30	13,000	295	12,600	99.2
7	40	12,200	<20	13,000	107.0
7	40	<20			
	slope		(380)	348	
Batch 4					
1	0	11,100	6,300	4,890	101.0
2	10	10,800	2,740	8,000	99.4
3	20	10,800	1,370	10,900	114.0
4	30	11,200	645	11,400	108.0
4	30	11,000	520	12,400	117.0
5	40	10,100	<20	11,000	109.0
6	60	12,300	<20	10,900	88.6
7		11,500	<20	13,500	117.0
	slope		(247)	301	

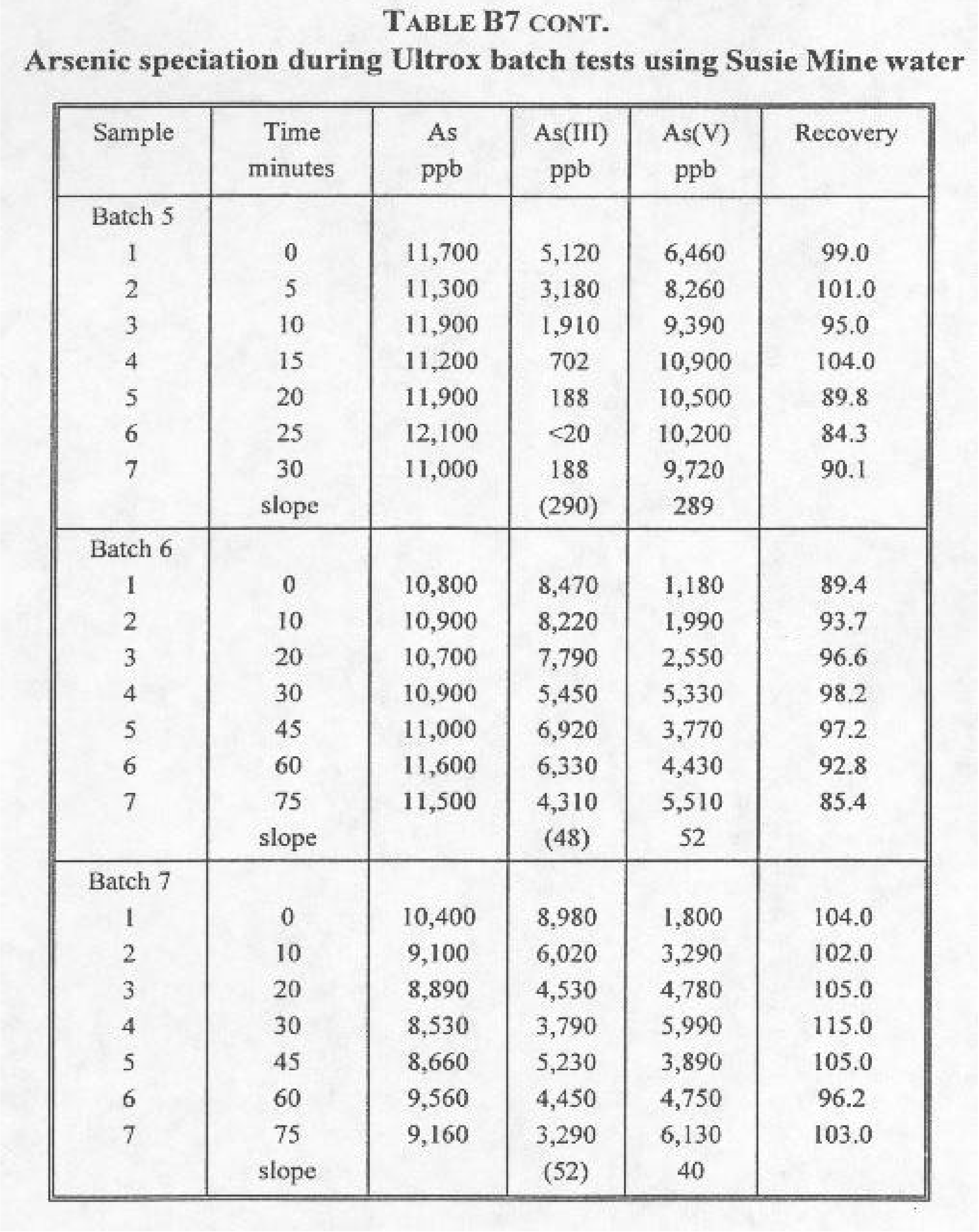

TABLE B7 CONT.

Arsenic speciation during Ultrox batch tests using Susie Mine water

Sample	Time minutes	As ppb	As(III) ppb	As(V) ppb	Recovery
Batch 5					
1	0	11,700	5,120	6,460	99.0
2	5	11,300	3,180	8,260	101.0
3	10	11,900	1,910	9,390	95.0
4	15	11,200	702	10,900	104.0
5	20	11,900	188	10,500	89.8
6	25	12,100	<20	10,200	84.3
7	30	11,000	188	9,720	90.1
	slope		(290)	289	
Batch 6					
1	0	10,800	8,470	1,180	89.4
2	10	10,900	8,220	1,990	93.7
3	20	10,700	7,790	2,550	96.6
4	30	10,900	5,450	5,330	98.2
5	45	11,000	6,920	3,770	97.2
6	60	11,600	6,330	4,430	92.8
7	75	11,500	4,310	5,510	85.4
	slope		(48)	52	
Batch 7					
1	0	10,400	8,980	1,800	104.0
2	10	9,100	6,020	3,290	102.0
3	20	8,890	4,530	4,780	105.0
4	30	8,530	3,790	5,990	115.0
5	45	8,660	5,230	3,890	105.0
6	60	9,560	4,450	4,750	96.2
7	75	9,160	3,290	6,130	103.0
	slope		(52)	40	

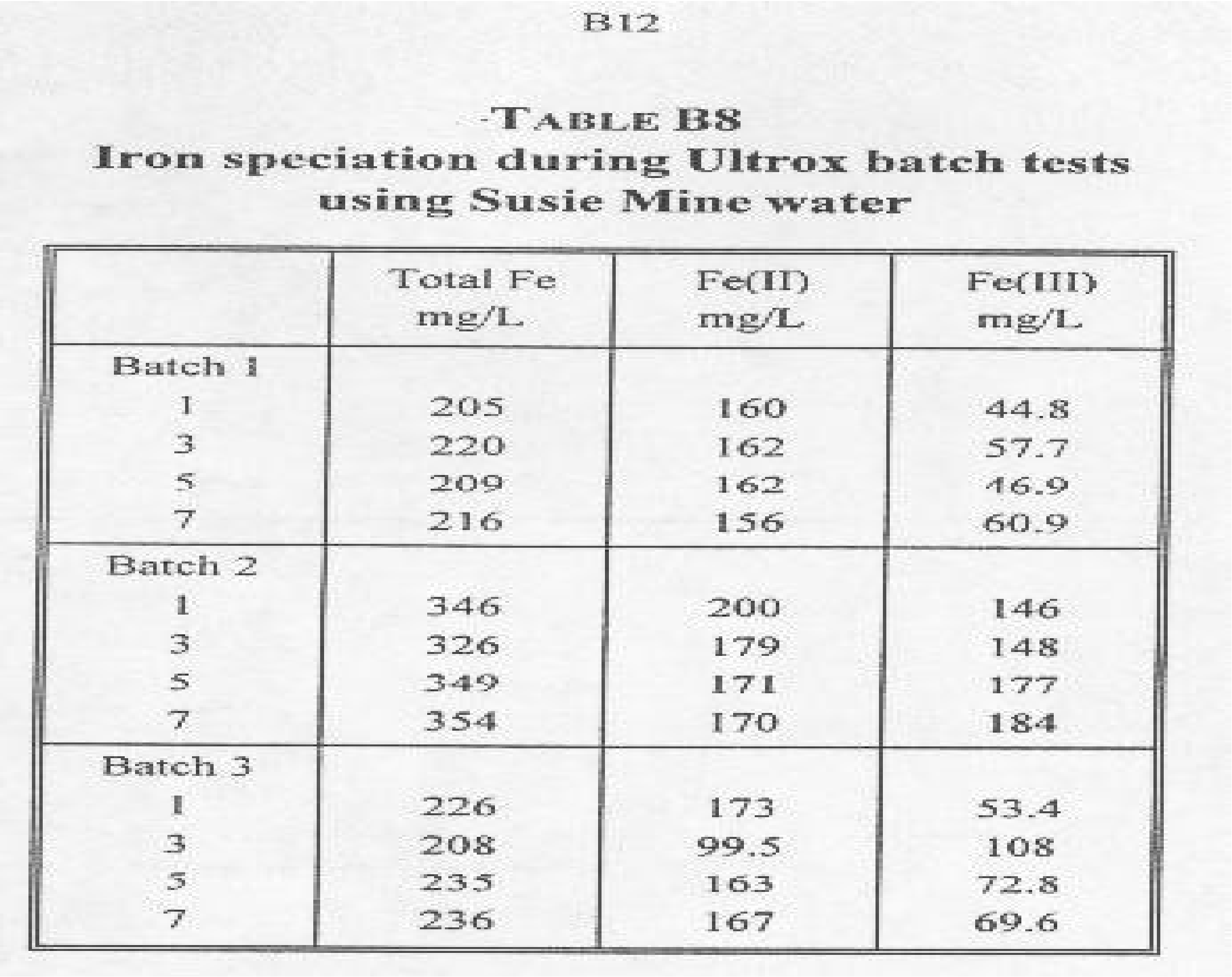

TABLE B8
Iron speciation during Ultrox batch tests using Susie Mine water

	Total Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1			
1	205	160	44.8
3	220	162	57.7
5	209	162	46.9
7	216	156	60.9
Batch 2			
1	346	200	146
3	326	179	148
5	349	171	177
7	354	170	184
Batch 3			
1	226	173	53.4
3	208	99.5	108
5	235	163	72.8
7	236	167	69.6

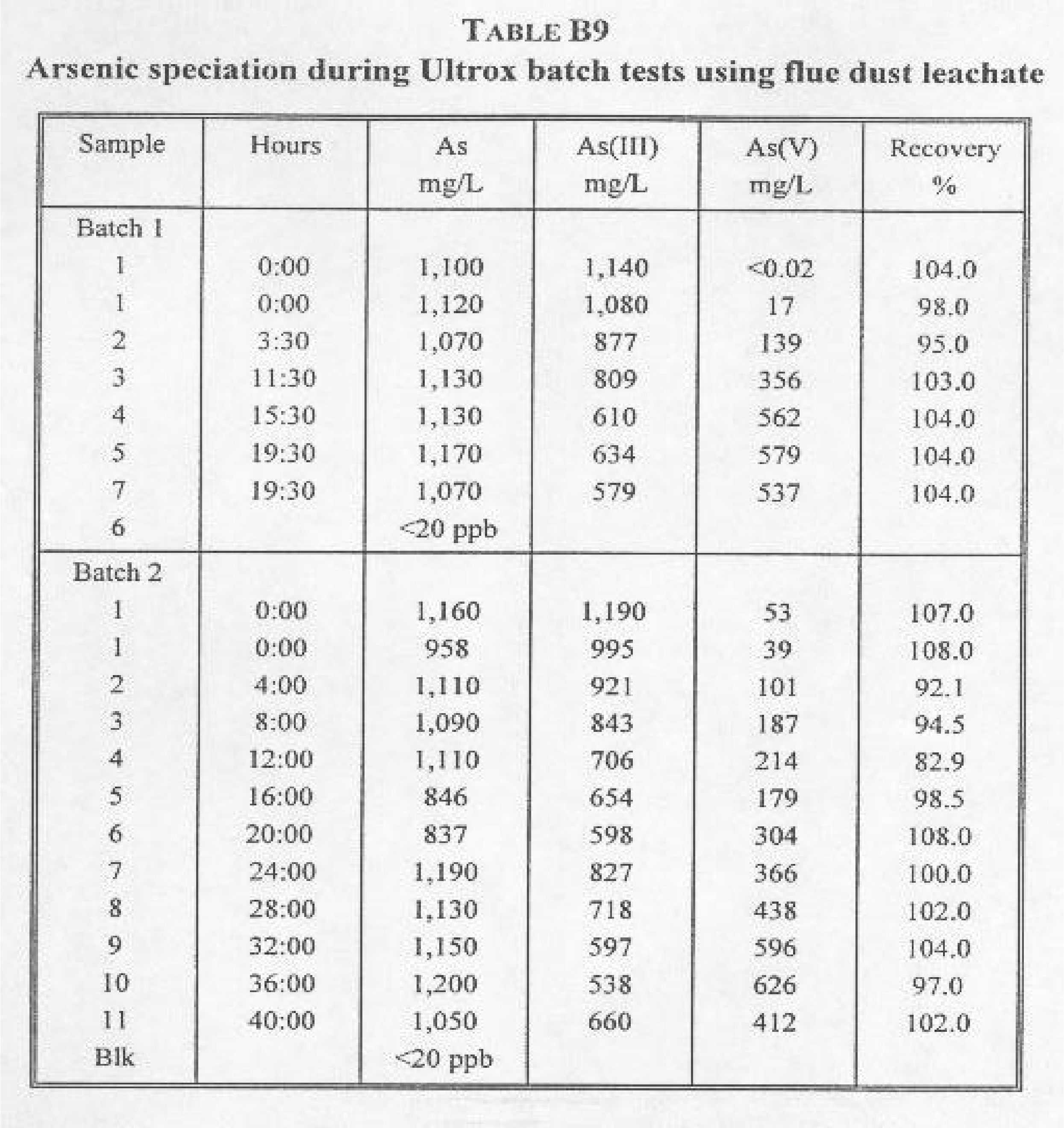

TABLE B9

Arsenic speciation during Ultrox batch tests using flue dust leachate

Sample	Hours	As mg/L	As(III) mg/L	As(V) mg/L	Recovery %
Batch 1					
1	0:00	1,100	1,140	<0.02	104.0
1	0:00	1,120	1,080	17	98.0
2	3:30	1,070	877	139	95.0
3	11:30	1,130	809	356	103.0
4	15:30	1,130	610	562	104.0
5	19:30	1,170	634	579	104.0
7	19:30	1,070	579	537	104.0
6		<20 ppb			
Batch 2					
1	0:00	1,160	1,190	53	107.0
1	0:00	958	995	39	108.0
2	4:00	1,110	921	101	92.1
3	8:00	1,090	843	187	94.5
4	12:00	1,110	706	214	82.9
5	16:00	846	654	179	98.5
6	20:00	837	598	304	108.0
7	24:00	1,190	827	366	100.0
8	28:00	1,130	718	438	102.0
9	32:00	1,150	597	596	104.0
10	36:00	1,200	538	626	97.0
11	40:00	1,050	660	412	102.0
Blk		<20 ppb			

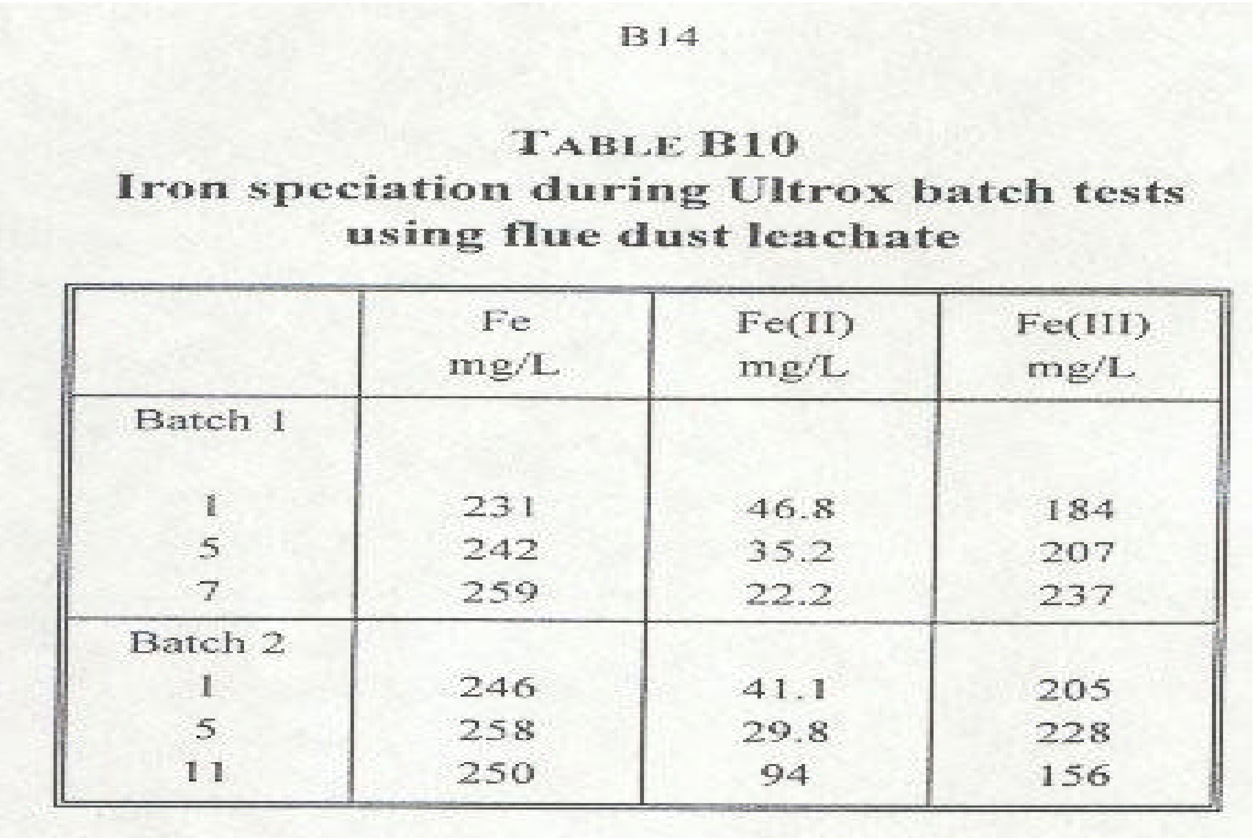

TABLE B10
Iron speciation during Ultrox batch tests using flue dust leachate

	Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
Batch 1			
1	231	46.8	184
5	242	35.2	207
7	259	22.2	237
Batch 2			
1	246	41.1	205
5	258	29.8	228
11	250	94	156

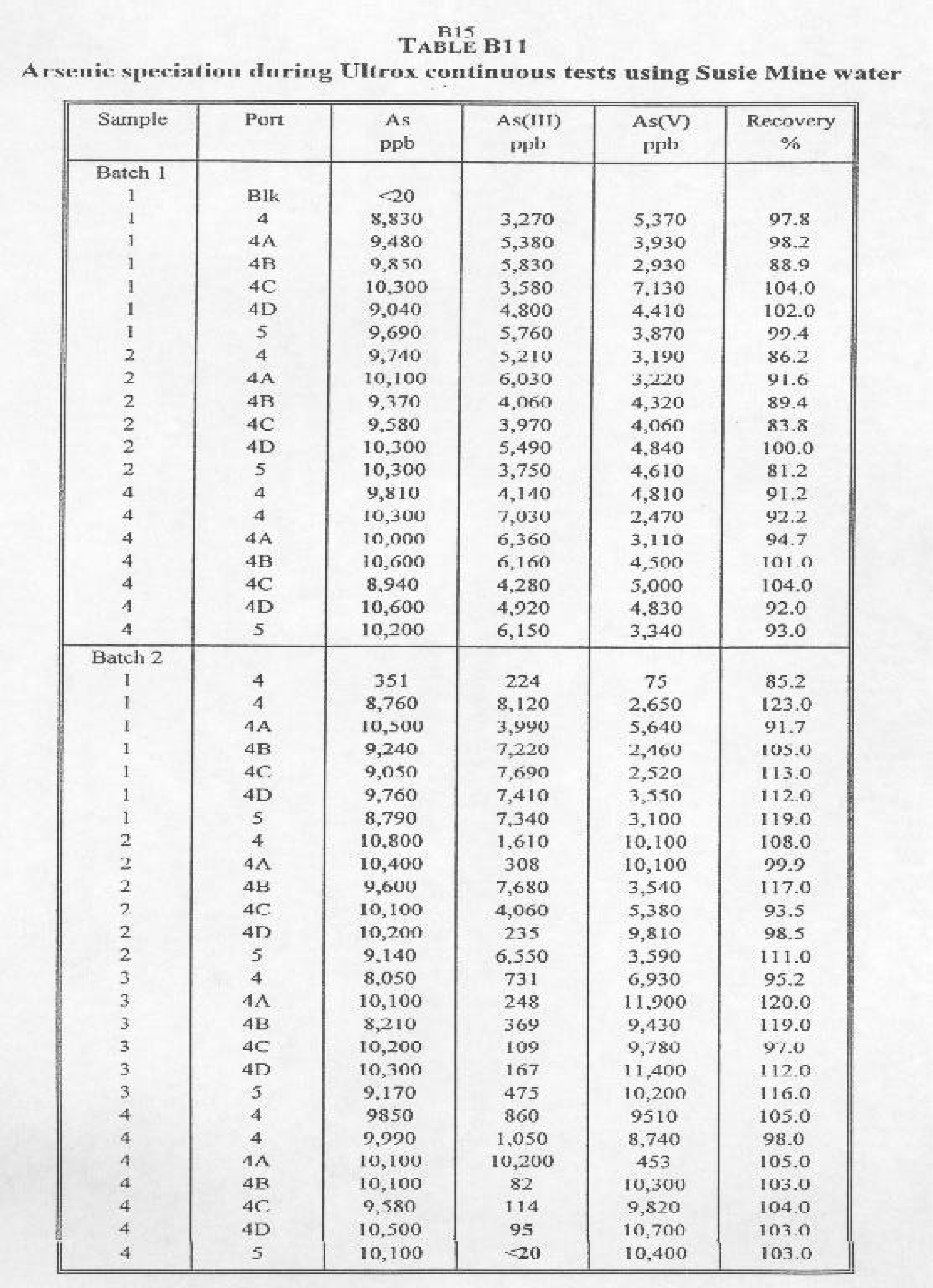

TABLE B11

Arsenic speciation during Ultrox continuous tests using Susie Mine water

Sample	Port	As ppb	As(III) ppb	As(V) ppb	Recovery %
Batch 1					
1	Blk	<20			
1	4	8,830	3,270	5,370	97.8
1	4A	9,480	5,380	3,930	98.2
1	4B	9,850	5,830	2,930	88.9
1	4C	10,300	3,580	7,130	104.0
1	4D	9,040	4,800	4,410	102.0
1	5	9,690	5,760	3,870	99.4
2	4	9,740	5,210	3,190	86.2
2	4A	10,100	6,030	3,220	91.6
2	4B	9,370	4,060	4,320	89.4
2	4C	9,580	3,970	4,060	83.8
2	4D	10,300	5,490	4,840	100.0
2	5	10,300	3,750	4,610	81.2
4	4	9,810	4,140	4,810	91.2
4	4	10,300	7,030	2,470	92.2
4	4A	10,000	6,360	3,110	94.7
4	4B	10,600	6,160	4,500	101.0
4	4C	8,940	4,280	5,000	104.0
4	4D	10,600	4,920	4,830	92.0
4	5	10,200	6,150	3,340	93.0
Batch 2					
1	4	351	224	75	85.2
1	4	8,760	8,120	2,650	123.0
1	4A	10,500	3,990	5,640	91.7
1	4B	9,240	7,220	2,460	105.0
1	4C	9,050	7,690	2,520	113.0
1	4D	9,760	7,410	3,550	112.0
1	5	8,790	7,340	3,100	119.0
2	4	10,800	1,610	10,100	108.0
2	4A	10,400	308	10,100	99.9
2	4B	9,600	7,680	3,540	117.0
2	4C	10,100	4,060	5,380	93.5
2	4D	10,200	235	9,810	98.5
2	5	9,140	6,550	3,590	111.0
3	4	8,050	731	6,930	95.2
3	4A	10,100	248	11,900	120.0
3	4B	8,210	369	9,430	119.0
3	4C	10,200	109	9,780	97.0
3	4D	10,300	167	11,400	112.0
3	5	9,170	475	10,200	116.0
4	4	9850	860	9510	105.0
4	4	9,990	1,050	8,740	98.0
4	4A	10,100	10,200	453	105.0
4	4B	10,100	82	10,300	103.0
4	4C	9,580	114	9,820	104.0
4	4D	10,500	95	10,700	103.0
4	5	10,100	<20	10,400	103.0

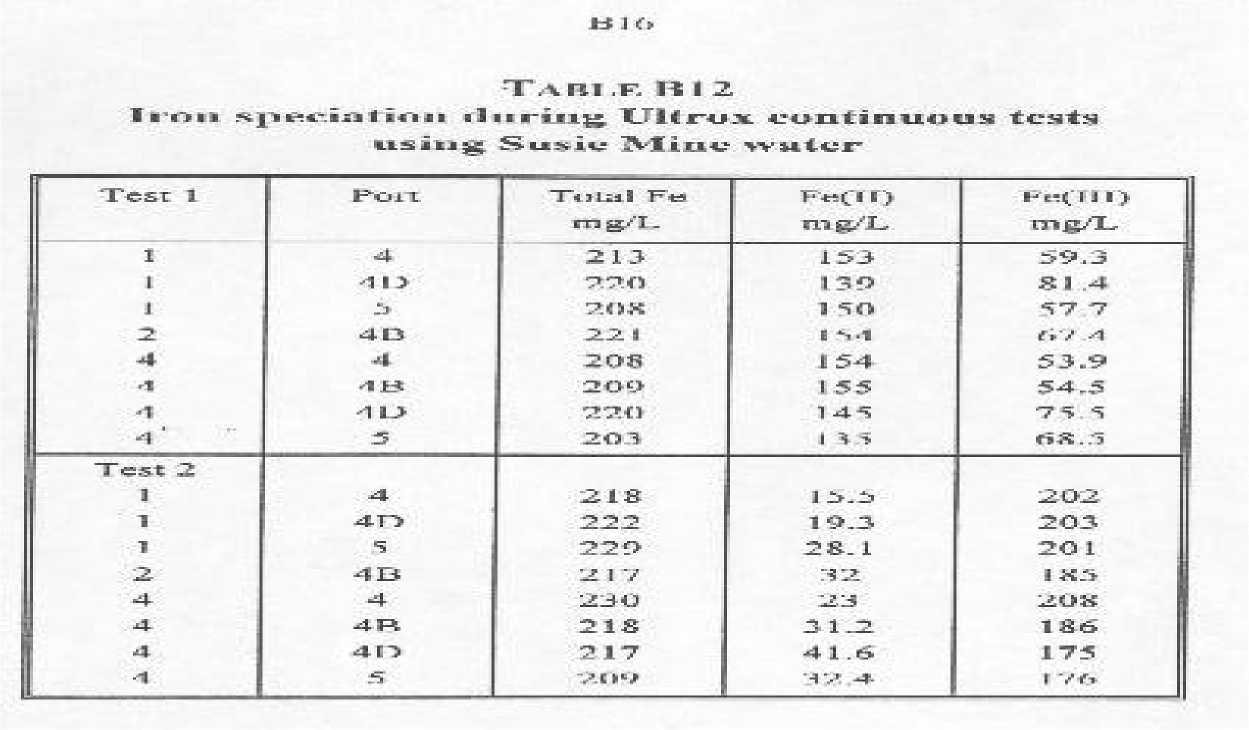

TABLE B12
Iron speciation during Ultrox continuous tests using Susie Mine water

Test 1	Port	Total Fe mg/L	Fe(II) mg/L	Fe(III) mg/L
1	4	213	153	59.3
1	4D	220	139	81.4
1	5	208	150	57.7
2	4B	221	154	67.4
4	4	208	154	53.9
4	4B	209	155	54.5
4	4D	220	145	75.5
4	5	203	135	68.5
Test 2				
1	4	218	15.5	202
1	4D	222	19.3	203
1	5	229	28.1	201
2	4B	217	32	185
4	4	230	23	208
4	4B	218	31.2	186
4	4D	217	41.6	175
4	5	209	32.4	176

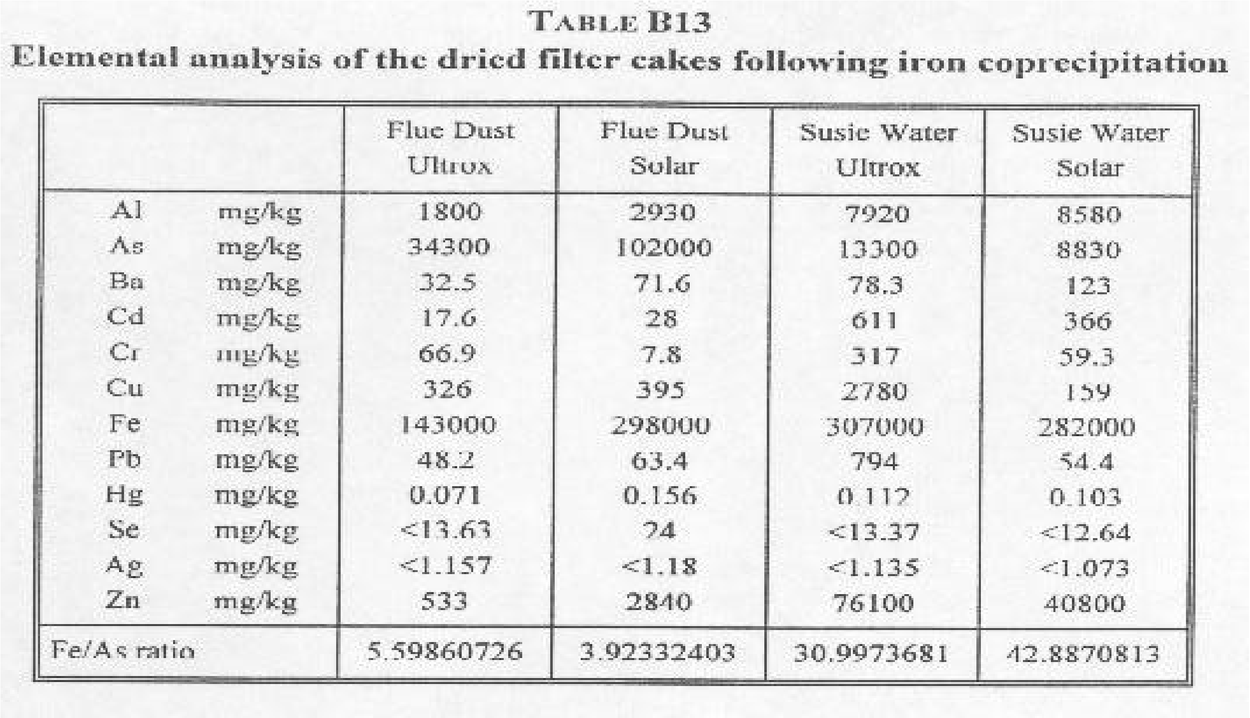

TABLE B13
Elemental analysis of the dried filter cakes following iron coprecipitation

		Flue Dust Ultrox	Flue Dust Solar	Susie Water Ultrox	Susie Water Solar
Al	mg/kg	1800	2930	7920	8580
As	mg/kg	34300	102000	13300	8830
Ba	mg/kg	32.5	71.6	78.3	123
Cd	mg/kg	17.6	28	611	366
Cr	mg/kg	66.9	7.8	317	59.3
Cu	mg/kg	326	395	2780	159
Fe	mg/kg	143000	298000	307000	282000
Pb	mg/kg	48.2	63.4	794	54.4
Hg	mg/kg	0.071	0.156	0.112	0.103
Se	mg/kg	<13.63	24	<13.37	<12.64
Ag	mg/kg	<1.157	<1.18	<1.135	<1.073
Zn	mg/kg	533	2840	76100	40800
Fe/As ratio		5.59860726	3.92332403	30.9973681	42.8870813

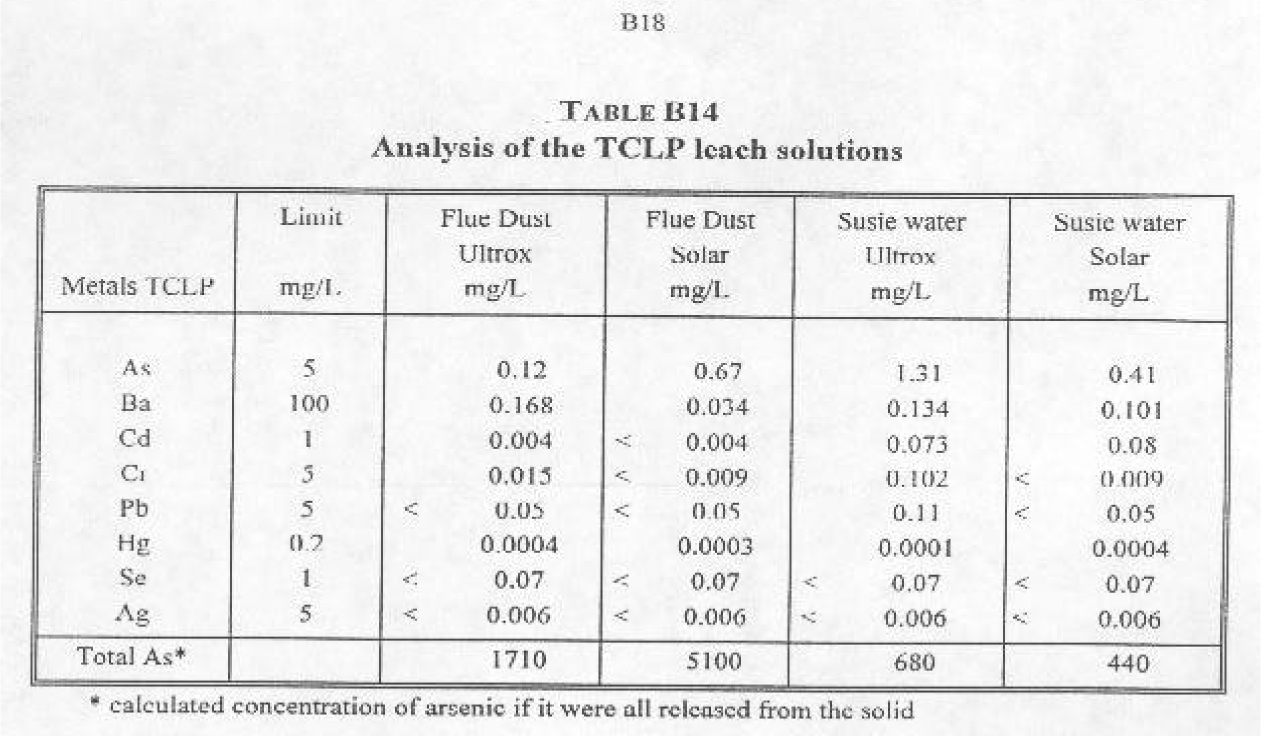

TABLE B14
Analysis of the TCLP leach solutions

Metals TCLP	Limit mg/L	Flue Dust Ultrox mg/L	Flue Dust Solar mg/L	Susie water Ultrox mg/L	Susie water Solar mg/L
As	5	0.12	0.67	1.31	0.41
Ba	100	0.168	0.034	0.134	0.101
Cd	1	0.004	< 0.004	0.073	0.08
Cr	5	0.015	< 0.009	0.102	< 0.009
Pb	5	< 0.05	< 0.05	0.11	< 0.05
Hg	0.2	0.0004	0.0003	0.0001	0.0004
Se	1	< 0.07	< 0.07	< 0.07	< 0.07
Ag	5	< 0.006	< 0.006	< 0.006	< 0.006
Total As*		1710	5100	680	440

* calculated concentration of arsenic if it were all released from the solid

APPENDIX C

Solidification Using Portland Cement

APPENDIX C

SOLIDIFICATION USING PORTLAND CEMENT

For the preparation of cement solidified samples, the dried filter cakes were weighed and then mixed with ordinary Portland cement (supplied by Blue Circle Southern, Berrima plant, NSW) and lime. Subsequently, a measured quantity of water was added to give the mass ratios of dried filter cake : cement : lime : water of 4:0.8:0.2:3. The mixture was mixed for three minutes and was packed in a 125 cubic centimetre PVC mould. The mixture plus mould were then placed in a plastic bag during the 28 days of curing.

TCLP TESTS

Tests were carried out using the dried filter cakes and the cement solidified wastes. The leachates were filtered through GF/F glass fibre membrane filter (0.6-0.8 μm porosity) followed by acidification to pH~1.5 and then analyzed for metal concentrations using ICP-MS, ICP-AES and AAS-HG.

LEACH TESTS USING AERATED WATER

To investigate the susceptibility of the filter cake samples to reaction with dissolved carbon dioxide, the solid samples were placed in water in a 2L measuring cylinder. The original dried filter cakes (Susie Ultrox and Flue Dust Solar Filter Cakes were selected) and the corresponding cement-solidified monoliths were crushed into 1-9 mm sized particles. 100 g of each type was placed in a PVC ring (5.5 cm internal diameter and ~5 cm height) which was covered with a piece of propyltex cloth of 125 μm pore size. Each assembly was suspended in a 2 L measuring cylinder as shown in **Figure C.1**. Demineralised water (pH 5.9) was added to give a leachate to solid ratio of 20 to 1. Air was continuously bubbled (0.25 ± 0.05 L/L of sample solution/min) throughout the experiment. In the 'control' experiments, CO_2-free air was bubbled at the same rate. The CO_2-free air was prepared by sequentially passing normal air through 6 M NaOH solution and demineralized water. The sodium hydroxide concentration ($\geq$ 6 M) was maintained by the weekly addition of NaOH solids. The experiments were performed in duplicate for all samples except 'control' samples.

ELEMENTAL ANALYSES OF LEACHATES SAMPLED DURING LEACH TESTING USING AERATED WATER

Sample legends as used in the tables below:

SUCT indicates Susie Ultrox Cement (Control)
SUC indicates Susie Ultrox Cement
SUT indicates Susie Ultrox (Control)
SU indicates Susie Ultrox Sample

FSCT indicates Flue Dust Solar Cement (Control)
FSC indicates Flue Dust Solar Cement
FST indicates Flue Dust Solar (Control)
FS indicates Flue Dust Solar.

Table C.7

Selenium concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	0.0292	0.0166	0.0184	0.0176	0.0110	0.0081	0.0145	0.0144	0.0163	0.0231	0.0217	0.0220
3	0.0025	0.0021	0.0026	0.0027	0.0032	0.0025	0.0151	0.0171	0.0186	0.0251	0.0258	0.0243
8	0.0027	0.0031	0.0028	0.0029	0.0220	0.0017	0.0130	0.0182	0.0174	0.0201	0.0190	0.0206
16	0.0016	0.0020	0.0019	0.0014	0.0013	0.0009	0.0147	0.0272	0.0277	0.0279	0.0280	0.0250
27	0.0006	0.0024	0.0023	0.0007	0.0007	0.0006	0.0095	0.0211	0.0197	0.0176	0.0189	0.0174
41	<0.0001	0.0013	0.0005	0.0009	0.0022	0.0002	0.0109	0.0195	0.0191	0.0157	0.0184	0.0176
57	<0.0001	<0.0001	0.0008	<0.0001	0.0005	0.0007	0.0121	0.0177	0.0204	0.0178	0.0179	0.0178
72	0.0008	0.0003	0.0023	0.0027	0.0002	0.0002	0.0126	0.0165	0.0203	0.0170	0.0171	0.0194
93	0.0008	0.0012	0.0013	0.0006	<0.0001	0.0006	0.0131	0.0155	0.0200	0.0207	0.0160	0.0193

Table C.8

Arsenic concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	0.067	0.076	0.081	0.001	0.003	0.003	1.550	1.610	1.700	0.276	0.298	0.291
3	0.070	0.078	0.075	0.002	0.004	0.009	2.010	2.120	2.220	0.277	0.294	0.278
8	0.075	0.078	0.080	0.005	0.009	0.009	2.070	2.800	3.020	0.314	0.335	0.325
16	0.060	0.070	0.068	0.007	0.008	0.010	2.190	2.860	3.160	0.310	0.322	0.293
27	0.062	0.065	0.058	0.008	0.012	0.008	2.200	3.500	3.850	0.275	0.290	0.300
41	0.068	0.074	0.079	0.008	0.012	0.009	2.300	3.800	3.900	0.280	0.295	0.265
57	0.080	0.080	0.084	0.008	0.010	0.009	2.470	4.160	4.200	0.314	0.352	0.340
72	0.040	0.028	0.032	0.010	0.007	0.007	2.860	4.200	4.220	0.360	0.390	0.390
93	0.041	0.024	0.028	0.010	0.008	0.007	2.800	4.200	3.920	0.360	0.350	0.360

Table C.9

Calcium concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	56.2	84.5	47.2	246	255	241	551	606	693	984	964	966
3	92.2	51.5	73.8	258	261	250	685	737	690	948	1020	969
8	114	141	108	272	254	253	756	818	815	940	977	1000
16	117	153	138	248	231	223	735	781	757	938	943	941
27	200	231	153	242	217	230	698	748	745	918	920	898
41	182	216	155	236	219	215	707	750	728	820	868	897
57	185	224	185	216	201	212	706	765	772	915	926	876
72	206	222	197	226	203	203	734	756	742	916	871	894
93	166	184	189	232	203	200	669	705	700	894	872	868

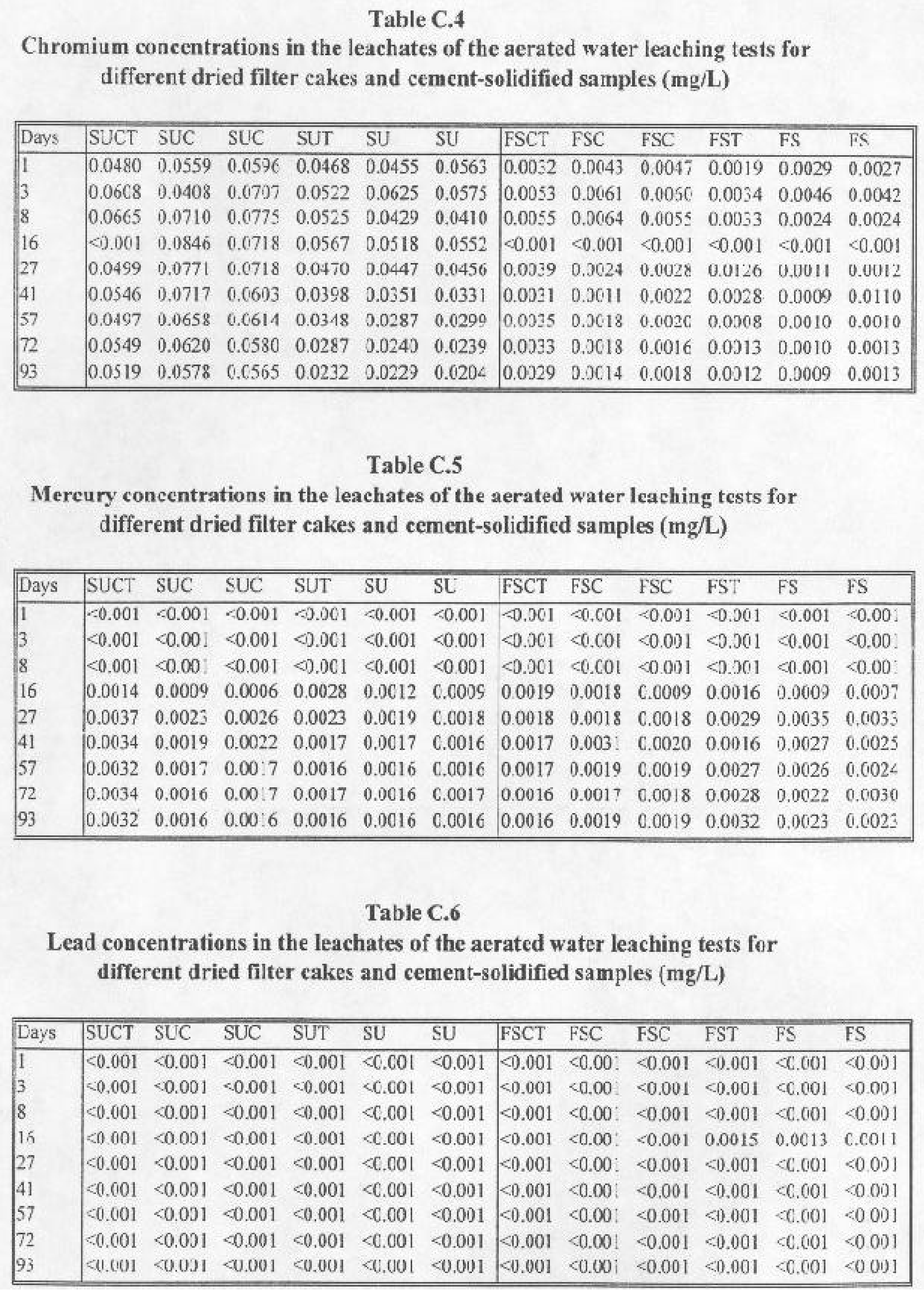

Table C.4

Chromium concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	0.0480	0.0559	0.0596	0.0468	0.0455	0.0563	0.0032	0.0043	0.0047	0.0019	0.0029	0.0027
3	0.0608	0.0408	0.0707	0.0522	0.0625	0.0575	0.0053	0.0061	0.0050	0.0034	0.0046	0.0042
8	0.0665	0.0710	0.0775	0.0525	0.0429	0.0410	0.0055	0.0064	0.0055	0.0033	0.0024	0.0024
16	<0.001	0.0846	0.0718	0.0567	0.0518	0.0552	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
27	0.0499	0.0771	0.0718	0.0470	0.0447	0.0456	0.0039	0.0024	0.0028	0.0126	0.0011	0.0012
41	0.0546	0.0717	0.0603	0.0398	0.0351	0.0331	0.0031	0.0011	0.0022	0.0028	0.0009	0.0110
57	0.0497	0.0658	0.0614	0.0348	0.0287	0.0299	0.0035	0.0018	0.0020	0.0008	0.0010	0.0010
72	0.0549	0.0620	0.0580	0.0287	0.0240	0.0239	0.0033	0.0018	0.0016	0.0013	0.0010	0.0013
93	0.0519	0.0578	0.0565	0.0232	0.0229	0.0204	0.0029	0.0014	0.0018	0.0012	0.0009	0.0013

Table C.5

Mercury concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
16	0.0014	0.0009	0.0006	0.0028	0.0012	0.0009	0.0019	0.0018	0.0009	0.0016	0.0009	0.0007
27	0.0037	0.0023	0.0026	0.0023	0.0019	0.0018	0.0018	0.0018	0.0018	0.0029	0.0035	0.0033
41	0.0034	0.0019	0.0022	0.0017	0.0017	0.0016	0.0017	0.0031	0.0020	0.0016	0.0027	0.0025
57	0.0032	0.0017	0.0017	0.0016	0.0016	0.0016	0.0017	0.0019	0.0019	0.0027	0.0026	0.0024
72	0.0034	0.0016	0.0017	0.0017	0.0016	0.0017	0.0016	0.0017	0.0018	0.0028	0.0022	0.0030
93	0.0032	0.0016	0.0016	0.0016	0.0016	0.0016	0.0016	0.0019	0.0019	0.0032	0.0023	0.0023

Table C.6

Lead concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
16	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.0015	0.0013	0.0011
27	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
41	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
57	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
72	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
93	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table C.1

Silver concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
16	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
27	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
41	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
57	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
72	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
93	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table C.2

Barium concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	0.0054	0.0070	0.0064	0.0107	0.0113	0.0128	0.0152	0.0155	0.0167	0.0135	0.0144	0.0132
3	0.0080	0.0081	0.0066	0.0126	0.0133	0.0128	0.0148	0.0157	0.0157	0.0143	0.0152	0.0144
8	0.0103	0.0090	0.0081	0.0137	0.0150	0.0148	0.0140	0.0142	0.0137	0.0166	0.0171	0.0171
16	0.0109	0.0096	0.0100	0.0129	0.0141	0.0139	0.0164	0.0118	0.0116	0.0174	0.0186	0.0179
27	0.0099	0.0129	0.0124	0.0160	0.0161	0.0159	0.0170	0.0128	0.0124	0.0192	0.0209	0.0180
41	0.0102	0.0140	0.0117	0.0144	0.0161	0.0158	0.0148	0.0215	0.0106	0.0105	0.0192	0.0182
57	0.0080	0.0161	0.0152	0.0143	0.0150	0.0159	0.0150	0.0112	0.0125	0.0196	0.0198	0.0183
72	0.0075	0.0158	0.0142	0.0137	0.0139	0.0141	0.0143	0.0104	0.0098	0.0192	0.0187	0.0192
93	0.0065	0.0166	0.0153	0.0127	0.0143	0.0153	0.0136	0.0097	0.0094	0.0205	0.0189	0.0181

Table C.3

Cadmium concentrations in the leachates of the aerated water leaching tests for different dried filter cakes and cement-solidified samples (mg/L)

Days	SUCT	SUC	SUC	SUT	SU	SU	FSCT	FSC	FSC	FST	FS	FS
1	0.0057	0.0066	0.0069	0.0065	0.0073	0.0078	0.0002	0.0002	0.0002	0.0008	0.0008	0.0007
3	0.0075	0.0084	0.0083	0.0080	0.0090	0.0087	0.0003	0.0003	0.0003	0.0008	0.0008	0.0007
8	0.0070	0.0107	0.0101	0.0094	0.0091	0.0083	0.0002	0.0003	0.0007	0.0008	0.0007	0.0007
16	0.0088	0.0109	0.0109	0.0098	0.0102	0.0105	0.0005	0.0006	0.0004	0.0011	0.0010	0.0010
27	0.0018	0.0023	0.0026	0.0032	0.0043	0.0093	<0.0001	0.0001	0.0001	0.0006	0.0008	0.0009
41	0.0016	0.0023	0.0023	0.0028	0.0045	0.0039	<0.0001	0.0008	0.0005	0.0001	0.0006	0.0005
57	0.0014	0.0027	0.0026	0.0028	0.0038	0.0041	<0.0001	0.0001	0.0003	0.0006	0.0005	0.0005
72	0.0013	0.0025	0.0028	0.0029	0.0038	0.0042	0.0001	<0.0001	<0.0001	0.0005	0.0006	0.0006
93	0.0013	0.0024	0.0026	0.0026	0.0047	0.0044	<0.0001	<0.0001	0.0001	0.0008	0.0005	0.0019

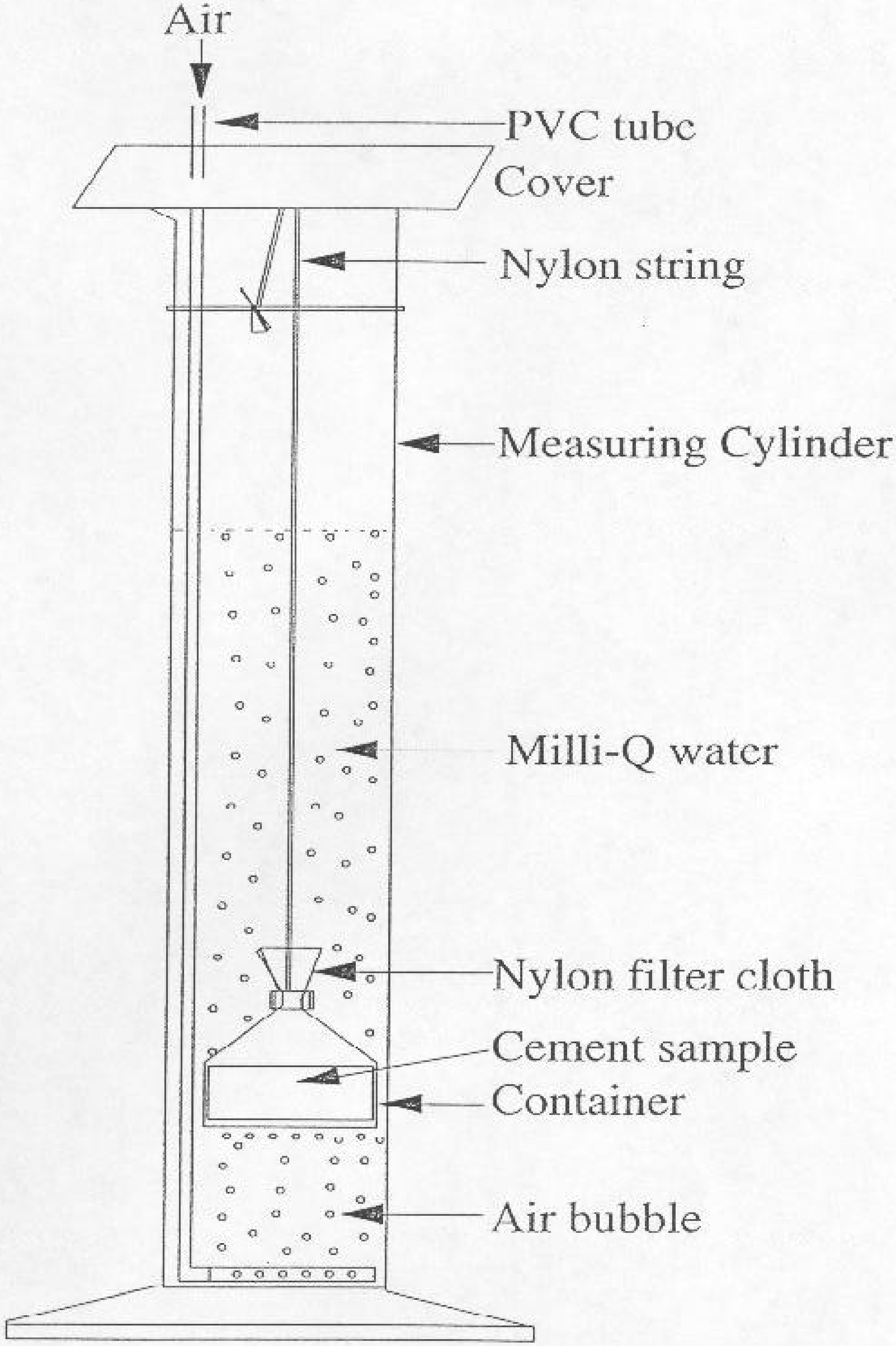

Figure C.1 Schematic diagram of the aerated water leaching apparatus

APPENDIX D

Calcium Hypochlorite

APPENDIX D
Process Economics

Calcium hypochlorite

$$Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2$$

$$H^+ + HOCl + As^{3+} \rightarrow As^{5+} + Cl^- + H_2O$$

$$H^+ + HOCl + 2Fe^{2+} \rightarrow 2Fe^{3+} + Cl^- + H_2O$$

at pH > 2 when Fe^{3+} hydrolyzes to give $Fe(OH)_3$

$$HOCl + 5H_2O + 2Fe^{2+} \rightarrow 2Fe(OH)_3 + Cl^- + 5H^+$$

Thus the oxidation of 1 mole of As^{3+} to As^{5+} requires 0.5 mole of $Ca(OCl)_2$ or the oxidation of 1 gram of As^{3+} to As^{5+} requires 0.955 gram of $Ca(OCl)_2$

The oxidation of 1 mole of Fe^{2+} to Fe^{3+} requires 0.25 mole of $Ca(OCl)_2$ or the oxidation of 1 gram of Fe^{2+} to Fe^{3+} requires 0.64 gram of $Ca(OCl)_2$

Basis: 1000 gallon of Susie Mine water containing 12 mg/L As(III) and 200 mg/L of Fe(II). Calcium hypochlorite is available at $1670 per ton (2000 lb) or $1.84 per kg.

Since 12 mg/L of As(III) requires 11.95 mg/L of $Ca(OCl)_2$, and 200 mg/L of Fe(II) requires 127.9 mg/L of $Ca(OCl)_2$, 1000 gallon of Susie Mine water would require (with 20% excess reagent):
1.2 x 3785 x (11.95 + 127.9)/1000 x $1.84/1000 = $1.17 per 1000 gallons..

If the mole ratio of Fe(II)/As(III) in the water was 39/1 (as in the Susie Mine water sampled before this project), Fe(II) concentration would be 349 mg/L. The corresponding cost per 1000 gallons would be:
1.2 x 3785 x (11.95 + 223.5)/1000 x $1.84/1000 = $1.97.