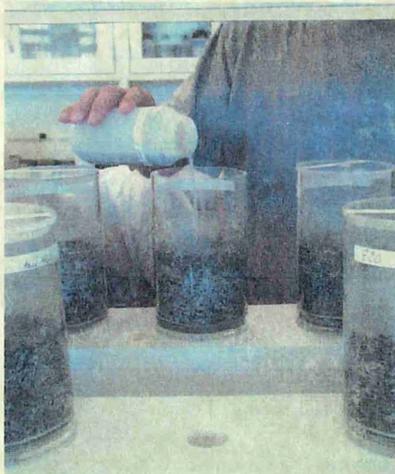


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Use of Microencapsulation to Prevent Acid Rock Drainage



Final Report to MSE Technology Applications, Inc.

September 2004

Minnesota Department of Natural Resources
Division of Lands and Minerals
St. Paul, MN

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St. Paul, MN

Table of Contents

List of Tables	iii
List of Figures	iii
List of Appendices	iv
EXECUTIVE SUMMARY	1
1. INTRODUCTION.....	2
1.1 Acid Mine Drainage.....	2
1.2 The Problem.....	3
1.3 Microencapsulation.....	3
2. OBJECTIVES	4
3. APPROACH	4
4. METHODS	5
4.1. Materials	5
4.1.1 Greenstone Rock.....	5
4.1.2. Chemicals.....	6
4.1.2.1. KB-SEA™	6
4.1.2.2. EcoBond-ARD™	6
4.2. Solid Phase Analyses	6
4.3. Apparatus	7
4.4 Experimental Procedure.....	7
4.4.1. Cell Loading.....	7
4.4.2. Initial Rinse.....	7
4.4.3. Application of Encapsulation Products.....	8
4.4.3.1. Application of KB-SEA™	8
4.4.3.2. Application of EcoBond-ARD™	8
4.4.4. Drainage Quality Sampling.....	9
4.5 Aqueous Analyses.....	9
4.6. Reaction Conditions.....	9
4.7. Microscope Observations.....	10
5. RESULTS	11
5.1. Solid-Phase Analyses.....	11
5.2 Application of Microencapsulation Products.....	11
5.3. Drainage Quality	11
5.3.1 pH.....	12

Table of Contents (cont.)

5.3.1.1.	Control Cells.....	12
5.3.1.2.	KEECO KB-SEA™ Cells.....	12
5.3.1.3.	EcoBond-ARD™ Cells.....	12
5.3.2.	Sulfate.....	13
5.3.2.1.	Control Cells.....	13
5.3.2.2.	KEECO KB-SEA™ Cells.....	13
5.3.2.3.	EcoBond-ARD™ Cells.....	13
5.3.3.	Calcium and Magnesium Data.....	13
5.3.3.1.	Control Cells.....	13
5.3.3.2.	KEECO KB-SEA™ Cells.....	14
5.3.3.3.	EcoBond-ARD™ Cells.....	14
5.3.4.	Metals.....	14
5.3.4.1.	Control Cells.....	14
5.3.4.2.	KEECO KB-SEA™ Cells.....	14
5.3.4.3.	EcoBond-ARD™ Cells.....	15
5.3.5.	Phosphorus.....	15
5.4.	Mass Release.....	16
5.4.1	Total Mass Release.....	16
5.4.2	Release Rates.....	16
5.5.	Microscope Evaluation.....	17
5.5.1	KEECO KB-SEA™.....	17
5.5.1.1	Unleached Reactor.....	17
5.5.1.1.1	Product.....	17
5.5.1.1.2	Pyrite Cubes.....	17
5.5.1.2	Leached Reactor.....	18
5.5.1.2.1	Pyrite Cubes.....	18
5.5.1.2.2	Oxidized Samples.....	18
5.5.2	Ecobond-ARD™.....	19
5.5.2.1	Unleached Reactor.....	19
5.5.2.1.1	Pyrite Cubes.....	19
5.5.2.2	Leached Reactor.....	19
5.5.2.2.1	Pyrite Cubes.....	19
6.	DISCUSSION.....	20
6.1.	Controls.....	20
6.2.	EcoBond-ARD™.....	20
6.3.	KEECO KB-SEA™.....	22
7.	CONCLUSIONS.....	24
8.	ACKNOWLEDGMENTS.....	25
9.	REFERENCES.....	25

LIST OF TABLES

1.	Total sulfur and dissolved carbon dioxide analyses of high sulfur, low sulfur, and blended greenstone samples	28
2.	Particle size distribution of blended greenstone sample	28
3.	Average whole rock chemistry of blended greenstone samples.....	29
4.	Average drainage quality data for KEECO humidity cells	30
5.	Average drainage quality data for Ecobond humidity cells	31
6.	Total mass release, control and KEECO humidity cells	32
7.	Rates of sulfate, calcium and magnesium release for microencapsulation cells.....	33
8.	Additional drainage quality parameters of concern	34

LIST OF FIGURES

1.	Schematic of humidity cell for laboratory Greenstone experiment	35
2.	Application of microencapsulation products, overview	36
3.	Addition of KEECO KB-SEA™ to a reactor	37
4.	Cell storage, constant temperature and humidity room	38
5.	KB-SEA™ treated cells, side view	39
6.	Drainage quality results; pH vs time for all cells.....	40
7.	Drainage quality results; sulfate vs time for all cells	41
8.	Drainage quality results; calcium vs time for all cells	42
9.	Drainage quality results; magnesium vs time for all cells	43
10.	Rock coated with KEECO; macro coating	44
11.	Polished cross sections of rock fragments shown in Figure 10 with KEECO product coating.....	45
12.	Detailed backscattered electron image of the KEECO product between two rock fragments.....	46
13.	Pyrite cubes from unleached KEECO reactor.....	47
14.	Pyrite Cubes from Figure 13 that have been imbedded and polished.....	47
15.	Portion of pyrite cube from a KEECO unleached reactor.....	48
16.	Microprobe results for pyrite crystal from unleached KEECO reactor, Face A	49
17.	Microprobe analyses for pyrite cube from unleached KEECO reactor, Face D	50
18.	Pyrite cubes selected for analyses from leached KEECO reactor	51
19.	Pyrite cube 1 with oxidized zone from the KEECO reactor	52
20.	Pyrite cube with KEECO coating showing no visible oxidized zone.....	53
21.	Pyrite cube 1, location of microprobe analyses and elemental composition.	54
22.	Pyrite cube 2, location of microprobe analyses and elemental composition.	55
23.	Oxidized areas from KEECO leached reactor	56
24.	Oxidized zone from area 2 in Figure 23 and microprobe element profile.....	57
25.	Pyrite cubes from Ecobond unleached reactor.....	58
26.	Microprobe results for pyrite from unleached Ecobond reactor	59
27.	Pyrite cubes selected for analyses from leached Ecobond reactor	60

LIST OF FIGURES (cont.)

28.	Pyrite Cube 1 from leached Ecobond reactor and microprobe element profile	61
29.	Pyrite Cube 2 from leached Ecobond reactor and microprobe element profile	62
30.	Comparison of control cell with cell treated with 1.5% EcoBond-ARD TM , 1/10/02 and 8/19/02.....	63
31.	Comparison of control cell with cell treated with 3% EcoBond-ARD TM , 1/10/02 and 8/19/02.....	64
32.	Comparison of control cell with cell treated with 4.5% EcoBond-ARD TM , 1/10/02 and 8/19/02.....	65
33.	Comparison of control cell with cell treated with 1% KB-SEA TM , 1/10/02, 8/19/02, and 8/9/04	66
34.	Comparison of control cell with cell treated with 3% KB-SEA TM , 1/10/02, 8/19/02, and 8/9/04	67
35.	Comparison of control cell with cell treated with 5% KB-SEA TM , 1/10/02 8/19/02, and 8/9/04	68
36.	Closeup of 1% and 5% KEECO reactors, 8/9/04.....	69
37.	Material treated with 1% KB-SEA TM . Grains were coated and cemented together but some oxidation had occurred	70

LIST OF APPENDICES

1.	Solids composition of rock from laboratory experiment
2.	Information on chemicals
3.	Microscope evaluation
4.	Drainage quality
5.	Concentration vs. time
6.	Cumulative mass release
7.	Laboratory methods
8.	Quality assurance program
9.	Miscellaneous photographs
10.	Calcium release
11.	Proposal for additional work

EXECUTIVE SUMMARY

Two commercially available microencapsulation products were tested for their ability to coat unoxidized pyrite and prevent its oxidation. EcoBond-ARD™, a phosphate based compound and KEECO KB-SEA™, a silica based product, were each applied to an unoxidized acid generating waste rock. Three application rates were selected by each company and represented a low, optimum and high application. Laboratory testing has been conducted in humidity cells for 168 weeks.

Cells with untreated waste rock (controls) produced drainage below pH 6.0 after 1 week and had an average pH of about 3.3 after 60 weeks. EcoBond-ARD™ delayed the onset of acidification but it was not successful in preventing acid drainage. The pH in all cells treated with EcoBond-ARD™ decreased to below 6 after 12-16 weeks. These cells were terminated after 59 weeks when the pH had decreased to around 3.5, essentially the same as in the controls. Possible explanations for the failure of the EcoBond-ARD™ included insufficient contact time to oxidize the surface of the pyrite or the absence of a durable coating. Additional concerns with the EcoBond-ARD™ were elevated levels of phosphorus and arsenic in the drainage. Initial arsenic concentrations ranged from 400 to 800 ug/L, well above the newly proposed federal drinking water standard of 10 ug/L. Initial phosphate concentrations were 1300 to 3900 mg/L and water of this quality could cause algal blooms in downstream receiving waters. Concentrations did not decrease to below the concern level of 0.03 mg/L until about 30 weeks.

KB-SEA™ was successful in preventing acid drainage at all levels of treatment. However, the pH from all cells treated with this product were initially around 12. Although pH has decreased in all cells, the cells treated with 5% had pH values consistently above 9 for about 75 weeks. The rate of sulfide oxidation in these cells was about 10% of the rate measured in the untreated controls and visually there was little sulfide oxidation in the cells treated with the optimum and high application rates (3%, 5%). The pH in the low application rate reactors (1%) has declined slowly and was below 6.5 at 168 weeks. Some oxidation is visible in the reactors and the sulfate release rates had increased slightly.

The exact mechanism for the success of this product has not yet been determined. Possible explanations include one or more of the following: high pH, due to the presence of lime in the product, cementation of the material, resulting in a macro encapsulation of the rock grains, and microencapsulation of the surfaces with silica.

At least 60% of the calcium associated with the quicklime (CaO) initially applied as a component of the KEECO product remained in the reactor. Some of the lime may have reacted to produce less reactive alkaline compounds, like Ca(OH)₂ and CaCO₃, and any or all of these compounds could be responsible for maintaining the neutral pH in the reactors. Microscopic evaluation of samples from one of the reactors with optimum treatment (3%) did not clearly identify a mechanism. Silica was generally present along the edge of the pyrite crystals but oxygen penetration into the pyrite had still occurred.

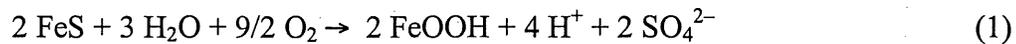
These cells should be continued to assess the long term effectiveness of the treatment. The treatment will be considered effective as long as the pH remains above 6.0. Additional work to determine the mechanism should be conducted and cost information needs to be developed.

1. INTRODUCTION

Managing mine waste to control and prevent environmental impacts has become a major issue in new mine development. Extensive characterization and laboratory testing are required to evaluate a given material's potential to generate problematic drainage. Reclamation plans must include provisions to prevent, control or treat any water quality problems that could be produced at the site.

1.1. Acid Mine Drainage

The primary mine drainage problem is produced by the oxidation of iron sulfide minerals that are generally associated with base and trace metal deposits. When these minerals are exposed to air, they oxidize to release metals, sulfate and acid. This reaction can be represented by the following reaction:



If the mine waste does not contain a sufficient amount of neutralizing minerals (e.g., calcium carbonate), drainage from the mine waste will be acidic and may contain elevated concentrations of trace metals. The production of acidic drainage requires iron sulfides, oxygen, and water. To stop the production of acid, at least one of these three components must be controlled or eliminated.

Minimizing the volume of water that contacts the mine waste, and thereby reducing the transport of reaction products, has been implemented at various mine sites. A cover with low permeability is placed over the mine waste to limit water infiltration. Cover types include synthetic membrane materials, such as high-density polyethylene, compacted clay or a combination of these materials (Eger, 1999; Wilson et al., 1997). In order to ensure that these covers are maintained, an ongoing monitoring and maintenance program is required. In dry climates, covers can be designed to store water during the wet season, and evaporate the water during the dry season (Swanson et al., 1997). Currently, the most widely accepted approach for controlling acid generation from mine waste is to limit oxygen diffusion by utilizing a water cover. This method has been most commonly used for tailings disposal (Li et al., 1997). Oxygen concentrations in water are generally less than 10 mg/L, or a factor of 20,000 less than the concentration in air. General recommendations call for a water cover of at least 1 meter in depth (Feasby et al., 1997). Although this approach has drastically reduced the oxidation of tailings, and has generally prevented acid conditions, metal release has still occurred (Aubé et al., 1995). While keeping the tailings totally submerged during operation is achievable, long-term maintenance of water holding dams becomes a concern when mining is completed (Aubertin et al., 1997).

For some underground operations, where the volume of waste rock is small, the waste rock can be placed with the tailings in the tailings basin. For large open pits, acid generating waste rock can be backfilled into the pit at closure. The water level in the pit rises and eventually covers the acid generating material. This approach has been used at the Flambeau Mine in Wisconsin, and the Brewer Mine in South Carolina. Although this approach may be effective, it is very expensive. Rock must be handled twice, and since the sulfide oxidation process has already begun, lime must be added to neutralize the rock either during or after placement.

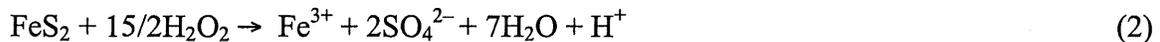
1.2. The Problem

Currently, there is no proven way to prevent water quality drainage problems from large waste rock piles unless the material can be stored immediately under water. Even with underwater disposal, some amount of metal release occurs, and care must be taken to ensure the material stays submerged after mine closure. The only other widely accepted approach is drainage collection and lime treatment. However, once acid generation begins, collection and treatment may be required for hundreds of years. New methods of preventing acid generation are needed. This study examined the use of commercial microencapsulation products to prevent acid generation from sulfide mine waste.

1.3. Microencapsulation

Reactive mine wastes can be isolated from oxidizing agents (i.e. O_2 , Fe^{3+}) by chemically precipitating a ferric coating on the surface of the waste material. This process, often called microencapsulation, prevents further oxidation of sulfide minerals by blocking the transport of oxidants to the sulfide surface and consuming ferric iron before it can become an oxidant.

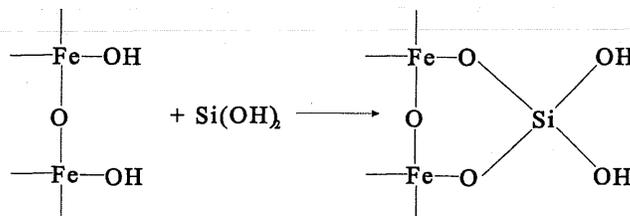
The coating can be produced by reacting sulfidic material with low concentrations of an oxidizing agent in the presence of soluble phosphate or silica in a buffered solution. Hydrogen peroxide or calcium hypochlorite have been typically used as oxidizing agents. The oxidizing agent reacts with the sulfide to produce ferric ions:



Sodium acetate has been used to buffer the solution at a pH of 5 to 6. At this pH, dissolved ferric iron is unstable and precipitates as ferric hydroxide. If dissolved phosphate is present it will scavenge ferric ions and ferric phosphate will precipitate:



If silicic acid is present in the solution, it will react with the ferric hydroxides, producing an insoluble ferric silicate precipitate that is chemically stable at low pH (Evangelou, 1996):



(5)

Most of the previous studies have dealt with the feasibility of chemically producing coatings on reactive mine wastes and tailings. Reasonably successful coatings were reported in laboratory studies using phosphates (Evangelou, 1994; Georgopoulou et al., 1995; Roy and Worrall, 1999), silicates (Zhang and Evangelou, 1998; Fytas et al., 1999), and various organic materials (Adams et al., 1994; Moskalyk, 1995). Generally, the presence of coatings on rock and tailing surfaces were confirmed using scanning electron microscopy (SEM), although decreased iron levels in drainage was often cited as evidence of coating formation.

Two products developed recently have been effective in reducing metal release from oxidized mine wastes and metal contaminated soils (Vandiviere and Evangelou, 1998; Conca et al., 1999, Jensen et al., 1999; Gobla, et al. 2000). These are a silica-based compound produced by Klean Earth Environmental Company (KEECO), and a phosphate-based compound produced by Metals Treatment Technologies, LLC (MT²). Although they have been effective in limiting metal release from oxidized material, no data is available to predict their ability to sufficiently limit sulfide oxidation and to prevent acid generation from unoxidized waste rock. This laboratory investigation was designed to evaluate both of these compounds for their ability to prevent acid generation and to evaluate application rates and treatment lifetime.

2. OBJECTIVES

The overall objectives of this study were:

1. To maintain drainage pH above 6.0
2. To reduce the rate of sulfide oxidation
3. To determine an appropriate application rate for each compound, and
4. To determine the longevity of the treatment

3. APPROACH

In order to determine the effectiveness of the microencapsulation products to prevent acid drainage, a laboratory investigation using humidity cells was conducted. Each company specified three application rates. The objective was to compare the recommended rate with a higher and lower application.

4. METHODS

4.1. Materials

4.1.1. Greenstone Rock

The desired rock type for this experiment was an acid-generating material that could be associated with future metal mining in Minnesota. When the University of Minnesota initiated a project to enlarge its underground physics laboratory at the Soudan Mine in northeastern Minnesota, an opportunity to collect samples with varying amounts of pyrite was presented. This excavation resulted in the removal of approximately 22,000 cubic yards of pyrite-bearing Archean greenstone rock. The Archean metavolcanics and metasedimentary formations, or greenstone belts, of Minnesota extend north into Canada, where they have yielded substantial mineral production. These formations are potential hosts for gold, zinc-copper massive sulfides with various by-products, and magmatic sulfide deposits containing copper, nickel and platinum group elements. Recent exploration of greenstone belt metasedimentary formations has focused on gold, base metals, and silver-cobalt-copper deposits.

Prior to excavation of the cavern, a drill hole was bored through the center of the future cavern area to characterize the rock. This data was used to identify zones containing material that would be suitable for environmental testing. Material with varying sulfur content was selected and about 450 tons were transported to the Hibbing office of Minnesota Department of Natural Resources (MN DNR). Detail on the excavation and data from the drill hole and associated testing on the material can be found in another report (Lapakko et al., 2002).

The rock used in the experiment was hand selected from material which had a bulk sulfur content of 0.67%. The target sulfur content for the laboratory study was 2%. A MN DNR geologist hand selected two five-gallon samples. One sample contained visible pyrite and was estimated to contain approximately 3% sulfur. The second sample contained little visible pyrite and was expected to be relatively low in sulfur. The two samples were analyzed for total sulfur and evolved carbon dioxide at Lerch Brothers in Hibbing, MN (Table 1). Based on these analyses it was determined that if the two samples were blended, the result would be a sample that would be close to the 2% target sulfur content. To determine variability in the blended sample, six splits were analyzed for total sulfur and evolved carbon dioxide at Lerch Brothers (Table 1).

The sample was crushed to -0.64 cm at Lerch Brothers. A stage crushing process was used to limit generation of fines. The sample was screened to -0.64 cm and the oversize material was crushed in three steps (large jaw crusher set at 1.92 cm, small jaw crusher set at 0.95 cm, roll crusher set at 0.64 cm). After each of the first two crushing steps, the -0.64 cm fraction was collected and the oversize was passed to the next crushing phase. Five 250-gram samples and one 300-gram sample was split from the bulk sample. The five 250-gram samples were stored in sealed plastic bags until filling the cells. The 300-gram split was pulped for subsequent analysis.

4.1.2. Chemicals

4.1.2.1. KEECO KB-SEA™

KB-SEA™ is a proprietary chemical produced by the Klean Earth Environmental Company (KEECO). Given the proprietary nature of the material, only general information (listed in the following paragraph) on the chemical was available from the company. Appendix 2 contains the material data safety sheet (MSDS) for this product.

KB-SEA™ is a calcium, silica based powder which is composed of several types of particles which are designed to work together. Microscopically, KB-SEA™ particles consist of translucent spheres that contain the various component materials. Some components dissolve immediately in water and modify the pH of the material and assist in the chemical dispersion of the other active components throughout the material being treated. Other components do not immediately dissolve. However, once the pH is adjusted, these components begin to react with the goal of encapsulating the metal-containing particle surfaces with a gelatinous coating composed primarily of silica. Individual KB-SEA™ particles react with solid particles and then begin to consolidate, forming larger aggregated particles via bridging.

4.1.2.2. EcoBond-ARD™

EcoBond-ARD™ is a proprietary chemical developed by Metals Treatment Technologies. Given the proprietary nature of the material, only general information (listed in following paragraph) on the chemical was available from the company. Appendix 2 contains the material data safety sheet (MSDS) for this product.

EcoBond-ARD™ is a phosphate based material that was developed to inhibit the oxidation of pyrite. The theory is that the phosphate in the EcoBond-ARD™ will combine with ferric iron (Fe^{+3}) to produce a stable, insoluble iron-phosphate compound. The goal is to produce a new compound that would render the Fe^{+3} in the pyrite unavailable for oxidation by coating all available pyrite surfaces. EcoBond-ARD™ is also designed to react with ferrous iron (Fe^{+2}) to form a second stable compound.

4.2. Solid Phase Analyses

Particle size distribution was determined by Lerch Brothers using method ASTM E-276-93 (ASTM, 2000). Lerch also conducted the initial sulfur analysis that was used to screen the samples. The rock samples selected for the cells were analyzed by Activation Laboratories Ltd. (ACTLABS) in Tucson AZ. Analyses included total sulfur, sulfate, and sulfide (determined by difference), and evolved carbon dioxide, using ASTM E-1915-97 (ASTM 2000). A 10% hydrochloric acid solution was used to solubilize the carbonate minerals, and the carbonate present was quantified as the difference between total carbon in the initial sample and that in the residue.

The remaining solid-phase constituents were determined by ACTLABS in Ancaster, ON. Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E886-94 (ASTM 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash ENVIRO II ICP. Concentrations of Ag, Cd, Cu, Ni, Pb, Zn, and Bi were determined using a total digestion modified from Crock et al. (1983), with analysis by ICP-AES. Other trace elements were determined using instrumental neutron activation analysis (Hoffman 1992).

4.3. Apparatus

Cylindrical cells (I.D. = 10.2 cm, h = 19.0 cm) constructed of acrylic plastic were used in the experiment (Figure 1). A 0.64-cm high acrylic sleeve was glued into the bottom of the cell to support a 0.16-cm thick PVC plate, which was perforated with 0.32-cm holes spaced 0.48 cm on center. The plate was covered with a polypropylene filter (22 micron, National Filter Media Corporation, Polymax B, Style 226-075-2) which supported the solids. The bottom was sealed with an acrylic plate with a 0.85-cm outlet port in the center, and a removable cover with a 0.85-cm vent hole was placed on top of the cell. Prior to filling, the cells were acid washed with 10% HNO₃ and then rinsed three times with distilled water. The cells were weighed and the weight was recorded.

4.4. Experimental Procedure

4.4.1. Cell Loading

On 11 May 2001 twenty-one cells were each filled with 1000 grams of rock, which was added in increments of approximately 250 grams. Fourteen of the cells were used for long term testing, and seven for initial microscopic evaluation. The seven included a control, and one cell for each of the application rates. A plastic pan was placed on a scale and four of the 250-gram splits were added. The weight was generally about 50 grams over the desired 1000-gram sample size. A plastic spoon was used to randomly remove the excess, which was retained with other unused sample. The samples were very dry and some of the very fine dust was lost due to suction from the exhaust hood. The plastic pan and spoon were rinsed with distilled water after each cell was filled. The cells with dry solids were weighed and the tared weight recorded.

4.4.2. Initial Rinse

Starting on 14 May 2001 the solids were rinsed daily for three days to remove oxidation products accumulated on the solids from the time they were crushed until the beginning of the experiment. A rubber cap was placed on the outlet port, and 500 mL of distilled water was slowly poured into each cell with a graduated cylinder. The cells were allowed to sit for ten minutes after the last one was filled, and then they were uncapped and allowed to drain.

Effluent (or drainage) samples were weighed and analyzed for pH and specific conductance at the MN DNR laboratory in Hibbing, MN (Table A4.2). From the remaining drainage, samples were collected and filtered for subsequent determinations of sulfate and metal concentrations. After

filtration, samples to be analyzed for metals were preserved with 0.2 mL Baker Instra-Analyzed nitric acid per 50 mL sample. The volume-weighted concentration for the initial three rinses was calculated to represent the drainage quality for the initial rinses to remove oxidation products (Table A4.2).

A sixty-eight parameter ICP-MS scan was conducted on the composite of the three initial rinses (prior to application) by ACTLABS (Table A4.3). The sulfate content of the composite was determined at the Minnesota Department of Agriculture (MDA) in St. Paul, MN.

4.4.3. Application of Encapsulation Products

On 17 May 2001 the encapsulation products were added to each cell (the cell was plugged, and the rock was flooded; Figures 2, 3). The cell was unplugged after 10 minutes and the treatment solution allowed to drain. The effluent was analyzed for pH at the MN DNR laboratory, and represents week 0 (Table A4.4). The cells were then placed in a constant temperature and humidity room for a week before the start of the experiment (week 1; Figure 4).

4.4.3.1. Application of KEECO KB-SEA™

Application rates were determined by KEECO to be 1%, 3% and 5% by weight (1% = 10 grams of product per 1000 grams of rock). The KB-SEA™ was weighed with an electronic balance and mixed with 150 mL of distilled water) and placed in an HDPE bottle. The bottle was shaken and placed on a shaker table, then agitated for 60 minutes. (This allowed the solutions to cool due to the exothermic nature of some of the reactions. The slurry was slightly warm after the product was added and the bottle shaken). The bottle was removed from the shaker table and then shaken immediately prior to application. The slurry was poured slowly from the bottle until water began to drip from the cell. The cell was then plugged, the bottle shaken and the remaining slurry applied to the cell. For the higher treatments (3% and 5%) it was necessary to shake the bottle one or more times to prevent settling. The bottle was then rinsed with 50 mL of distilled water to remove any residual product and this water was added to the top of the cell. No product remained in the bottles. The cells were then allowed to sit in contact with the product for 10 minutes before draining.

4.4.3.2. Application of EcoBond-ARD™

Application rates were determined by MT² to be 1.5%, 3.0% and 4.5% by weight. (For the 3% application, 30 grams of the reactive reagent was added to the 1000 grams of rock in the cell.) Preparation of the solutions was done by MT² staff. Staff from MT² used two sources of chemicals to make the treatment solutions. Cells 9, 11 and 13 were treated with material from the company's office in Colorado, while cells 10, 12 and 14 were treated with chemicals obtained from Lerch Brothers Laboratories in Hibbing. The chemicals were dissolved in distilled water, and additional water was added to bring the final volume to about 200 mL (It took about 150 mL of solution to fill the bed, but since the solids were not level, some additional solution needed to be added to ensure that all the solids were contacted).

Once the solutions were prepared, the bottles were placed on a shaker table until they were added to the cells. The addition procedure was similar to that used for the KEECO product. However, since EcoBond-ARD™ is a solution it was not necessary to shake the bottle as frequently or rinse the bottle at the end of the application. There were no visible residual chemicals remaining in the bottles.

4.4.4. Drainage Quality Sampling

Beginning on 24 May 2002 (week 1) the cells were rinsed weekly using the same procedure that was used in week 0 (initial rinse) with the exception that the rinse water was applied with a separatory funnel instead of a graduated cylinder and slowly dripped into the cell. Effluent samples were collected and analyzed for pH, specific conductance and alkalinity at the MN DNR laboratory. Samples were analyzed at weeks 1, 2, 3, 4, 6, 8, 10, 12, 14, 16, 18, 20 and 24, and at 4 week intervals through week 102 and every 8 weeks through 168 (period of record). Through week 8, effluents were analyzed for sulfate, Ca, Mg, Na, K, Fe, Cu, Ni, Co and Zn. Subsequently, the effluents were analyzed for SO₄, Ca, Mg and Fe by MDA. Additional selected samples for the EcoBond-ARD™ cells were analyzed for total phosphate, orthophosphate and arsenic by MDA.

A sixty-eight parameter ICP-MS scan was also conducted on the week 1 samples at ACTLABS (Table A4.6).

4.5. Aqueous Analyses

Water samples were analyzed for specific conductance, pH, alkalinity, and acidity at the MN DNR laboratory. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA et al. 1992).

The remaining sample was filtered for metals and sulfate analyses. Additional 100 mL samples for the EcoBond-ARD cells were filtered for total phosphate and orthophosphate analyses and were analyzed at MDA. Total phosphorus samples were acidified with 0.4 mLs of sulfuric acid and orthophosphate samples were frozen.

Calcium, magnesium, sodium and potassium were determined with a Varian 400 SPECTRAA. An inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A) was used for the remaining metals analyses. Sulfate concentrations were determined using a Lachat QuickChem 8000 or, for [SO₄] < 5 mg/L, a Dionex ion chromatograph. For total phosphorus and orthophosphate analyses the Ascorbic Acid Method (Wastewater Method 4500-P E) on a Perkin Elmer 552 Spectrophotometer was used.

4.6. Reaction Conditions

Between rinses the samples were retained in the cells to oxidize. The cells were stored in a room in

which temperature and humidity were controlled. Temperature was regulated by a thermostatically-controlled heater, and humidity was controlled by a humidifier and dehumidifier, both of which were controlled by humidistats. Over the 168-week period of record, temperature and relative humidity were measured three to four times a week ($n = 158$) with a Taylor wet-bulb, dry-bulb hygrometer. Temperature ranged from 22.2°C to 27.5°C and averaged 24.5°C, with a standard deviation of 1.2°C. Relative humidity ranged from 51.3 to 63.5 and averaged 57.3, with a standard deviation of 1.8%.

4.7. Microscope Observations

An initial microscopic evaluation was conducted with an environmental scanning electron microscope (ESEM) at the University of Minnesota. Several samples were hand picked from the top of the unleached control and the cell treated with 1% KB-SEA™.

The unleached cell treated with 3% KB-SEA™ was dismantled to provide additional samples for microscopic evaluation. During this process, samples were examined with an optical microscope. Additional samples were selected from this cell and analyzed by Peter McSwiggen of McSwiggen and Associates. Analyses were done with a JEOL Electron Probe Microanalyzer (electron microprobe), model 8600, using an accelerating voltage of 15 kV and a beam current of 20 nanoamps. Mineral and metal standards were used for all calibrations.

Sulfide mineral grains were hand-picked from the samples. Whenever possible iron oxide clusters were also collected. These hand-picked items were then embedded in an epoxy mount and polished for analyses. After polishing, each mount was carbon coated to ensure that they had a conductive surface to eliminate charging from the electron beam.

A number of sulfide mineral grains were analyzed in order to determine the amount and nature of the reaction between the commercial products and the sulfide grains. For each sulfide grain, a backscattered electron image was collected for the area surrounding the analysis location. A line analysis was then made from the inner portion of the sulfide grain, across its outer edge and into the surrounding epoxy. These line analyses show the relative variations in Fe, S, and components of the commercial products. They also show the degree of oxidation that took place at the interface, and the degree to which the commercial product was still coating the surface.

For the KEECO product the pyrite grains that were analyzed came from bottom quarter of the reactor (layer 4). Two chunks of iron oxide were also analyzed in an attempt to determine the differences between these and the non-reacted sulfide grains. These came from layer 2 in the reactor, which was the second quarter from the top. One set of element maps was collected from one of the iron oxide chunks. This was to show the nature of the iron coating and how it surrounded rock fragments and cemented them together (Appendix 3).

For the Ecobond product, no good samples of oxidized pyrite grains (iron oxides) were found. Several were examined but they appeared to be from oxidized steel, and were most likely from the grinding process. The pyrite grains that were used came from layers 3 and 4.

5. RESULTS

5.1. Solid-Phase Analyses

Ninety percent of the material was within the target size distribution of -1/4", +65 mesh. Only about 5% was less than 200 mesh (Table 2). Six sub-samples of the material used in the cells were analyzed for total sulfur and sulfate. Total sulfur averaged 2.04% and ranged from 1.55-2.45% (Table 3, Appendix 1). About 98% of the sulfur was present as sulfide.

Evolved CO₂ measurements were very low and indicated the absence of carbonate in the material. Values ranged from less than detection (<0.05%) to 0.11%.

The major elements in the greenstone samples were silica (73.4% SiO₂), aluminum (8.7% Al₂O₃) and iron (8.6% Fe₂O₃; Table 3). Although detailed mineralogy was not conducted on this sample, mineralogic analyses of other samples from the area have shown that the major minerals present are quartz (Si O₂), sericite (K Al₂Si₃ O₁₀ (OH)₂) and chlorite (a complex Mg, Al, Fe silicate) (Lakappo et al., 2002) (Additional work is under way to determine the exact composition of the chlorite in this formation (Lapakko et al., 2002). Since this material was not associated with any ore body, the trace metal content was low. Chromium was present in the highest concentration (226 mg/kg), followed by Zn (102 mg/kg; Table A1.5).

Acid production potential (APP) was calculated from the average sulfide content (2%) to be 62.5 kg CaCO₃ equivalents/metric ton. The average neutralization potential was 5.5 kg CaCO₃/metric ton and was determined using the Sobek procedure and back titrating to an endpoint of 8.3 (Attachment A1.1).

5.2. Application of Microencapsulation Products

EcoBond-ARDTM dissolved completely and was very easy to apply. The material in the cell was flooded and when the cell was drained, there was no evidence of preferential flow or uneven application.

The KB-SEATM was applied as a slurry. This material needed to be shaken periodically and was more difficult to apply than EcoBond-ARDTM. Although the material in the cell appeared to wet completely, the suspended material from this slurry was not evenly distributed throughout the cells and it is possible that some of the rock was not completely treated with this application method. Material had accumulated on top of the cells and in layers in parts of the cells (Figure 5, Appendix 9). The amount of material visible in the cells increased with increasing application rate.

5.3. Drainage Quality

In the September 2002 report (Eger and Antonson, 2002), water quality results from the beginning of the experiment through week 60 were presented for the controls and the cells treated with KB-SEATM. Results for the cells treated with EcoBond-ARDTM were presented through week 59 since

the product had not been able to prevent the generation of acid drainage and the reactors had been terminated. New data from the reactors treated with the KEECO product and control reactor 1 for weeks 60 through 168 will be presented in this report. Control reactor 8, and three of the original Ecobond reactors were shipped to MT² in January 2003. MT² had agreed to retreat the reactors to see if their product could stop the acid generation from the oxidized material.

5.3.1. pH

5.3.1.1. Control Cells (Cells 1, 8)

There was some difference in the initial water quality from the untreated controls (cells 1,8). The initial pH varied from 6.54 in cell 1 to 5.6 in cell 8. However, pH decreased quickly in both controls and was less than 4 in both cells after 10 weeks. The pH then decreased to about 3.3 after 19 weeks and has remained at that level for the duration of the experiment (Figure 6, Tables 4, 5).

5.3.1.2. KEECO KB-SEATM (Cells 2, 3, 4, 5, 6, 7)

The initial pH from all the cells treated with KB-SEATM, was essentially 12 or greater. The pH declined slowly and the rate of decrease was correlated to the application rate. In the cells treated with 1%, pH declined to below 10 after 5 weeks, while in cells treated with 5%, the pH did not remain consistently below 10 until week 34. After 60 weeks pH ranged from 7.6 to 7.74 for the cells treated with 1%, and from 9.1 to 9.5 for cells treated with 5% (Figure 6).

The pH continued to decrease in all the KEECO reactors. By week 140, the pH in the reactors treated with 1% KB-SEATM had dropped to below 7, and continued to decrease to about 6.5 at week 168 (Figure 6).

The pH was higher in the reactors treated with 3 and 5% KB-SEATM. In the reactor treated with 3% product, the pH leveled out at about 8 at week 80 and remained at that level through week 168 (Figure 6).

It took about 75 weeks for the pH from the reactors treated with 5% product to decrease below 9. Since that time, the pH has fluctuated between 8 and 9, but the overall trend has been to lower values (Figure 6).

5.3.1.3. EcoBond-ARDTM (Cells 9, 10, 11, 12, 13, 14)

Initial pH from the cells treated with EcoBond-ARDTM ranged from 8.4 to 9.06. The cells treated with the material from the company office of MT² (cells 9,11,13) had a higher pH than the cells treated with the solution made from the chemicals obtained from Lerch. The pH decreased in all treated cells with time and the decrease was independent of application rate. The pH dropped to below 6 after 12-13 weeks, and was generally below 4 after 27-31 weeks. At week 59, when the cells were stopped, the pH in all the treated cells was within about 0.2 pH units of the untreated controls (Figure 6, Table 5).

5.3.2. Sulfate

5.3.2.1. Controls

Although the sulfate concentrations followed similar trends in both control cells, the average concentration in cell 8 was about 15% higher than cell 1 during the first 20 weeks (Tables 4, 5). Sulfate concentrations decreased after the initial rinse to around 60 mg/L but increased sharply after week 10, when the pH dropped below 4. Concentrations peaked between 180-200 mg/L during weeks 12-14, and then decreased to about 130 mg/L. Concentrations in both cells slowly decreased to around 100 mg/L at week 60, and continued to decrease with time in reactor 1 to around 70 mg/L at week 168 (Figure 7).

5.3.2.2. KEECO KB-SEA™

Sulfate concentrations were lower than the controls, and sulfate concentrations tended to decrease with increasing application rates, particularly during the first 12 weeks. In the 1% cells, sulfate concentrations ranged from 36 to 108 mg/L, but dropped to below 10 mg/L after week 20. At sixty weeks, sulfate concentrations were around 7 mg/L. Concentrations have increased slightly since week 60, and were about 12-13 mg/L after 168 weeks. In the cells that were treated with higher application rates, the initial concentrations were lower but concentrations decreased less quickly than the 1% cells. At sixty weeks, the sulfate concentration in these cells was around 10 mg/L, and concentrations continued to slowly decrease (Figure 7). At 160 weeks, concentrations ranged from around 2.5 mg/L for the reactor treated with 3% product to about 6 mg/L for the 5% reactors (Figure 7).

5.3.2.3. EcoBond-ARD™

Initial sulfate concentrations varied by a factor of two between the duplicate cells, with concentration increasing with application rate. The maximum concentration was 1510 mg/L. Concentrations dropped rapidly, with concentrations in all cells decreasing to around 40 mg/L by week 14. Concentrations remained relatively consistent throughout the remainder of the experiment. Average sulfate concentrations ranged from 41 to 52 mg/L in weeks 20 to 59, and were less than one-half the value of the control (Table 5).

5.3.3. Calcium, Magnesium

5.3.3.1. Control cells

Initially, calcium concentrations ranged from 10.6 to 13.9 mg/L and exceeded magnesium by about a factor of 3. Calcium fluctuated during the first 14 weeks, decreasing to less than 10 mg/L, then approaching or exceeding the initial value in weeks 12-14. After week 14, concentrations decreased and fell to < 4 mg/L and were less than magnesium (Figures 8, 9). Calcium continued to decrease reaching about 2 mg/L at week 160.

Initial magnesium concentrations were less than 5 mg/L in both cells. The maximum values were observed during weeks 12-14, when concentrations ranged from 11-12 mg/L. Concentrations then decreased and were generally between 5-6 mg/L at the end of 50-60 weeks (Figure 9), and decreased to around 3 mg/L at week 160.

5.3.3.2. KEECO KB-SEA™

Initial calcium concentrations were elevated in all cells, with concentrations increasing with application rate. Calcium ranged from 93-124 mg/L in the 1% cells, to 185-269 mg/L in the 5% cells. Concentrations decreased over time in all cells, with concentrations at 60 weeks ranging from 6-10 mg/L in all cells (Figure 8). Concentration decreased slowly after week 60. After 160 weeks calcium was about 5 mg/L in the 1% reactor, and ranged between 5 and 8 mg/L for the cells that received higher applications.

Magnesium concentrations were uniformly low in all treated cells. Concentrations ranged from less than 0.1 mg/L to 0.3 mg/L for the 1% cells, to generally <0.1 mg/L in the cells treated with higher (3-5%) application rates (Figure 9, Table 4). Magnesium concentration have remained low for the duration of the experiment and remained in the same range as observed at 60 weeks (Figure 9).

5.3.3.3. EcoBond-ARD™

Calcium and magnesium were uniformly low in all the treated cells, and generally ranged from 0.5 to 5 mg/L. With the exception of the first two samples in all cells, calcium generally exceeded magnesium (Figures 8, 9, Table 5).

5.3.4. Metals

Trace metals were only analyzed during the first ten weeks of the experiment. Concentration had decreased over time, and a decision was made to focus on pH and sulfate.

5.3.4.1. Controls

Select samples were analyzed for iron, aluminum, copper, nickel, cobalt, zinc and arsenic. With the exception of arsenic, which was always at or below the detection limit of 0.002 mg/L, metal concentrations increased as pH decreased and reached their maximum value between weeks 10 and 24 (Appendix 4). Aluminum increased from less than 0.02 mg/L to around 10 mg/L and exceeded calcium and magnesium. Although iron also increased, its maximum concentration was only about 1 mg/L. Maximum observed concentrations for the other metals were: copper 0.26 mg/L, nickel 0.19 mg/L, cobalt 0.14 mg/L, and zinc 0.20 mg/L (Appendix 4).

5.3.4.2. KEECO KB-SEA™

In contrast to the control cells, aluminum and iron generally decreased with time. The initial

aluminum concentrations were around 1 mg/L and increased to between 2 and 3.5 mg/L during weeks 3-4, and then decreased. Concentrations at 60 weeks ranged from 0.12-0.15 mg/L in the 1% cells to 0.8 to 0.96 in the 5% cells.

The maximum iron concentrations of 0.6-2.0 mg/L occurred in the initial samples. Concentrations decreased to less than 0.1 mg/L by week 6, and by week 60 all cells had iron concentrations less than 0.01 mg/L. Since week 60, iron concentrations have fluctuated slightly but have remained below 0.1 mg/L. Arsenic, copper, cobalt, nickel and zinc were all at or near the detection limit of 0.002 mg/L throughout the experiment (Appendix 4, Table 4).

5.3.4.3. EcoBond-ARD™

There was extreme variability in the metal concentrations for the cells treated with EcoBond-ARD™, although all cells had higher concentrations than the controls. Cells 9, 11, and 13 had substantially higher concentrations than the duplicate cells (cells 10, 12 and 14). Initial aluminum concentrations varied by an order of magnitude while iron varied by two orders of magnitude. Maximum concentrations were measured in cell 13 (4.5%), with 28.2 mg/L iron, and 4.0 mg/L aluminum. This cell also had the maximum concentrations of the other metals: arsenic 0.8 mg/L, copper 0.7 mg/L, nickel 0.1 mg/L, cobalt 0.02 mg/L and zinc 0.17 mg/L.

While copper, cobalt, nickel and zinc concentrations were about an order of magnitude lower in the even number cells, arsenic was elevated in all cells and ranged from about 0.4 to 0.8 mg/L and did not drop below 0.05 mg/L until after week 4. By week 4 the other trace metals had decreased to below the detection limit of 0.002 mg/L (Appendix 4, Table 5). Metal concentrations increased as pH decreased, and the average values during weeks 20-60 were about an order of magnitude higher than the average for the first twenty weeks (Table 5).

Iron concentrations also decreased initially but then increased as the pH continued to decrease. At week 51 iron concentrations ranged from around 1.5 to 10 mg/L and were almost an order of magnitude higher than the controls. Aluminum concentrations also increased and were generally between 2-3 mg/L at week 51.

5.3.5. Phosphorus

Phosphorus concentrations in the control were very low, and initially ranged from 0.01 - 0.02 mg/L. By week 10, the concentration had decreased to below the detection limit of 0.01 mg/L. In the cells treated with EcoBond-ARD™, phosphorus concentrations were elevated during the initial part of the experiment with almost all of the phosphorus in the ortho (biologically available) form. Initial phosphorus concentrations were extremely high and ranged from around 1300 to 3900 mg/L. Although phosphorus concentration decreased rapidly, concentrations did not decrease below 0.03 mg/L until after week 14 (Tables, 5, 7, Appendix 4).

5.4. Mass Release

5.4.1. Total Mass Release

The total mass of calcium, magnesium sulfate and alkalinity were calculated for the control reactor 1 and the KEECO reactors from the beginning of the experiment through week 168 (Appendix 6). A linear interpolation was used to estimate concentrations for dates when no samples had been collected.

Total sulfate release for the control reactor 1 was about 73 millimoles, about 7 times greater than the release from the 1% reactors (2, 3) and about 10 times the release from the reactors treated with 3 and 5% KB-SEA™ (Table 6).

Calcium release from the KEECO reactors was 2 to 5 times higher than the control and generally increased with application rate. Alkalinity release also tended to increase with application rate (Table 6).

5.4.2. Release Rates

The rates of release were determined from a linear regression of the cumulative mass released from the cell versus time plots (Appendix 6). Data from weeks 20-51 were used to determine rates for the EcoBond-ARD™ cells, while data from weeks 20-60 and for weeks 60-168 were used to determine rates for the KB-SEA™ cells and the control. Twenty weeks was chosen as the starting point for several reasons: it minimized the impact of the initial rinse phase; the mass release versus time plots were generally linear for this time period; and by choosing this time period, the release rates could be directly compared to those in a related study with similar material (Lapakko et al., 2002). Sixty weeks was chosen primarily because rates through week 60 were calculated in the September 2002 report and the mass release versus time plots were essentially linear for the 60-168 week interval.

Sulfate release, which is a direct measure of acid generation, was highest in the control cell and averaged 0.58 millimoles/kg/week for weeks 20 to 60 and decreased to 0.37 millimoles/kg/week for weeks 60-168 (Table 7). Rates for the cells treated with EcoBond-ARD™ were about 40% of the controls and ranged from an average of 0.22 millimoles/kg/week for the 4.5% cells to 0.26 millimoles/kg/week for the 1.5% cells. Rates were much lower for the material treated with KB-SEA™. During weeks 20 to 60, rates were lowest in the 1% cells (0.04 millimoles/kg/week) and highest in the 3% cells (0.10 millimoles/kg/week). Sulfate release rates increased by 25-40% during weeks 60 to 168 in the 1% cells, while rates in the 3 and 5 percent reactors decreased substantially. The largest decrease was observed in reactor 5 (3%) where the rate decreased from 0.10 millimole/kg/wk to 0.02 millimoles/kg/wk (minimum rate measured). Rates in the 5% reactors also decreased, but only by 20-40%. (Table 7).

In the first part of the experiment calcium release from the controls averaged 0.05 millimoles/kg/week and was slightly lower in the cells treated with EcoBond-ARD™ (0.03-0.04 millimoles/kg/week; Table 7). Rates were two to three times higher in cells treated with KB-

SEATM and ranged from 0.08 to 0.17 millimoles/kg/week, with the maximum release from the 3% cells. From week 60 to 168 calcium release decreased in all reactors but the release was still higher on the KEECO reactors than the control. The decrease ranged from about 20% for reactor 2 (1%) to about 50% for reactors 5 (3%). Calcium release increased with application rate (Table 7).

Initial magnesium release rates in the control cells averaged 0.12 millimoles/kg/week and was about three times higher than the rate calculated for the EcoBond-ARDTM cells (0.03-0.04 millimoles/kg/week) and over an order of magnitude higher than the 1% KB-SEATM cells (0.004-0.005 millimoles/kg/week). Magnesium rates decreased by about 40% in the controls and increased slightly on the 1% reactors. Magnesium concentrations in the other KB-SEATM cells were generally below the detection limit of 0.1 mg/L for the entire experiment, so the release rate could not be calculated.

5.5. Microscope Evaluation

Images obtained from the environmental scanning electron microscope (ESEM) revealed the presence of globular structures in the cell treated with 1% KEECO KB-SEATM (Appendix 3). The structures were not found in the control cell and appeared to be related to the application of the KEECO product. Although these structures were present on the sulfide surfaces, there appeared to be a general coating on the entire solid. Since it was not possible to visually distinguish the mineralogy of the surface, the specificity of the coating could not be determined.

Additional microscope evaluation, using a combination of a scanning electron microscope and a microprobe, did provide detailed chemical information on the surface.

5.5.1. KEECO KB-SEATM

5.5.1.1. Unleached

5.5.1.1.1. Product

A rock fragment with a visible coating of the KEECO product was selected to determine the general properties of the product (Figure 10, 11). The coating contained three macroscopic textures; a rounded “bead-like” structure (Figure 12), which was observed earlier using an environmental scanning electron microscope (Appendix 3), angular mineral fragments, and acicular (needle-like) grains. Electron microprobe analyses of the beads show that they are mostly Si, Al, and Ca (Appendix 3). The mineral fragments are quartz grains, and the acicular grains are also a Si, Al, Ca phase.

5.5.1.1.2. Pyrite Cubes.

Individual pyrite cubes were selected from the reactor and were mounted, cut and polished (Figure 13,14). Several cubes were examined to determine the interaction of the KEECO product with the sulfide surface.

The first surface that was examined had product “beads” on the outside of the surface and a “transitional zone” at the surface of the pyrite (Figure 15). In the transition zone, which was on the order of 15 microns, calcium and silica were mixed with sulfur (Figures 16).

Additional analyses of other surfaces did not show this type of transition zone. Although product was observed on most surfaces, possible interaction zones were much smaller; on the order of 2-3 microns (Figures 17).

The product was also observed as a coating on other rock fragments including quartz mineral grains. This indicated that the product had coated other mineral phases, even though it may not have actually chemically reacted with them. Additional data from the microscopic evaluation is presented in Appendix 3.

5.5.1.2. Leached Reactor

5.5.1.2.1. Pyrite Cubes

Several sites on five different pyrite grains were selected for microprobe analyses (Figure 18). Some of the sites had obvious zones of oxidation (Figure 19), while others did not have any apparent oxidation on the surface (Figure 20).

On the oxidized grains, elemental analyses revealed that oxygen had diffused into the pyrite and this reaction zone typically varied from about 2 to 15 microns. Some surfaces contain an abundance of sulfur in this oxidized zone (Figure 20) and others contain only a minimal amount (Figure 21). Silica was generally present along the edge of the crystal indicating the presence of the KEECO coating. However, oxygen penetration and the thickness of the reaction zone do not appear to be correlated with the presence of the silica on the pyrite surface. The immediate presence or absence of the KEECO product control does not appear to control whether an oxide layer develops on the surface of a pyrite grain, and other micro-chemical environmental changes must also play a role.

5.5.1.2.2. Oxidized samples

Samples were also chosen that were thought to be highly oxidized sulfide grains (Figure 23). However microscopic evaluation suggest the pyrite grains may not have actually been significantly oxidized themselves, even though the pyrite is surrounded by massive amounts of iron-oxide. The sulfide grain shown in Figure 24, though surrounded by iron-oxide, is still the same size and general shape as the neighboring pyrite grains that are contained in the rock fragment and isolated from the iron-oxide. The pyrite enclosed in the iron-oxide still has sharp, angular edges. Oxidized pyrite grains are generally irregular-shaped remnants of the former grains (P.McSwiggen, personal communication, 2004).

In addition, Si and Al (Figure 24) are present at the boundary between the sulfide grain and the iron-oxide (Figure 24). The Si and Al probably represents a thin coating of the KEECO product on

the original pyrite surface, and thereby marks the original crystal face. This suggests that the iron oxide is not a break down of this pyrite grain, but that this location is a nucleation site for oxide growth.

5.5.2. Ecobond-ARD™

5.5.2.1. Unleached Reactor

5.5.2.1.1. Pyrite Cubes

The Ecobond ARD was applied as a clear liquid, therefore there was no residual material visible in the reactor as was observed in the KEECO reactor. The pyrite grains from the unleached reactors do not appear to contain significant coatings of the Ecobond product (Figure 25). Electron microprobe analyses did show that many of these grains have a thin coating of K and P indicating the presence of the Ecobond product (Figure 26). In some cases the K and P concentrations are offset from the actual edge of the pyrite grain by about 5 to 7 microns (Figure 26). This offset is due to shrinkage within the epoxy.

As the mounting epoxy cures, it tends to shrink a small amount and it can pull away from the pyrite grain. This can leave a gap between the epoxy and the pyrite grain. This gap can be seen on many of the backscattered electron images. The fact that the K and P coating were easily pulled away from the pyrite grain indicates that it was a simple coating on the grain and was not chemically bonded to it. There is no evidence of P or K intermixing with the pyrite components.

5.5.2.2. Leached Reactor

5.5.2.2.1. Pyrite Cubes

The pyrite cubes from the Ecobond reactors have visible oxidation and contained an oxidized “rind” typically 5 to 10 microns thick (Figures 27-29). In some cases, the oxidized layer had been pulled away from the crystal face by the epoxy (Figure 28) while in other samples the oxidized layer adhered to the crystal face (Figure 29). The position of the layer is a measure of the tensile strength of the oxide layer. Those coatings with poor tensile strength may be secondary oxide coatings, while those that are strongly bonded to the crystals may represent early stages of oxidation of the pyrite crystal itself.

Low to trace amounts of P and K was present near the crystal edge and appeared to be generally associated with the oxidized iron layers (Figure 28 and 29). Silica was also observed in several of the oxidized areas (Figure 29) suggesting the formation of iron-silica-hydroxide. There was no obvious decrease in sulfur within the pyrite, but oxygen penetration had occurred and ranged in depth from 2-8 microns.

6. DISCUSSION

6.1. Controls

The ratio of acid production potential to the neutralization potential was 11.4, and as expected, the control cells produced acid drainage. Since the greenstone material contained almost no carbonates, the neutralization potential was very low. Only minor amounts of siderite (FeCO_3) were observed in mineralogic analyses of greenstone samples from this area (Lapakko et al., 2002).

With little to no carbonate, neutralization must come from the dissolution of silicate minerals, primarily chlorite (a complex magnesium, aluminum, iron silicate) and sericite (a potassium, aluminum silicate ($\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$)). Given the low neutralization potential for this material, calculated acid production potential exceeds the neutralization potential at 0.18% sulfide. The pH from greenstone samples from this area with 0.2% sulfur dropped below 6 after 20 weeks and decreased to around 4.2 at 60 weeks (Lapakko et al., 2002).

Sulfate release, which is directly proportional to the rate of sulfide oxidation, was 0.58 millimoles/kg/week for weeks 20 to 60. This rate was about two times higher than observed in laboratory experiments using greenstone samples with about one-half the sulfur content. Sulfate release rates in that study generally increased with increasing sulfur content, and ranged from 0.005 millimoles/kg/week for 0.04% sulfur to 0.25 millimoles/kg/week for 1.22% sulfur (Lapakko et al., 2002).

The release rates of calcium and magnesium were also about twice the rate measured from the cell with 1.22% sulfur. Initial calcium and magnesium release may come from carbonate phases contained within the small amounts of siderite present, but most of the magnesium release is believed to be due to the dissolution of the complex silicate minerals, particularly chlorite (Lapakko et al., 2002).

6.2. EcoBond-ARD™

Although the cells treated with EcoBond-ARD™ were initially successful in maintaining pH above 6.0, the treatment was not effective in preventing the formation of acid drainage. Although the specific nature of EcoBond-ARD™ is proprietary, the product contains phosphate and was developed based on the reaction of phosphate with ferric iron to form an insoluble iron phosphate compound. Ideally this compound would form on the surface of the iron sulfide minerals and render the remaining surface unreactive.

Phosphate application has been shown to reduce sulfide oxidation (Evangelou, 1995, 2001). Evangelou used hydrogen peroxide (H_2O_2) to oxidize pyrite to produce ferric iron ions which combined with phosphate in solution to form an insoluble compound (FePO_4). The amount of pyrite oxidized in the material treated with phosphate was over an order of magnitude lower than the control and about 99% of the iron released was retained in the test column (Evangelou, 2001). SEM photos confirmed the presence of an iron phosphate coating on the pyrite surface (Evangelou,

1995). Although the phosphate coating was initially successful in decreasing the rate of sulfide oxidation, the effect of the coating decreased as pH decreased. The decrease in treatment efficiency was thought to be the result of the dissolution of the ferric phosphate coating at low pH (pH <4; Evangelou, 1995). Once the coating dissolved, the rate of sulfide oxidation was essentially equal to the untreated control.

This was the first trial to use EcoBond-ARD™ to prevent sulfide oxidation. In previous trials with this product on mine waste, the waste was already oxidized and contained elevated concentrations of ferric iron and other trace metals. As a result, when these materials were treated, insoluble iron and phosphate compounds were formed and metal release decreased (Gobla et al., 2000).

Since the objective of this study was to determine if the microencapsulation chemicals would prevent acid drainage from unoxidized material, only small amounts of ferric iron were present initially in the cells. To compensate for the potential lack of ferric ions, the product contains an oxidizing agent which is designed to attack unreacted sulfide surfaces and generate ferric iron. Metals Treatment Technologies initially requested that the cells be saturated with their product for 24-48 hours. In Evangelou's study with phosphate, the samples were in contact with the applied chemical for 3-4 days (Evangelou, 2001). Since the long term goal of this project was to determine if these technologies could be applied to a large waste rock stockpile, the saturation time was restricted to 10 minutes. The time was arbitrarily chosen to ensure that, at a minimum, all the rock surfaces would be contacted. For a full scale stockpile, the product would most likely be sprayed onto the surface so there would be very few saturated areas. However, the first rinse did not occur until one week after application, while in an actual field setting rainfall could occur anytime after application.

Microscope evaluation of unleached pyrite cubes treated with Ecobond ARD™ did have phosphorus along the edge of the crystal, but there was no evidence of interaction with the pyrite. The presence of product along the edge may be an artifact of experimental conditions. The reactors were flooded with the product and then drained. No rinsing was done to remove any residual solution. As a result, as the interstitial water that was originally present evaporated during storage, product was left on all surfaces.

For some of the pyrite samples a crack developed as the epoxy pulled away from the crystal during drying and in several of the images the phosphorus peak was separated from the crystal. This suggests that the phosphorus had not reacted with the crystal but was more likely left on the surface when the residual product solution evaporated.

Oxidation was visible on the pyrite cubes from the leached reactors, which was expected since the Ecobond reactors had produced acid drainage. In general, there was evidence of product at the edge of the pyrite in the leached samples, but oxygen had penetrated into the pyrite, from about 2 to 15 microns. In some samples the sulfur in the pyrite decreased but in most the sulfur remained unchanged and suggested only minimal reaction.

The most likely explanation for the failure of Ecobond ARD is the absence of ferric iron in the fresh unoxidized material. The short application time (about 10 minutes) was not long enough to produce enough ferric iron to react with the phosphate in the Ecobond product.

Although the treatment did not prevent acid drainage, the sulfate release rates were less than half of the control cell. Visually there was less oxidation in the treated cells than in the controls, but the degree of oxidation increased with time (Figures 30, 31, 32).

After the cells began producing acid drainage, MT² was contacted and asked if they would be interested in retreating the cells. Although the product did not prevent acid drainage, it might still be an effective control. Some of the sulfides in the material had oxidized and might contain sufficient ferric iron to react with the phosphate in the EcoBond-ARDTM. The company was not interested and the cells were stopped at week 59. Later the company agreed to re-treat and run one of the duplicate sets of cells in their laboratory. A set of reactors was sent to the company in January 2003 but the tests were never done.

There were several other water quality issues associated with the use of EcoBond-ARDTM. Initial samples contained elevated levels of arsenic and some contained elevated copper (Table 8). Arsenic concentrations were about two orders of magnitude higher than the controls and ranged from 400-800 ug/L, well above the current federal drinking water standard of 50 ug/L and proposed drinking water standard of 10 ug/L. While the trace metal concentrations decreased by week 2, arsenic remained above 100 ug/L for the first 3-4 weeks and did not decrease to 10-20 ug/L until 8 weeks.

Since EcoBond-ARDTM is a phosphate-based chemical, both total and ortho phosphates were measured in the control cell (8) and in all treated cells. Phosphorus concentrations were elevated during the initial part of the experiment with almost all of the phosphorus in the ortho or biologically available form. Phosphorus is the limiting nutrient in aquatic systems and concentrations above 0.03 mg/L are generally believed to lead to excessive algal growth and eutrophication. Although phosphorus concentrations decreased rapidly, concentrations did not decrease below 0.03 mg/L until after week 14 (Table 8).

The elevated concentrations of arsenic and phosphorus would require that the drainage immediately following treatment be collected. It might be possible to use this water as process water, or some treatment or dilution would probably be required prior to discharge.

6.3. KEECO-KB-SEATM

All cells treated with KB-SEATM were successful in preventing acid drainage and reducing sulfide oxidation. Sulfate release rates were about an order of magnitude lower than the controls and after 168 weeks all pH's were still above 6. Silica treatments, although not with the KEECO product, have been shown to be effective in reducing sulfide oxidation (Evangelou, 2001). Evangelou's conceptual model includes two layers of silica coatings. Initially the silicate reacts with hydroxyl groups to form a silica polymer on the hydroxide surface that has formed on the pyrite. Once the surface has been coated, additional condensation of silica occurs to produce a surface silica film.

The feasibility of this theory was demonstrated by treating coated pyrite with different strength acids. Treating with 4 molar hydrochloric acid increased the rate of sulfide oxidation, but the rate was still only about half that of the control. When the sample was treated with 4 molar hydrofluoric acid all the silica was removed and the rate of oxidation was essentially the same as the control (Evangelou, 2001).

The treatment effect with KEECO KB-SEA™ may be related to several factors: high pH (due to the presence of quicklime in the product), cementation of the material (resulting in a macro encapsulation of the rock grains), and coating of the surfaces with silica. Visually there was little sulfide oxidation in the treated cells after 60 weeks but after 168 weeks, some oxidation was observed (Figures 33, 34, 35). The amount of visible oxidation decreases as the rate of application increased (Figure 36).

The solubility of silica increases with increasing pH, and in order to maintain pH and silica solubility, KB-SEA™ contains lime. In Evangelou's study, pH of the application solutions was adjusted to 6, and despite lower sulfide oxidation rates in the silica-treated columns, the pH dropped to below 4 (Evangelou 2001). In a laboratory humidity cell study, rotary kiln fines (a waste product generated when limestone is converted to lime (CaO)) were mixed with an unoxidized acid producing waste rock. Sulfide oxidation was reduced as long as the neutralizing capacity of the RK fines was present. However, once this capacity was depleted, sulfide oxidation rates increased to levels similar to those in the controls (Lapakko et al., 2000).

The KB-SEA™ contains 30-50% lime or CaO. Even at the lowest application rate (1%) and the lowest lime content (30%), only about 40% of the calcium applied initially has been removed from the reactor. At the current rate of calcium release it would take around 9 years to remove all the residual calcium from the reactor (Appendix 10).

When the unleached cell treated with 3% KB-SEA™ was dismantled to examine the material and collect samples for microscope analysis, about 50% of the rock grains were cemented together (Attachment A3.2). Many of the areas were so solid that water could not flow through the portion of the cell containing the cemented material. This cementation process effectively reduced the total area of sulfides in the cell and would reduce the overall sulfate release. The areas that were cemented tended to be composed of the areas with coarser rock grains. These areas had concentrated the suspended material that was part of the original slurry applied to the cell, and many of the grains were visibly coated (Figure 37). Despite this physical coating some sulfide oxidation could be observed, but overall there was very little visible oxidation (Figure 37; Appendix 3).

Microscope evaluation of the unleached and leached reactors did not clearly identify a mechanism or explain the success of the KEECO material. However, there was evidence for some interaction between the KEECO product and the pyrite, but in most images the product was on the outside of the crystal and oxygen had migrated into all the pyrite crystals.

One potential limitation of the microscope evaluation is that large pyrite crystals, although an easy crystal to analyze, have relatively little surface area and tend to be significantly less reactive than finer grained framboidal pyrite. Fine grained material is difficult to analyze since separating the original material from the secondary reaction products, is not straight forward. This is a particular problem with the KEECO product since many of the secondary reaction products contain silica, and silica peaks presumably from reaction products, were present in some of the oxidized zones in the Ecobond reactor. A more controlled experiment with pyrite crystals might provide a better model to determine the interaction of the KEECO product with the pyrite (Appendix 11).

In a field setting the high pH of drainage from an area treated with this product would need to be addressed. Since typically discharge limits for pH are 6-9, drainage from an area treated with KB-SEA™ might have to be collected, or, at a minimum, the effect of the drainage on the receiving waters would have to be evaluated.

7. CONCLUSIONS

Although EcoBond-ARD™ delayed the onset of acidification of an unoxidized greenstone rock containing 2% sulfur, it was not successful in preventing acid drainage. Untreated controls produced drainage with a pH below 6 after 1 week, while the pH in cells treated with EcoBond-ARD™ did not decrease to this level until week 12-16. Additional concerns with the EcoBond-ARD™ were elevated levels of phosphorus and arsenic in the drainage. Concentrations remained above concern levels for around 8 weeks for arsenic and 30 weeks for phosphorus.

KB-SEA™ was successful in preventing acid drainage at all levels of treatment and the rate of sulfide oxidation was about 10% of the rate measured in the untreated controls. However, the pH from all cells treated with this product were initially around 12 and although pH has decreased in all cells, the cells treated with 5% had pH values consistently above 9 for about 75 weeks.

The exact mechanism for the success of this product has not yet been determined. The pH has remained elevated due to the presence of lime in the product and much of the material in the cells has been cemented together, thereby reducing the flow of oxygen and water to pyrite surfaces. At least 60% of the calcium associated with the quicklime (CaO) applied with the KEECO product has been retained in the reactors and at the current calcium release rate it would take 9 years or longer to remove all the residual calcium.

Microscopic evaluation of pyrite crystals from one of the KEECO reactors treated with 3% KB-SEA™ found that although some silica was generally present on the surface of the pyrite crystals, oxygen had penetrated into the pyrite.

One potential limitation of the microscope evaluation is that large pyrite crystals, although an easy crystal to analyze, have relatively little surface area and tend to be significantly less reactive than finer grained framboidal pyrite.

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Table 1. Total sulfur and dissolved carbon dioxide analyses of high sulfur, low sulfur and blended samples. Analyses by Lerch Brothers.

TOTAL SULFUR (%)	DISSOLVED CARBON DIOXIDE (%)
High sulfur sample (3 analyses)	
2.58	0.08
2.32	0.04
2.42	0.02
Low sulfur sample (3 analyses)	
0.57	0.82
0.64	0.80
0.85	0.72
Blended sample (6 analyses)	
1.84	0.11
2.49	0.13
2.53	0.19
1.78	0.29
2.43	0.17
2.36	0.19

Mean analyses for blended sample: Total sulfur = 2.24 %
 Dissolved carbon dioxide = 0.18%

Table 2. Particle size distribution of blended sample. Analyses by Lerch Brothers.

SIZE FRACTION	PERCENT PASSING
¼"	100
4 M	84.9
10 M	40.8
20 M	26.1
28 M	19.8
35 M	16.4
48 M	12.5
65 M	9.9
100 M	7.9
150 M	6.3
200 M	5.1

Table 3. Average whole rock chemistry (percent) of blended greenstone sample. Analyses by ACTLABS, Inc.

Parameter	Result
S	2.04
S ²⁻ ¹	2.00
SO ₄ ²⁻ as S	0.04
CO ₂	0.06
Al ₂ O ₃	8.70
CaO	0.41
Fe ₂ O ₃ ²	8.63
K ₂ O	1.05
MgO	2.48
MnO	0.053
Na ₂ O	0.18
P ₂ O ₅	0.27
SiO ₂	73.36
TiO ₂	0.342
LOI	3.99
TOTAL ²	99.45

Average values of six replicate samples

¹Determined by difference.

²For parameters from Al₂O₃ through LOI2.

Table 4. Average drainage quality data for KEECO humidity cell. Concentrations reported in mg/L, pH in standard units, and specific conductance (SC) in $\mu\text{S}/\text{cm}$, (averages exclude anomalous values, Table A4.1). Values reported to be less than detection limit were multiplied by -0.5. (NA=not analyzed).

Cell	Period of Record (weeks)	pH	SC	ALK	ACY	SO ₄	Ca	Mg	Na	K	Al	Fe	As	Cu	Ni	Co	Zn
1	0 - 20	3.97	244	10	41	96	9.9	6.62	1.39	5.90	0.56	0.44	0.001	0.08	0.12	0.08	0.14
	21 - 60	3.34	320	NA	107	113	3.9	5.93	0.05	0.93	10.79	0.51	NA	0.193	0.159	0.112	0.082
	60-168	3.39	250	NA	79.4	77.7	2.6	3.65	NA	NA	6.42	0.28	NA	NA	NA	NA	NA
2	0 - 20	9.30	218	46	NA	44	29.7	0.13	1.48	4.01	2.12	0.03	0.001	0.003	0.001	0.001	0.002
	21 - 60	7.84	48	12.5	NA	7	7.1	0.21	0.00	0.67	0.13	0.002	NA	0.001	0.001	0.001	0.001
	60-168	7.08	36	5.3	NA	9.7	5.5	0.29	NA	NA	0.08	0.02	NA	NA	NA	NA	NA
3	0 - 20	9.42	265	55	NA	51	35.0	0.17	1.50	4.50	2.35	0.04	0.001	0.004	0.001	0.001	0.002
	21 - 60	8.23	57	16	NA	8	9.0	0.26	0.00	0.53	0.15	0.01	NA	0.001	0.001	0.001	0.001
	60-168	7.29	40	7.8	NA	10.5	6.3	0.29	NA	NA	0.16	0.02	NA	NA	NA	NA	NA
4	0 - 20	10.67	478	128	NA	21	49.1	0.05	3.13	5.85	1.93	0.06	0.001	0.003	0.001	0.001	0.001
	21 - 60	8.85	82	18	NA	19	13.8	0.06	0.20	1.12	0.65	0.01	NA	0.001	0.001	0.001	0.001
	60-168	7.92	35	13	NA	3.6	6.4	0.07	NA	NA	0.26	0.02	NA	NA	NA	NA	NA
5	0 - 20	10.74	474	138	NA	8	45.6	0.05	2.58	5.68	2.20	0.06	0.001	0.004	0.001	0.001	0.001
	21 - 60	9.09	82	15	NA	20	13.0	0.05	0.32	1.22	1.00	0.004	NA	0.001	0.001	0.001	0.001
	60-168	7.91	37	11	NA	5	6.7	0.07	NA	NA	0.31	0.02	NA	NA	NA	NA	NA
6	0 - 20	11.16	767	195	NA	18	79.9	0.05	4.74	10.60	2.10	0.12	0.001	0.004	0.002	0.001	0.001
	21 - 60	9.52	74	19	NA	13	10.5	0.05	0.57	1.96	1.16	0.003	NA	0.001	0.001	0.001	0.001
	60-168	8.69	48	15	NA	8	8.7	0.06	NA	NA	0.72	0.02	NA	NA	NA	NA	NA
7	0 - 20	10.85	495	111	NA	14	46.0	0.05	3.41	7.17	2.22	0.06	0.001	0.003	0.001	0.001	0.001
	21 - 60	9.41	62	16	NA	8	8.3	0.05	0.60	1.76	1.04	0.002	NA	0.001	0.001	0.001	0.001
	60-168	8.56	38	11	NA	7	6.8	0.05	NA	NA	0.66	0.02	NA	NA	NA	NA	NA

Table 5. Average drainage quality data for Ecobond humidity cells. Concentrations reported in mg/L, pH in standard units, and specific conductance (SC) in $\mu\text{S}/\text{cm}$ (Averages exclude anomalous values, Table A4.1.). Values reported to be less than detection limit were multiplied by 0.5. (NA = not analyzed)

Cell	Period of Record (weeks)	pH	SC	ALK	ACY	SO ₄	Ca	Mg	Na	K	Al	Fe	As	Cu	Ni	Co	Zn	OP	TP
8	0 - 20	4.14	269	31	NA	112	10.60	7.29	1.94	6.53	0.25	0.54	0.001	0.024	0.187	0.068	0.126	0.008	0.012
	21 - 60	3.37	327	NA	102	117	4.31	6.25	0.05	0.89	11.67	0.56	0.001	0.138	0.161	0.112	0.086	NA	0.011
9	0 - 20	6.32	374	360	2.5	93	1.52	0.72	0.90	137.4	0.11	0.28	0.094	0.011	0.001	0.001	0.002	265.4	239.3
	21 - 60	3.79	160	NA	35	50	3.07	1.84	0.00	4.87	1.30	5.84	0.001	0.186	0.084	0.077	0.084	NA	0.020
10	0 - 20	6.44	516	317	2.5	63	2.21	1.03	1.04	171.6	0.03	0.14	0.101	0.001	0.001	0.001	0.001	208.6	195.4
	21 - 60	3.76	168	NA	36	52	3.01	2.19	0.00	4.50	1.78	4.77	0.001	0.203	0.095	0.085	0.102	NA	0.022
11	0 - 20	6.19	1176	356	2.5	168	1.62	0.91	0.97	297.6	0.21	1.41	0.087	0.003	0.002	0.001	0.006	497.6	564.6
	21 - 60	3.80	156	NA	34	49	2.53	1.71	0.00	5.17	1.26	7.20	0.001	0.206	0.085	0.079	0.063	NA	0.017
12	0 - 20	6.53	867	503	2.5	94	1.84	0.90	0.95	274.7	0.05	0.10	0.087	0.001	0.001	0.001	0.001	387.8	331.4
	21 - 60	3.78	171	NA	34	48	2.99	1.89	0.00	4.84	1.37	5.96	0.001	0.231	0.096	0.086	0.104	NA	0.037
13	0 - 20	6.20	1210	889	2.5	172	1.55	0.82	1.13	173.1	0.18	1.19	0.077	0.002	0.001	0.001	0.004	576.5	561.2
	21 - 60	3.83	151	NA	33	47	2.37	1.54	0.00	5.48	1.07	8.08	0.001	0.193	0.078	0.075	0.063	NA	0.016
14	0 - 20	6.83	1214	714	2.5	164	1.11	0.68	1.30	436.6	0.03	0.01	0.082	0.001	0.001	0.001	0.001	8.98	487.0
	21 - 60	4.05	128	NA	22	41	3.26	1.71	0.00	5.98	0.69	5.06	0.001	0.164	0.068	0.062	0.067	NA	0.018

Table 6. Total mass release, control and KEECO humidity cells.

Treatment	Reactor	Mass released, millimoles		
		Sulfate	Calcium	Alkalinity
Control	1	72.7	7.45	NA
1 % KB-SEA	2	11.1	17.9	7.84
1 % KB-SEA	3	13.0	21.6	10.6
3 % KB-SEA	5	8.4	26.6	18.3
5 % KB-SEA	6	8.7	34.5	26.3
5 % KB-SEA	7	7.0	23.6 ¹	17.3

Notes

Cumulative release from the start of the experiment through week 168.

¹ Most of the difference in the calcium release between reactor 6 and 7 occurred during the first 20 weeks. (18.3 millimoles vs 10.7 millimoles) The initial calcium concentrations in reactor 7 were substantially less than in the rinse water from reactor 6.

Table 7. Rates of sulfate, calcium, and magnesium release for microencapsulation cells (rates in millimoles/kg/week).

Cell	Application rate	Period of record in weeks	n ¹	Sulfate		Calcium		Magnesium	
				rate	r ²	rate	r ²	rate	r ²
1	control	20-60	11	0.565	0.997	0.046	0.997	0.117	0.995
		60-168	18	0.368	0.998	0.030	0.997	0.068	0.996
2	KB-SEA™ 1%	20-60	11	0.035	0.999	0.084	0.994	0.004	0.999
		60-168	18	0.050	0.998	0.065	0.998	0.006	0.994
3	KB-SEA™ 1%	20-60	11	0.041	0.998	0.110	0.991	0.005	0.999
		60-168	18	0.052	0.912	0.069	0.912	0.006	0.910
4	KB-SEA™ 3%	20-60	11	0.095	0.895	0.172	0.973	0.001	0.997
		60-116	13	0.018	0.994	0.078	0.999	0.001	0.995
5	KB-SEA™ 3%	20-60	11	0.103	0.9935	0.164	0.9962	0.001	0.9999
		60-168	18	0.020	0.946	0.076	0.997	0.001	0.990
6	KB-SEA™ 5%	20-60	11	0.064	0.993	0.129	1.000	0.001	1.000
		60-168	18	0.038	0.985	0.103	0.997	0.001	0.980
7	KB-SEA™ 5%	20-60	11	0.043	0.991	0.104	0.998	0.001	1.000
		60-168	18	0.035	1.000	0.081	0.999	0.001	1.000
8	control	20-51	9	0.588	0.998	0.053	0.998	0.125	0.997
9	Ecobond-ARD™ 1.5%	20-51	9	0.255	0.997	0.040	0.975	0.037	1.000
10	Ecobond-ARD™ 1.5%	20-51	9	0.260	0.999	0.037	0.955	0.043	0.999
11	Ecobond-ARD™ 3%	20-51	9	0.242	0.999	0.031	0.969	0.033	0.999
12	Ecobond-ARD™ 3%	20-51	9	0.230	0.999	0.036	0.953	0.035	0.995
13	Ecobond-ARD™ 4.5%	20-51	9	0.233	1.000	0.029	0.967	0.030	0.997
14	Ecobond-ARD™ 4.5%	20-51	9	0.205	1.000	0.041	0.974	0.034	0.993

¹ n indicates the number of analyzed values during the rate period.

Rates were calculated from cumulative mass vs time plots; r² = correlation coefficient (Appendix 6).

Table 8. Additional water quality parameters of concern.

Cell #	Treatment	Parameter	Standard or level of concern (mg/L)	Initial concentration (mg/L)	Time required for concentration to decrease to standard (weeks)
EcoBond-ARD™					
9	1.5%	Arsenic	0.01 ^a	0.49	~8 ^d
		Copper	0.023 ^b	0.23	2
		Total phosphorus (Total-P)	0.03 ^c	1660	between 14 and 31 ^e
10	1.5%	Arsenic	0.01 ^a	0.45	~8 ^d
		Total-P	0.03 ^c	1340	between 14 and 31 ^e
11	3%	Arsenic	0.01 ^a	0.71	~8 ^d
		Copper	0.023 ^b	0.62	2
		Total-P	0.03 ^c	3930	between 14 and 31 ^e
12	3%	Arsenic	0.01 ^a	0.46	~8 ^d
		Total-P	0.03 ^c	2280	between 14 and 31 ^e
13	4.5%	Arsenic	0.01 ^a	0.79	~8 ^d
		Copper	0.023 ^b	0.72	2
		Total phosphorus (Total-P)	0.03 ^c	3910	between 14 and 31 ^e
14	4.5%	Arsenic	0.01 ^a	0.52	Between 8 and 14
		Total-P	0.03 ^c	3360	Between 14 and 31
KB-SEA™					
2, 3	1%	pH	6-9	12.0	7 ^f
4	3%	pH	6-9	12.3	28
5	3%	pH	6-9	12.4	52
6	5%	pH	6-9	12.4	74 ^g
7	5%	pH	6-9	12.3	70 ^g

^aRecently proposed federal drinking water standard.

^bMinnesota chronic aquatic toxicity standard, based on hardness 400 mg/L as CaCO₃.

^cGuideline, Total-P concentrations above this value can lead to excessive algal growth.

^dAt 8 weeks As was between 0.01-0.015 mg/L.

^eThe large time interval was due to limited sampling for this parameter.

^f1% cells were averaged, since there was essentially no difference between the cells.

^gpH fluctuated but was generally less than 9 after this time.

Figure 1. Schematic of humidity cell for laboratory Greenstone experiment.

All humidity cell materials are acrylic except the perforated plate (polyvinyl chloride) and the outlet pipe (high density polyethylene).

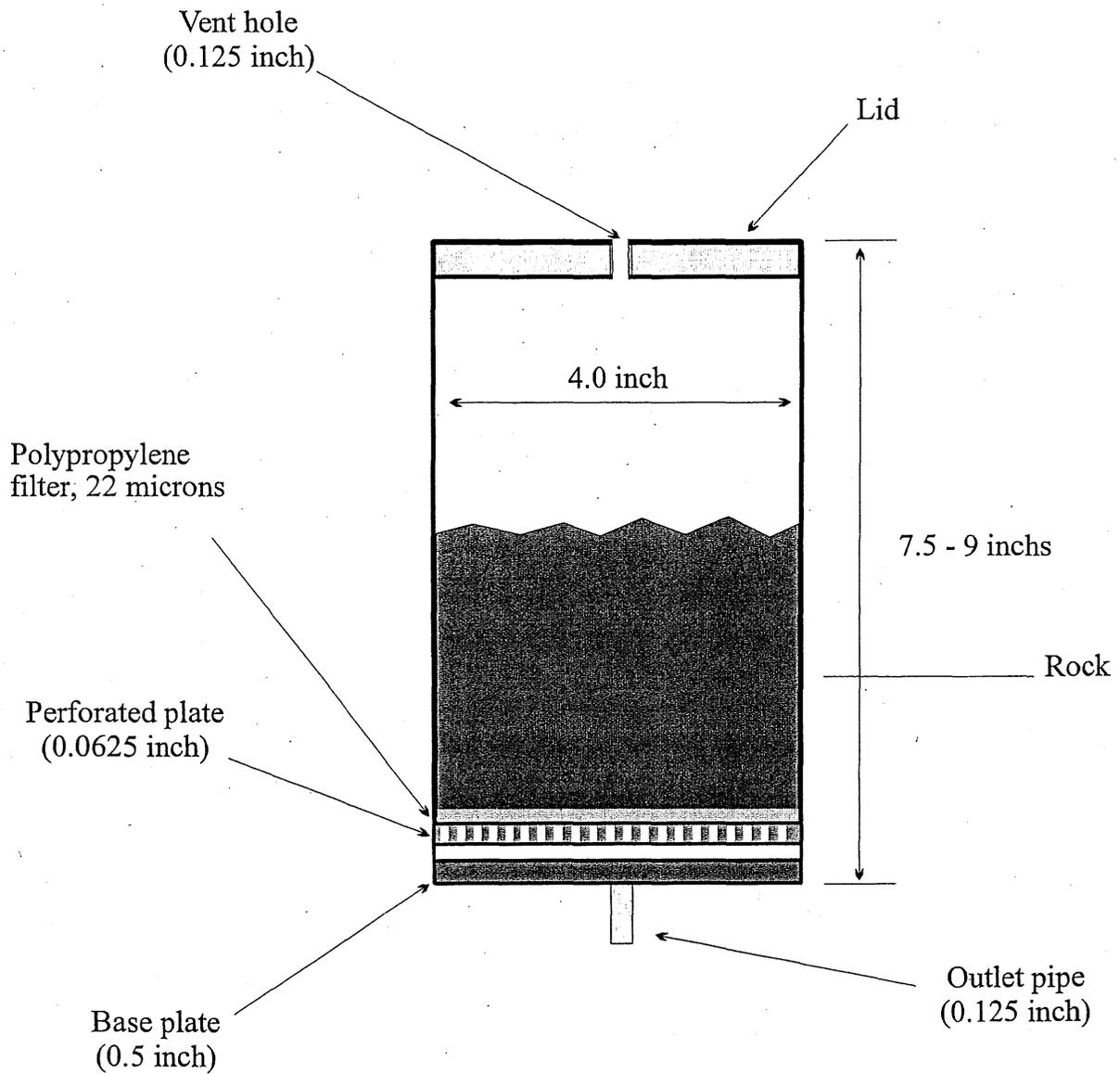


Figure 2. Application of microencapsulation products, overview. The bottom of the cell was left open until water began to drip out of the outlet port, then the port was plugged. The remaining solution was poured into the cell where it remained for 10 minutes. After this time, the outlet port was unplugged, and the solution was allowed to drain.

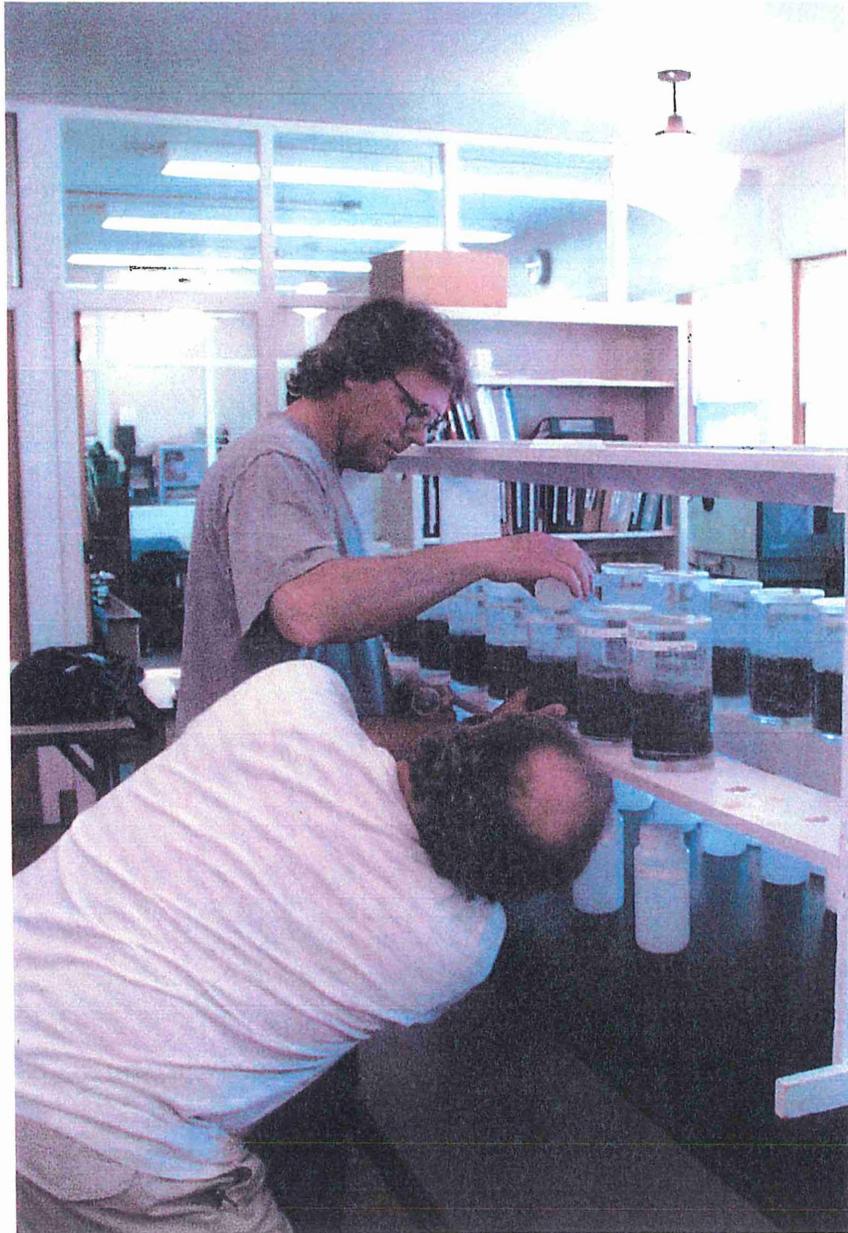


Figure 3. Addition of KEECO KB-SEA™



Figure 4. Cell storage in constant temperature and humidity room.



Figure 5. KB-SEA™ reactors, side view. Distribution of material in the KEECO cells reactors immediately after application. Since this was a slurry you could see the distribution within the reactor. Left to right, 5%, 3%, 1%.



Figure 6. Drainage quality results; pH vs. time for all cells.

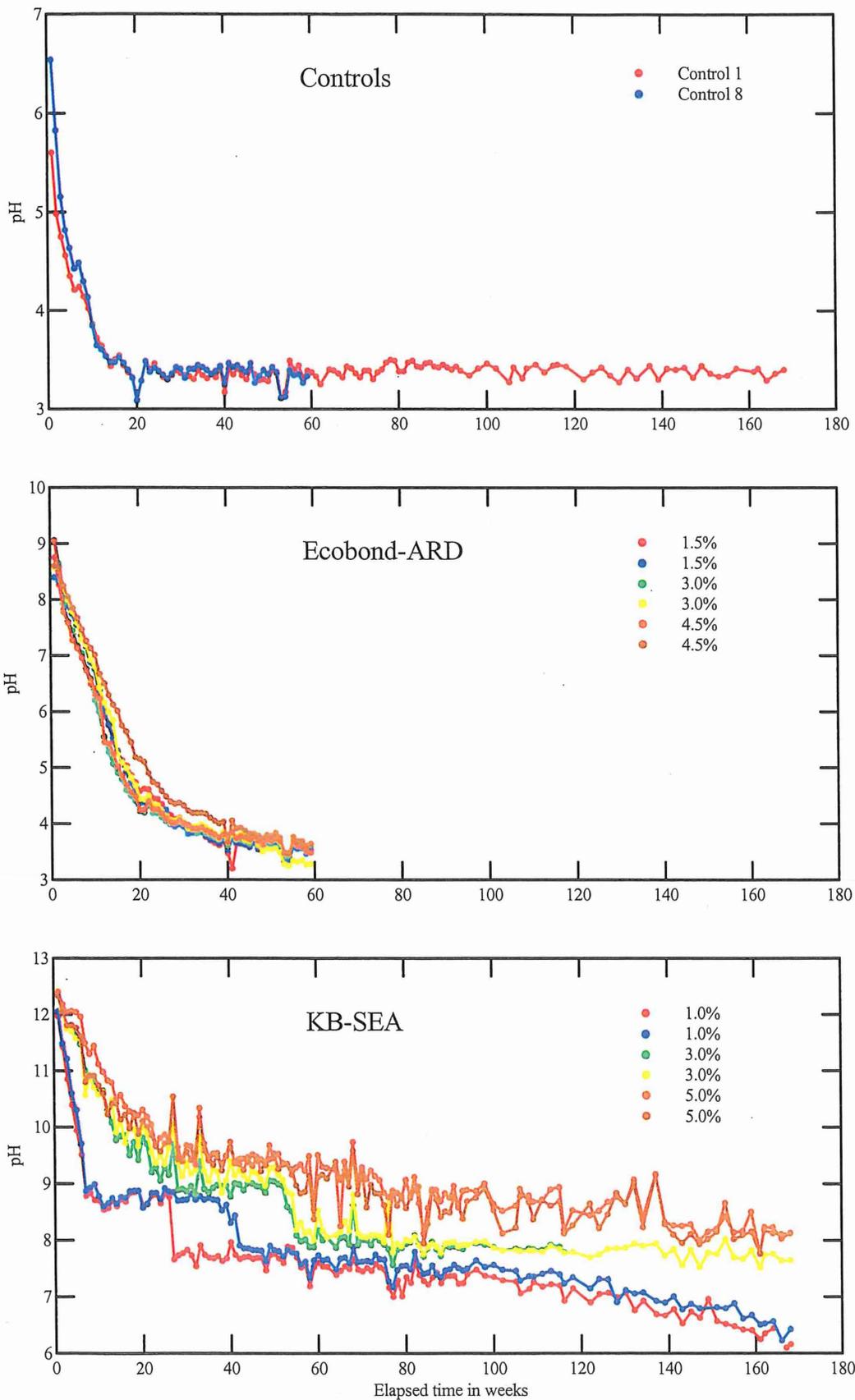


Figure 7. Drainage quality results; sulfate vs. time for all cells.

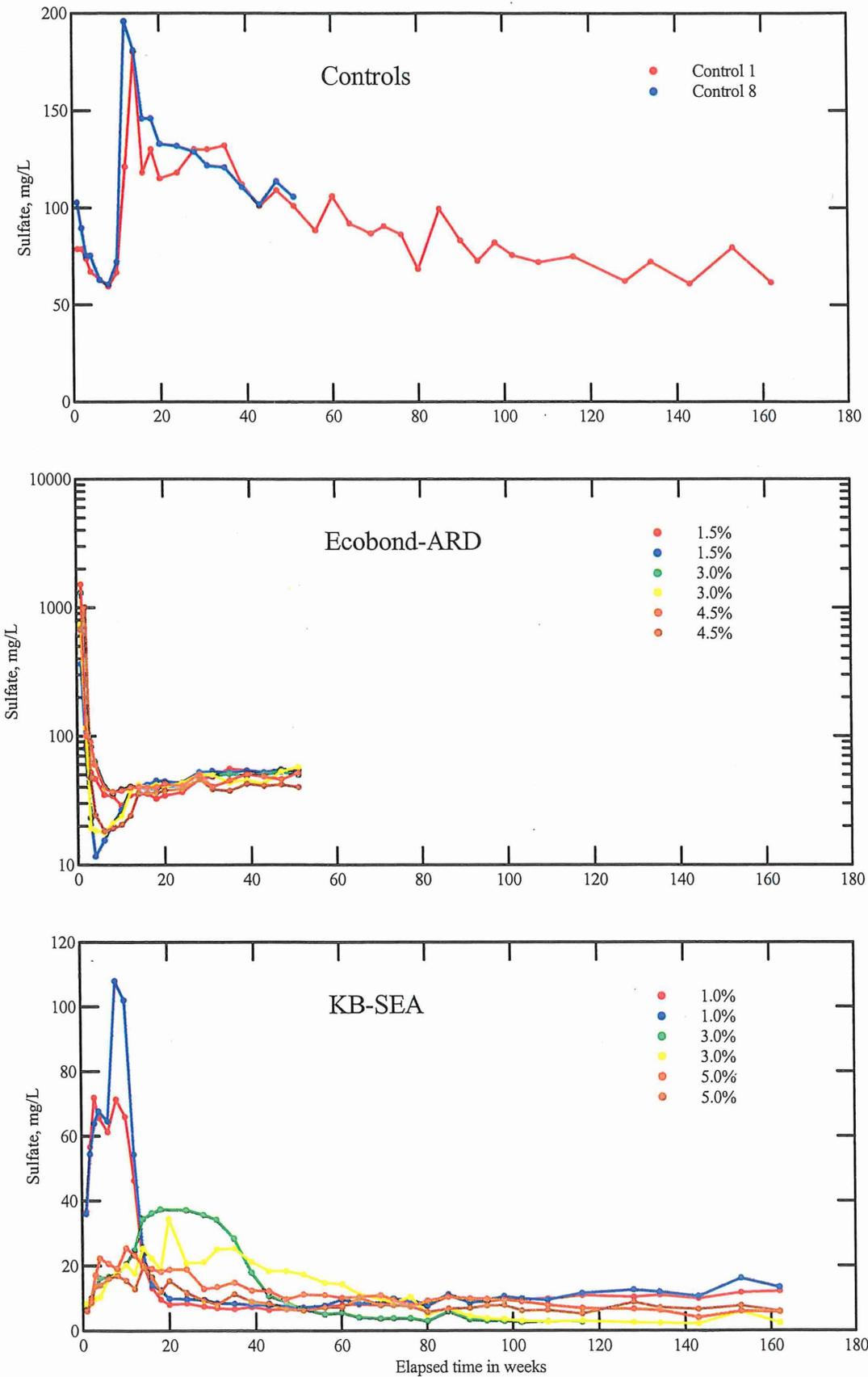


Figure 8. Drainage quality results; calcium vs. time for all cells.

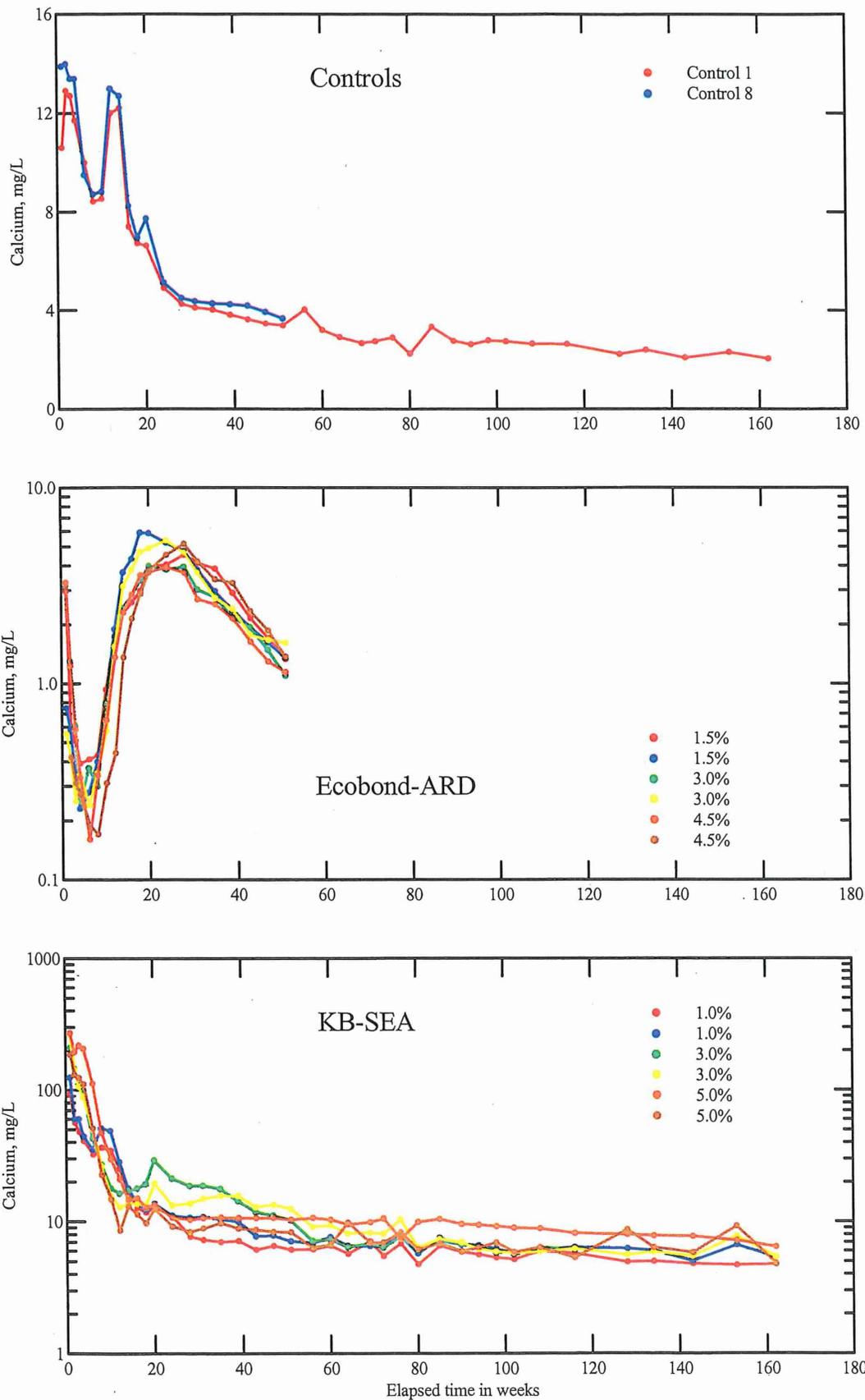
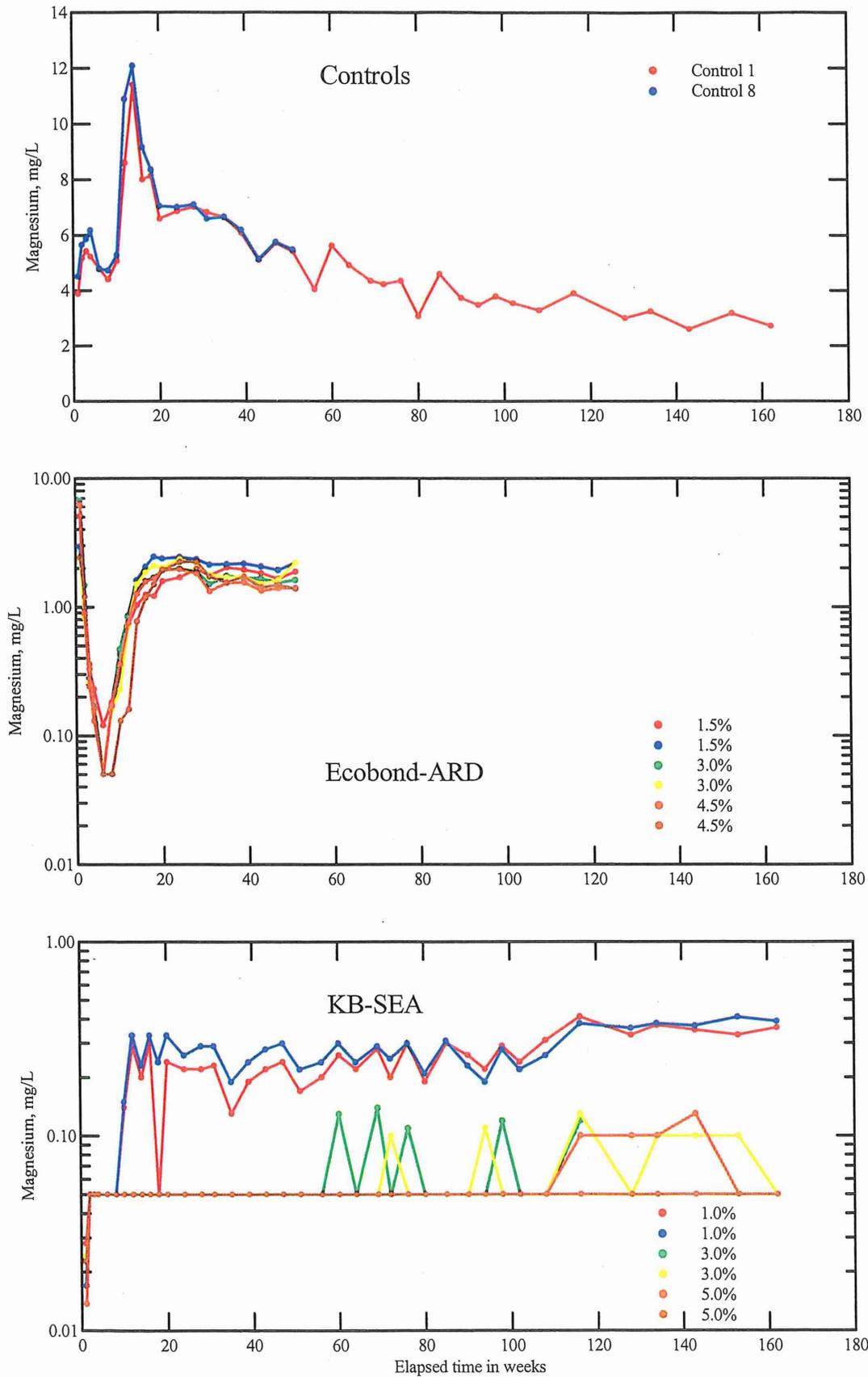


Figure 9. Drainage quality results; magnesium vs. time for all cells.



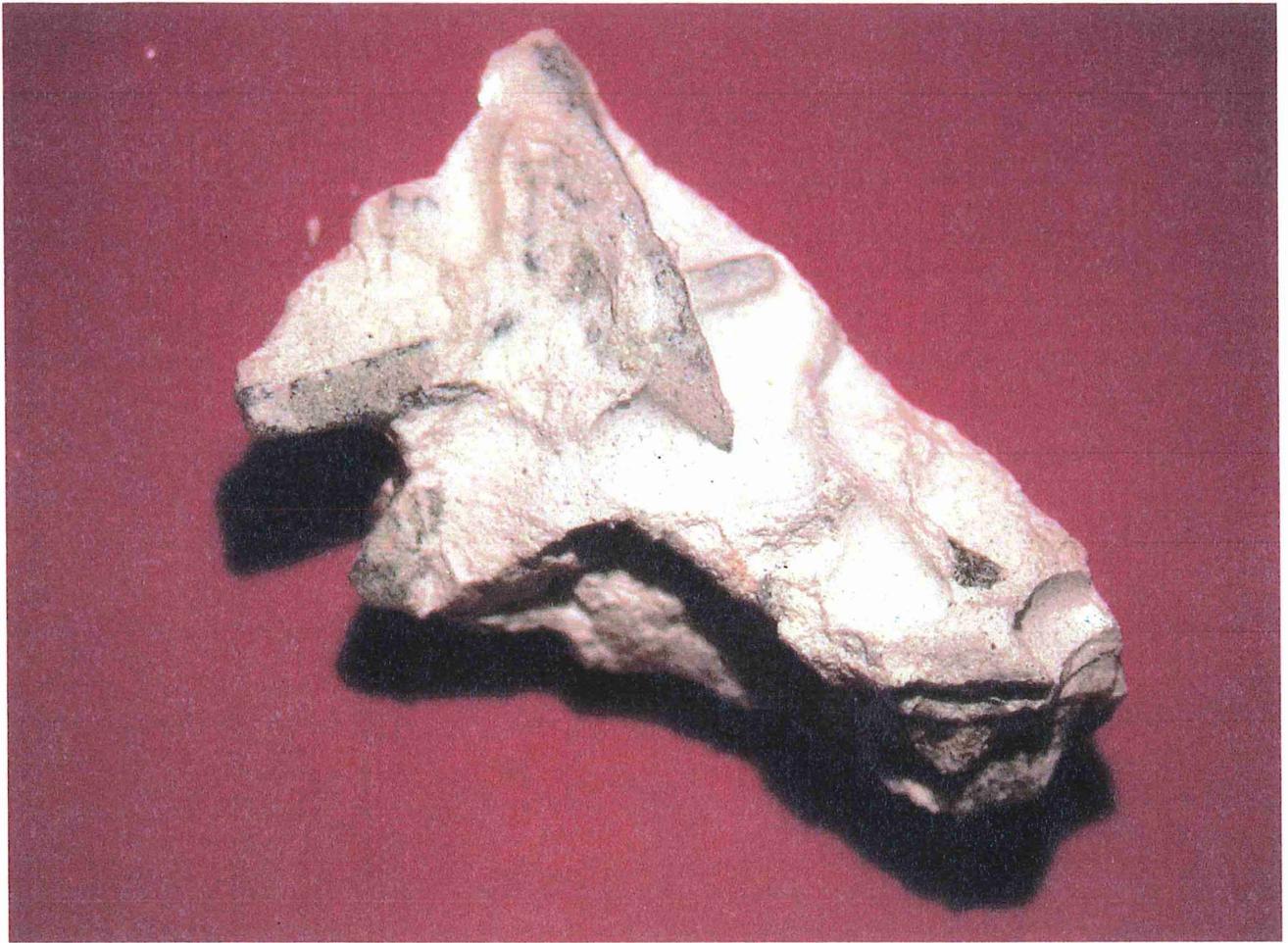


Figure 10. Rock coated with KEECO macro coating.

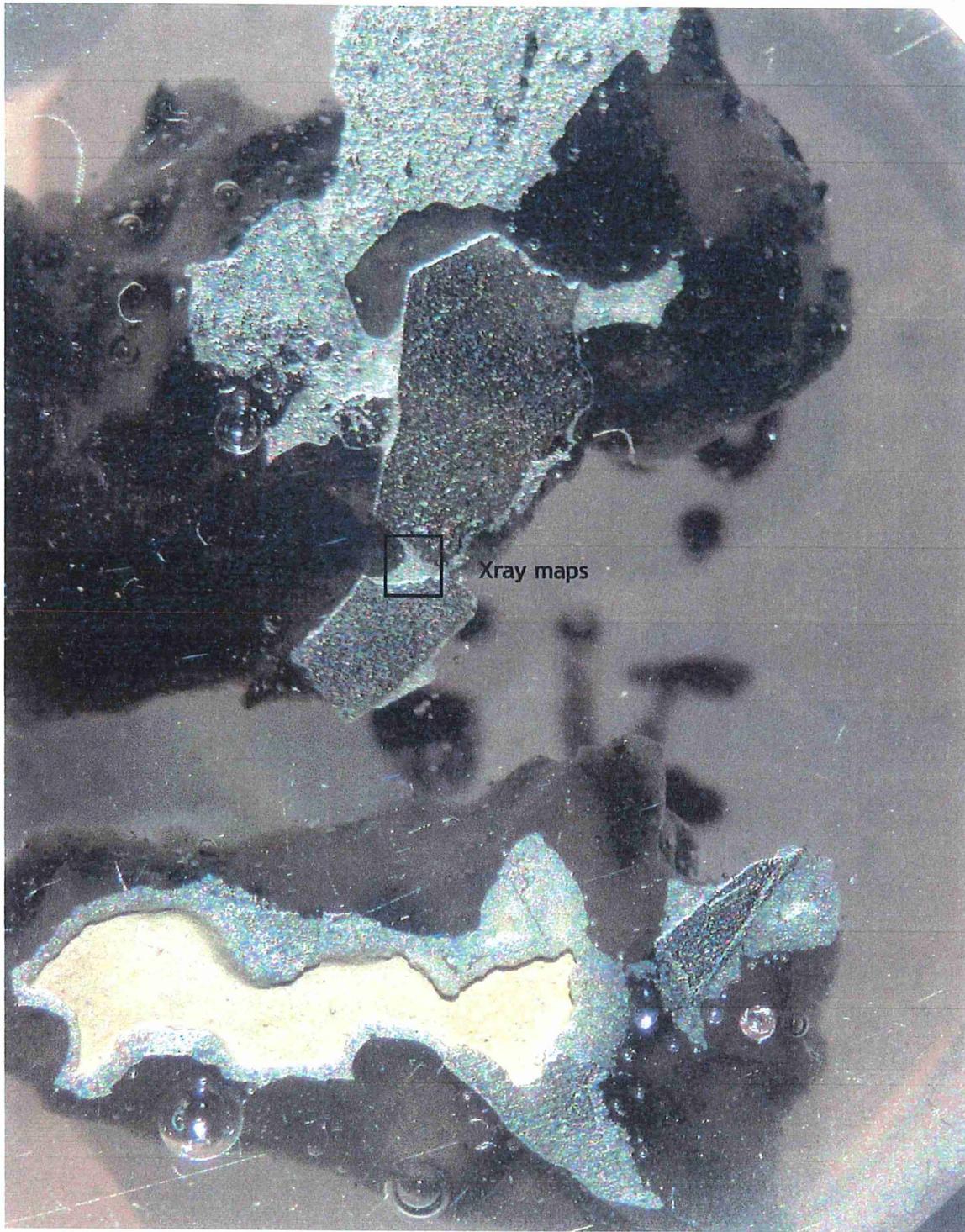


Figure 11. Polished cross sections of rock fragments shown in Figure 10 with KEECO product coating..

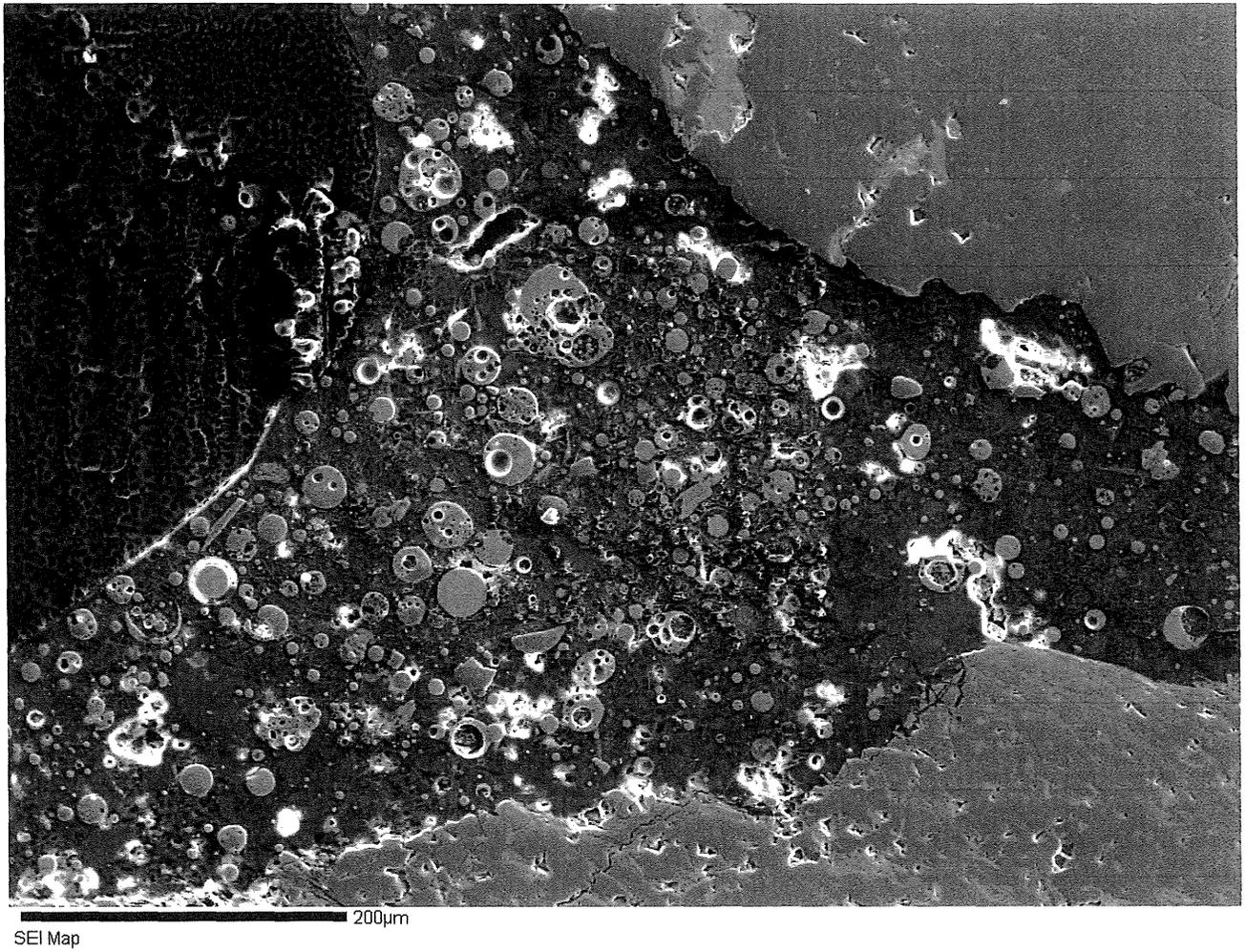


Figure 12. Detailed backscattered electron image of the KEECO product between two rock fragments.



Figure 13. Pyrite cubes from unleached KEECO reactor.

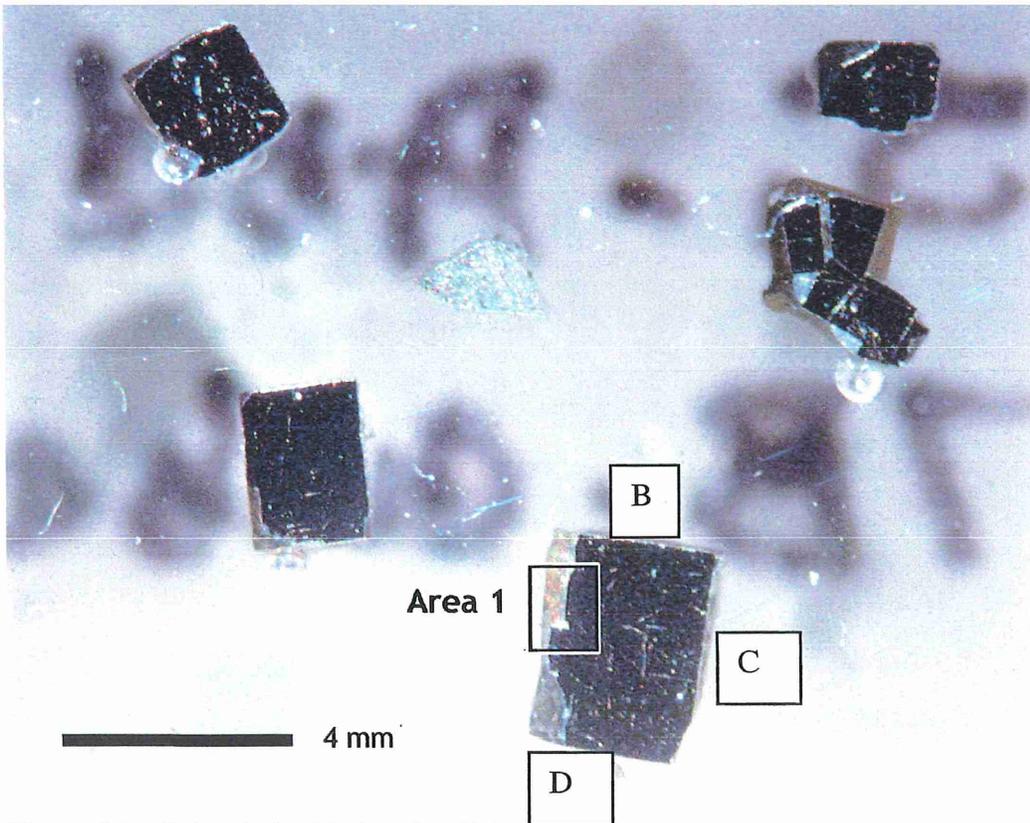


Figure 14. Cubes imbedded and polished.

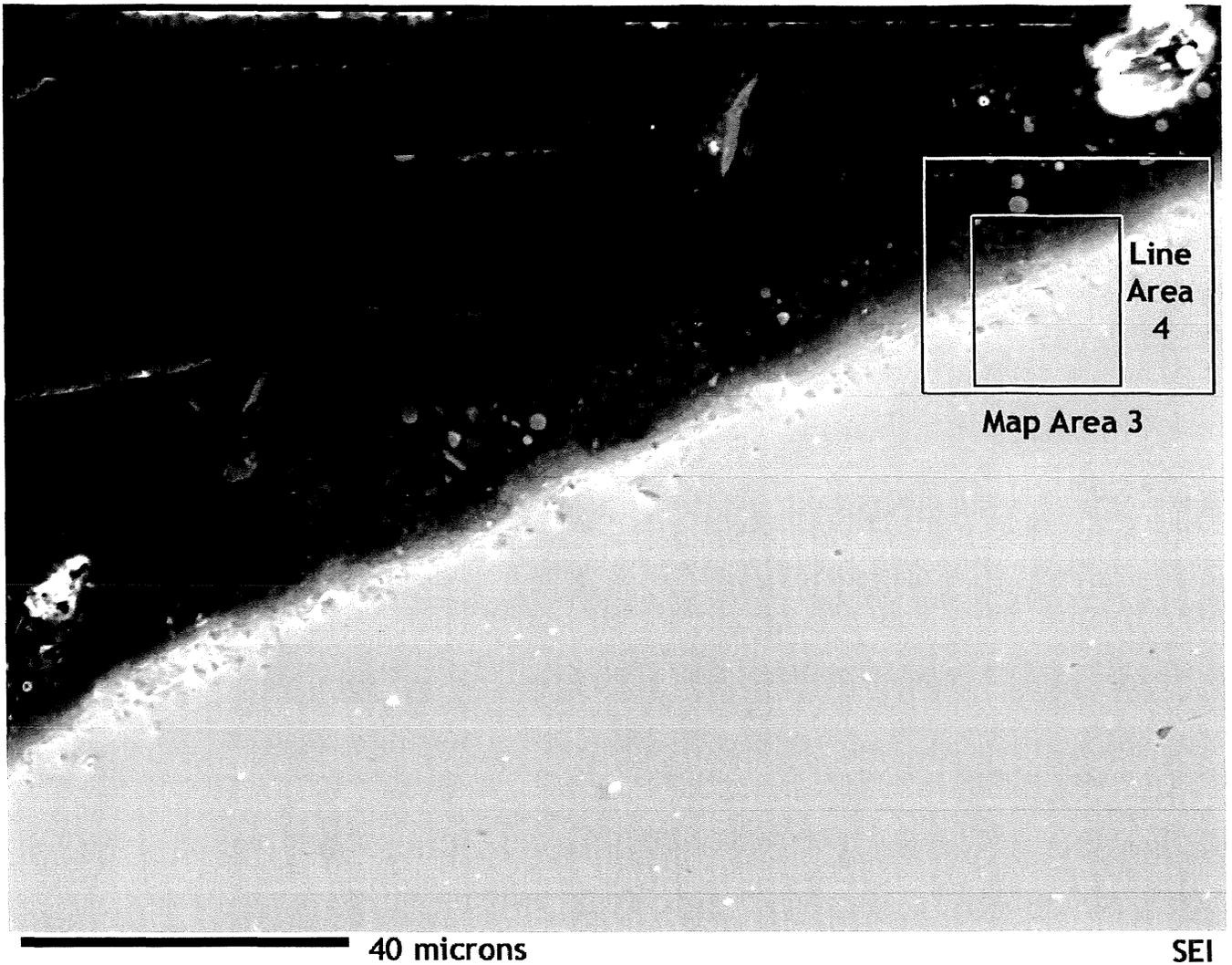


Figure 15. Portion of a pyrite cube from KEECO unleached reactor.

Note: Figure shows coating, pyrite grain, and a transition zone between the pyrite grain and the product. The transition zone contains a mix of Fe and S from the pyrite grain and Si, Al, Ca, and O from the KEECO product, indicating a chemical reaction between the KEECO product and the sulfide grain.

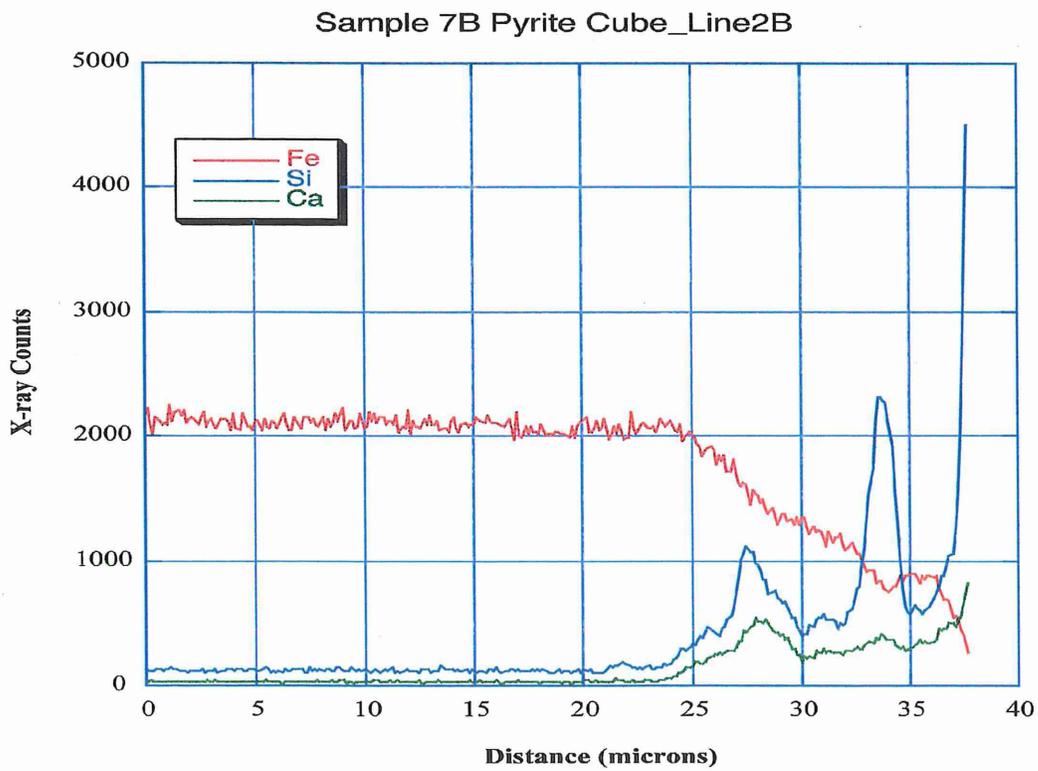
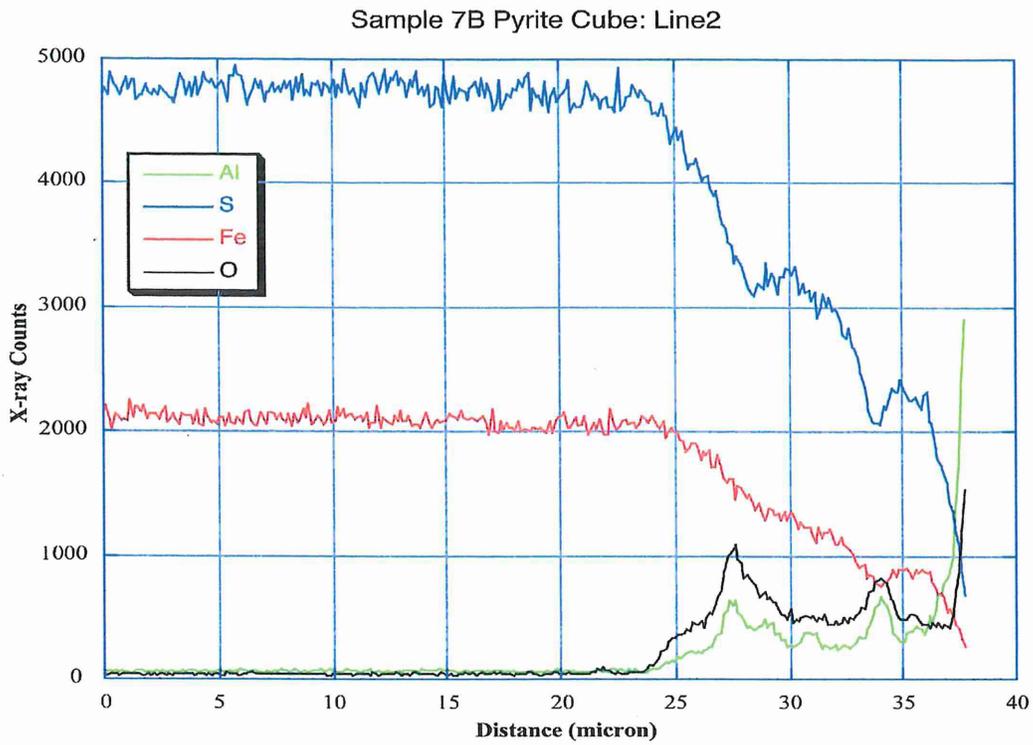


Figure 16. Microprobe results for pyrite crystal from unleached KEECO reaction.

Pyrite 1, Face D, Line 1

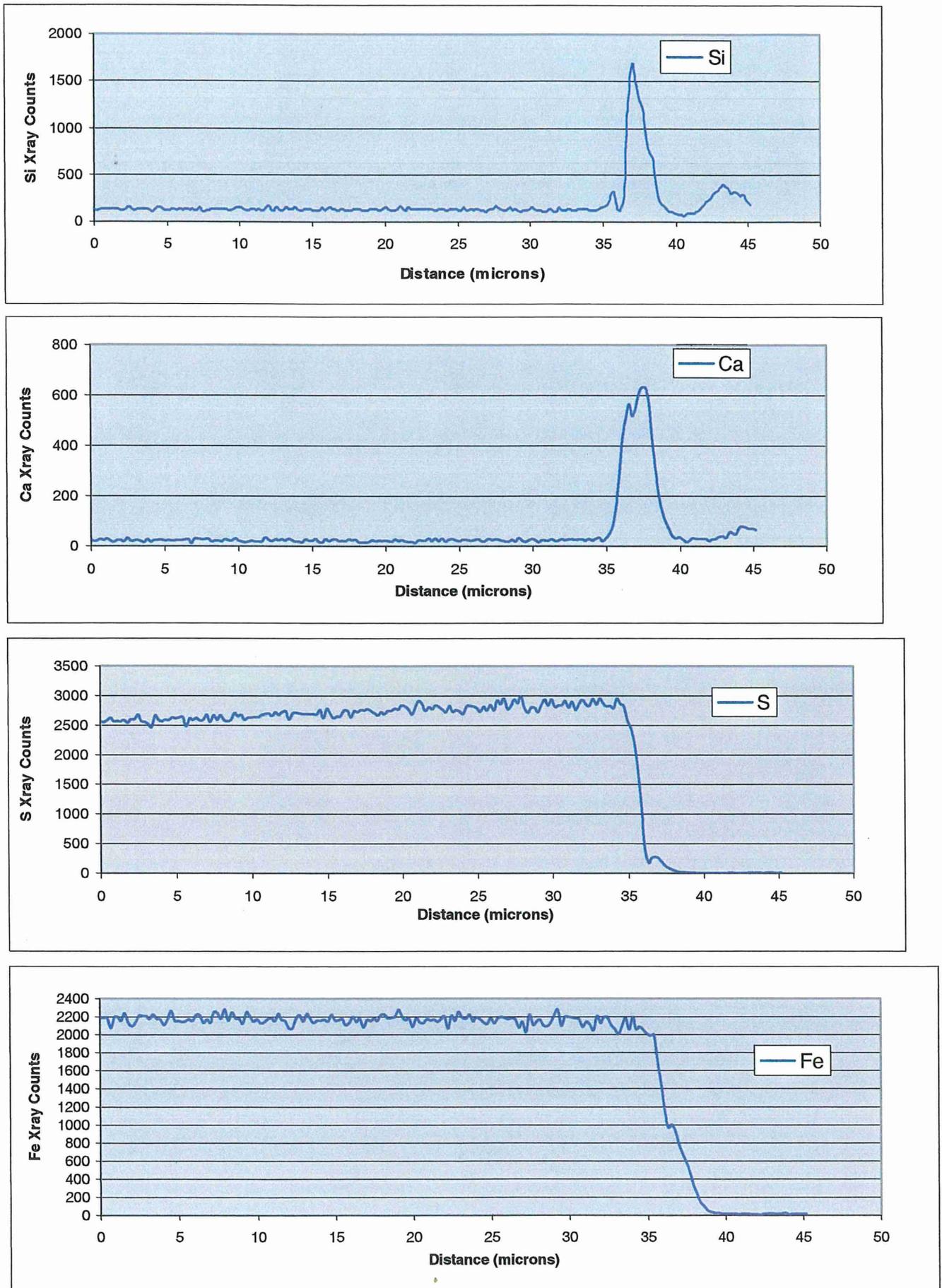


Figure 17. Microprobe analyses for pyrite cube from unleached KEECO reactor, Face D.

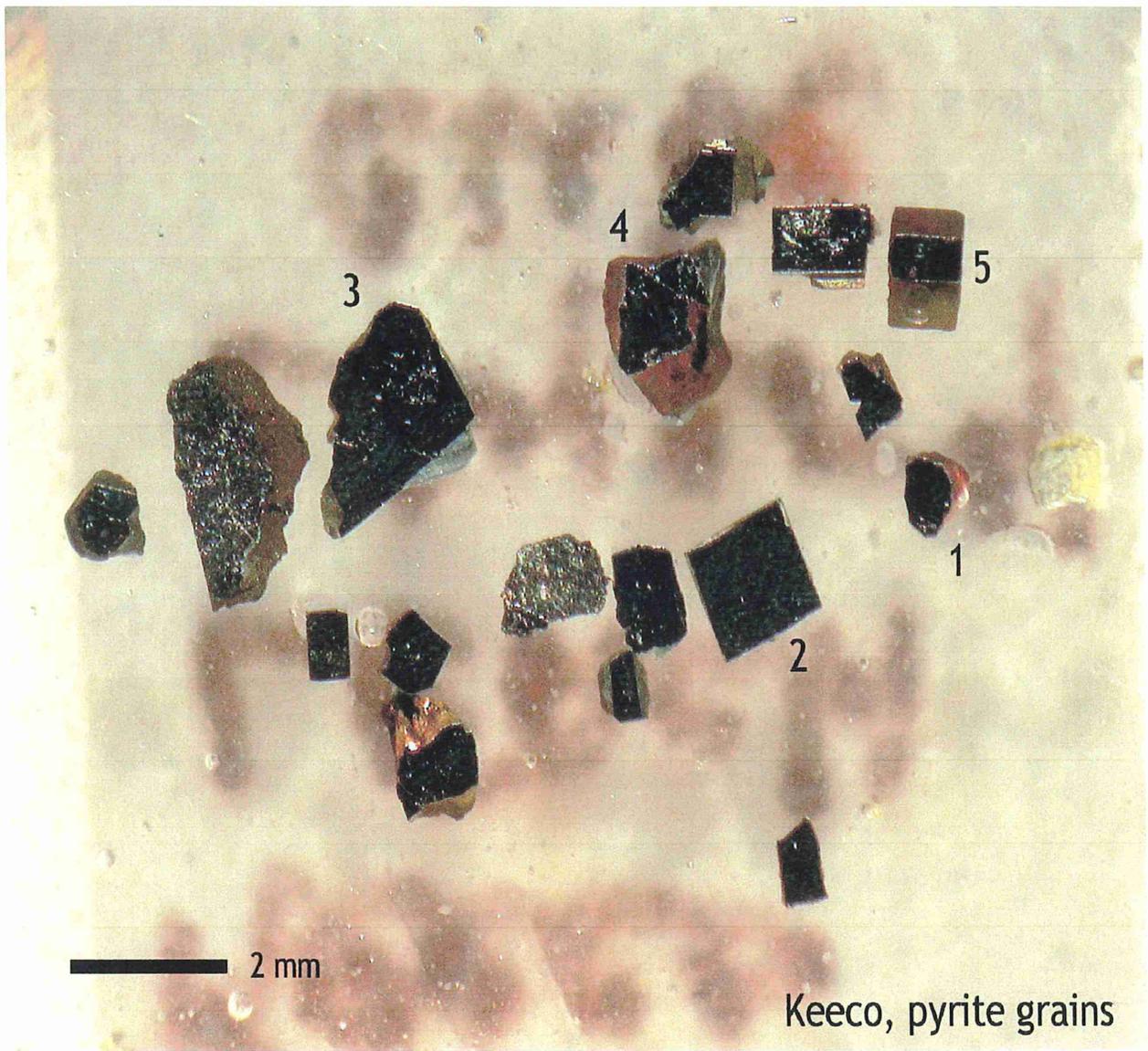


Figure 18. Pyrite cubes selected for analyses from leached KEECO reactor.

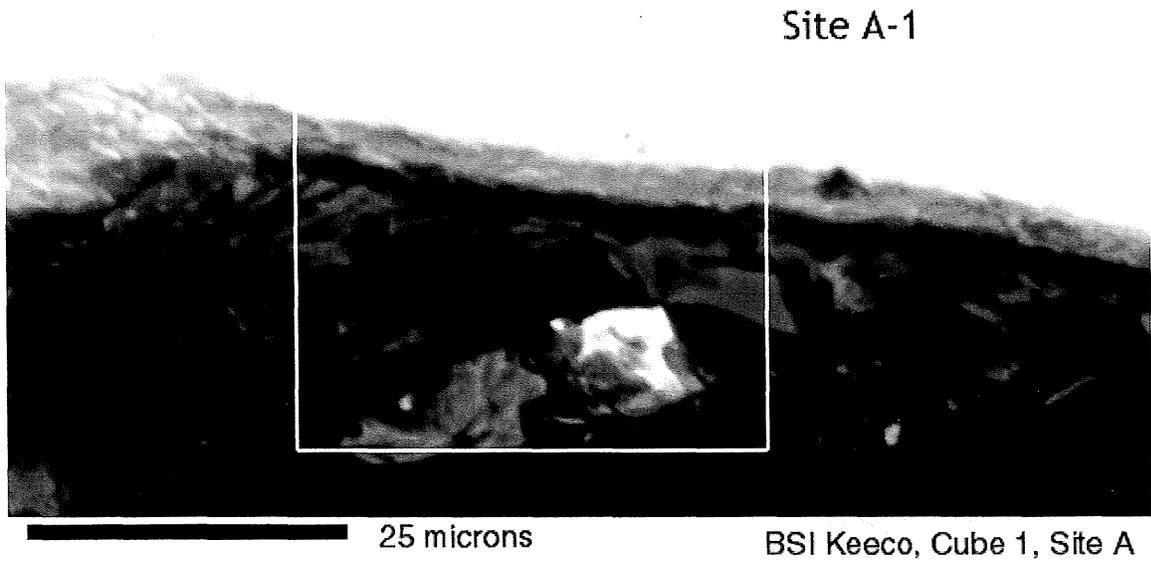


Figure 19. Pyrite cube 1, with an oxidized zone from the KEECO reactor.

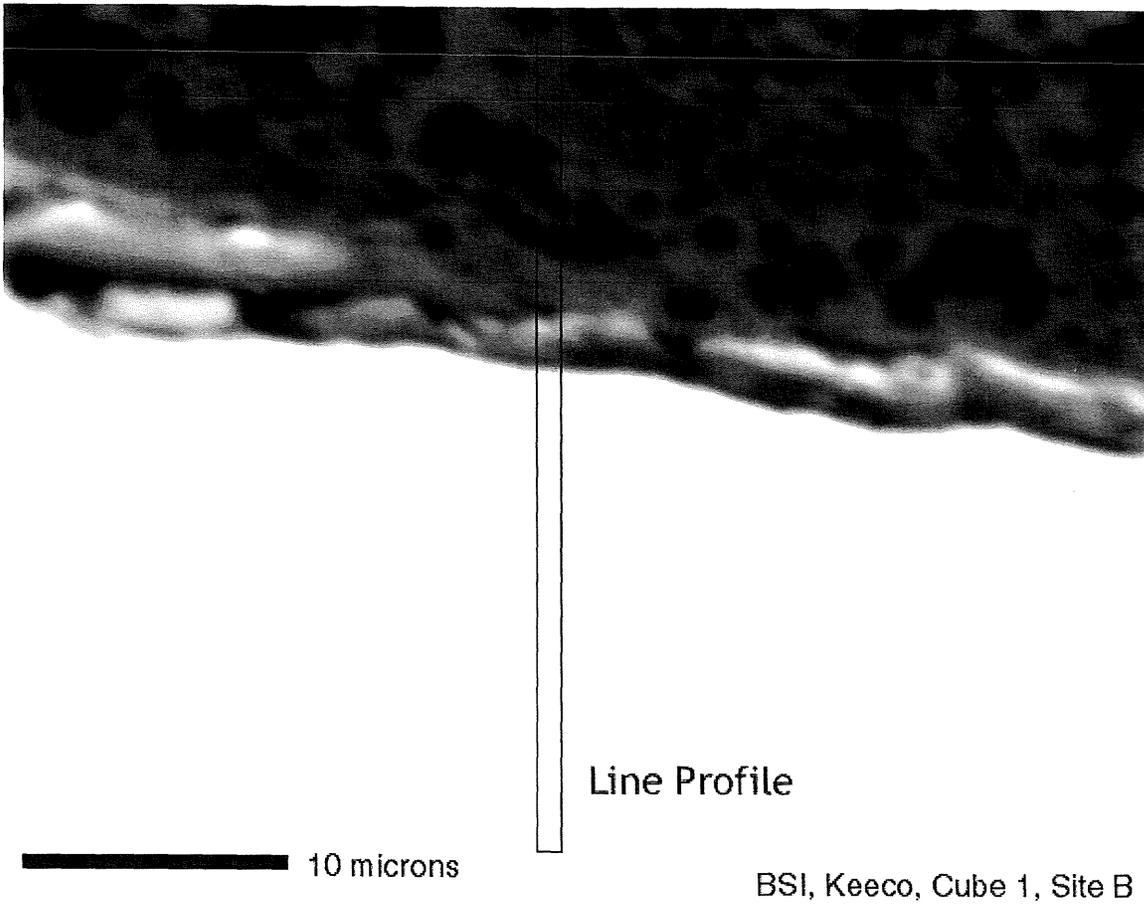
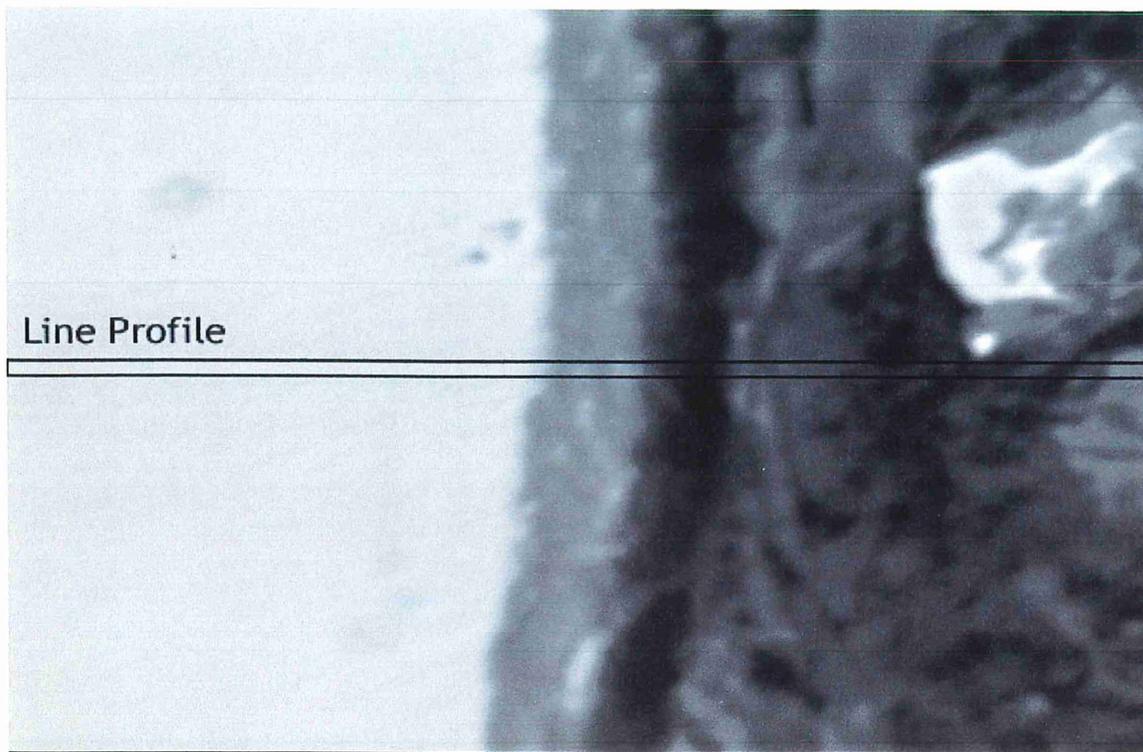


Figure 20. Pyrite cube with KEECO coating showing no visible oxidized zone.



Line Profile

10 microns

BSI Keeco, Cube 1, Site A-1

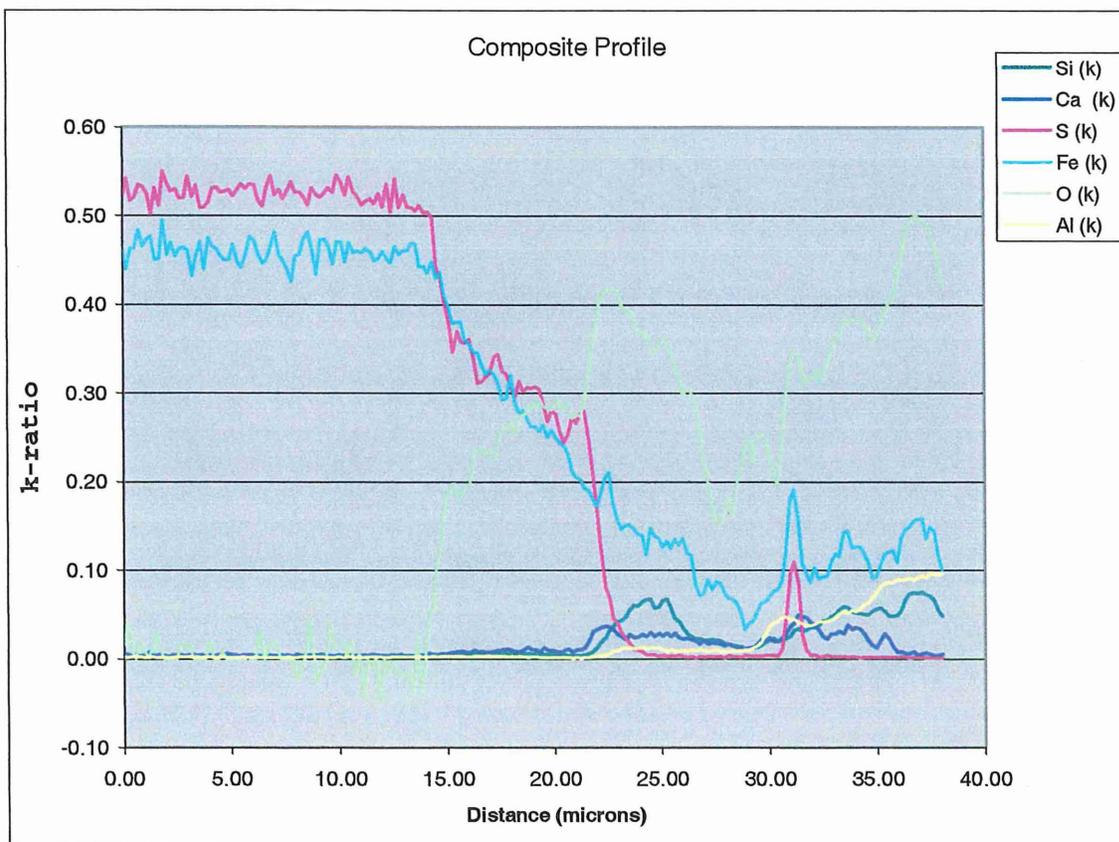


Figure 21. Pyrite cube 1, location of microprobe analysis and elemental composition.

Note: Figure shows the variation in compositions along a line profile from the pyrite grain into the epoxy on the right. The Y-axis is the weight fraction of each element uncorrected for matrix effects.

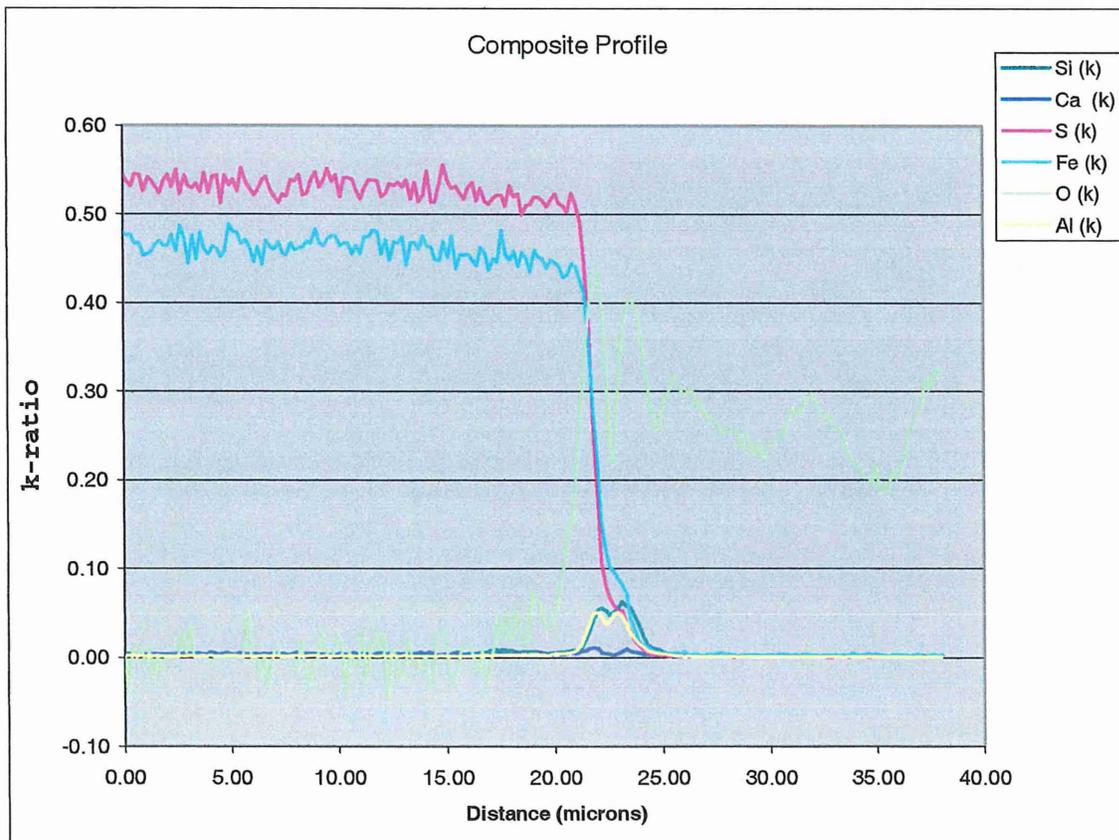
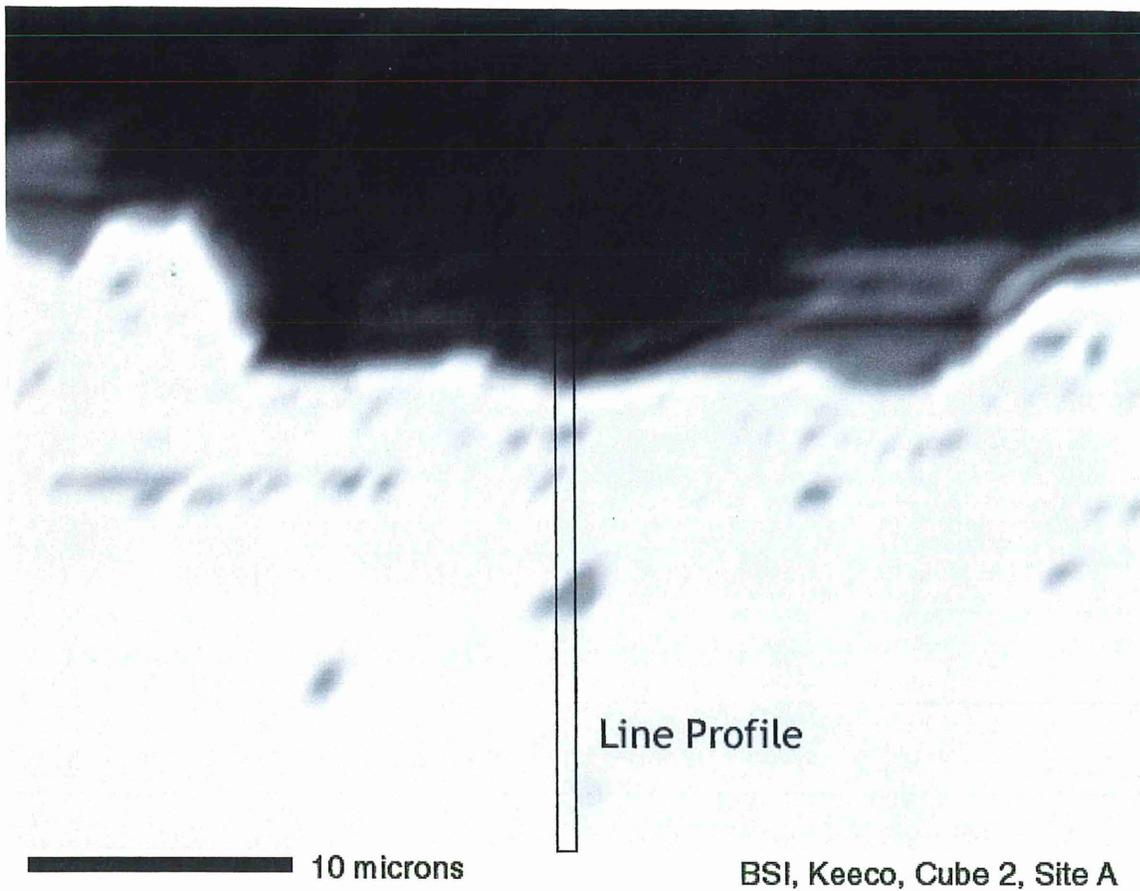


Figure 22. Pyrite cube 2, location of microprobe analysis and elemental composition.

Note: The Y-axis is the weight fraction of each element uncorrected for matrix effects.

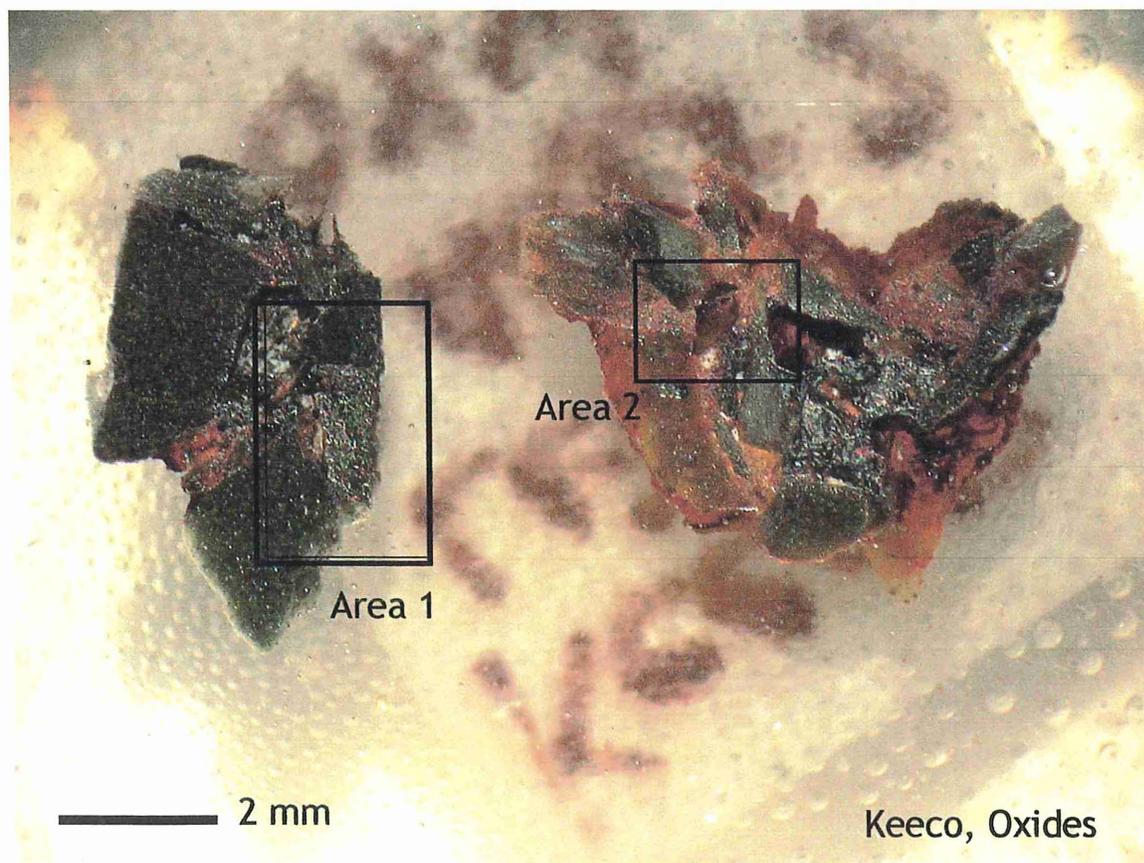


Figure 23. Oxidized areas from KEECO leached reactor.

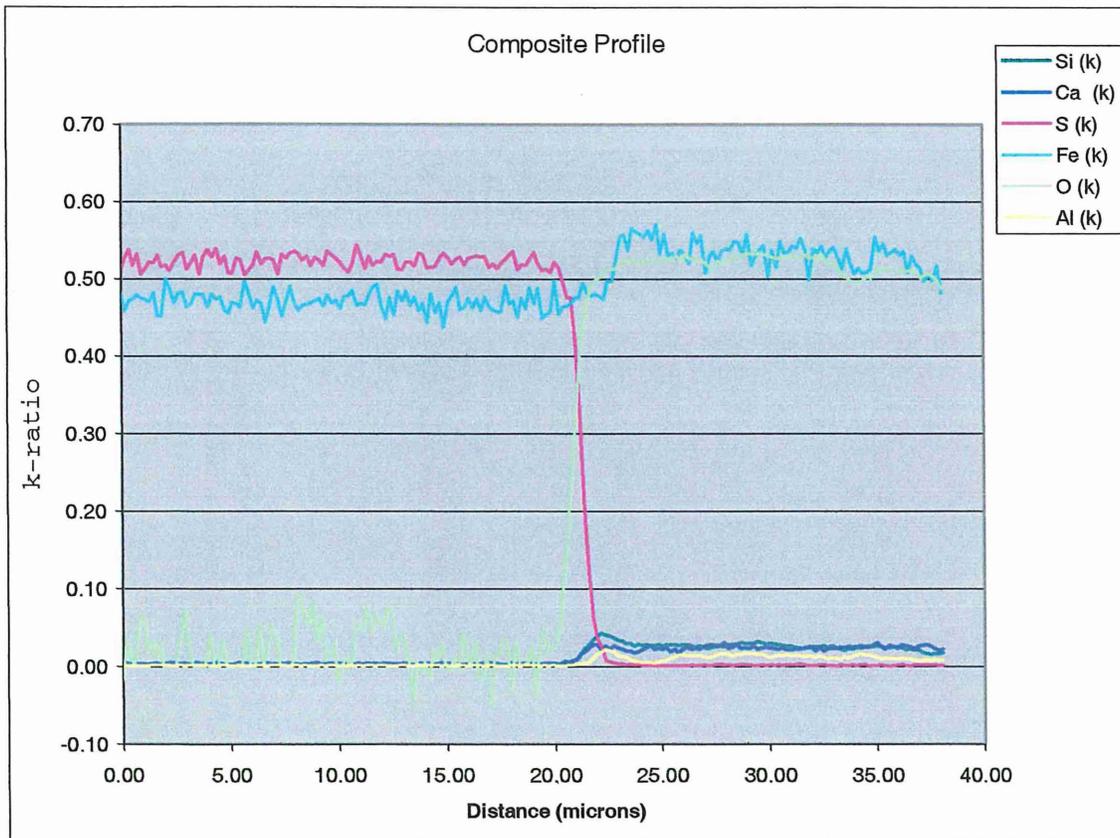
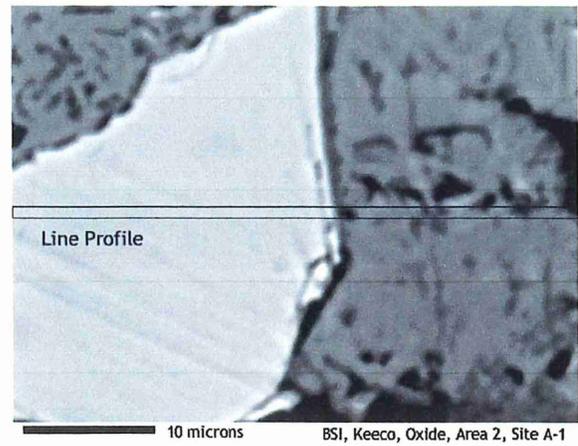
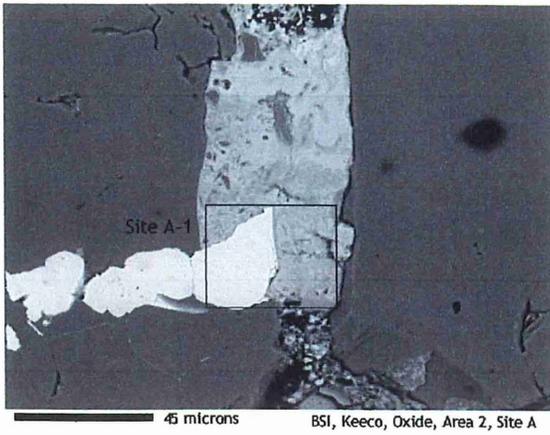


Figure 24. Oxidized zone from area 2 in Figure 23 and microprobe element profile.

Note: The Y-axis is the weight fraction of each element uncorrected for matrix effects.

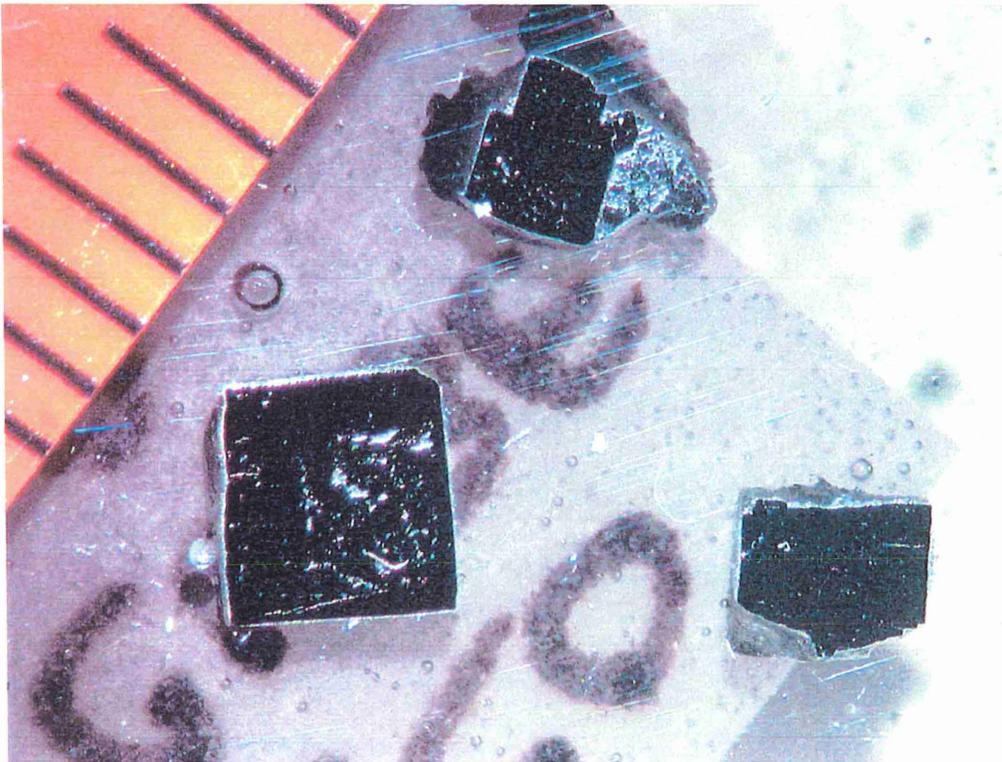
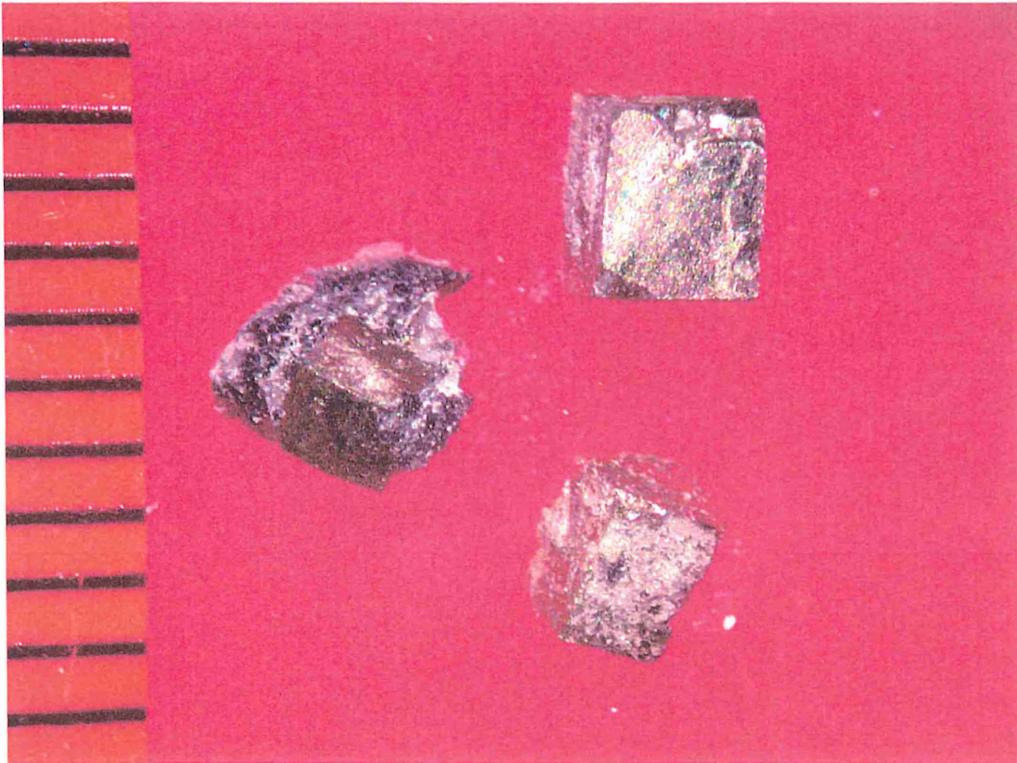


Figure 25. Pyrite Cubes from Ecobond unleached reactor

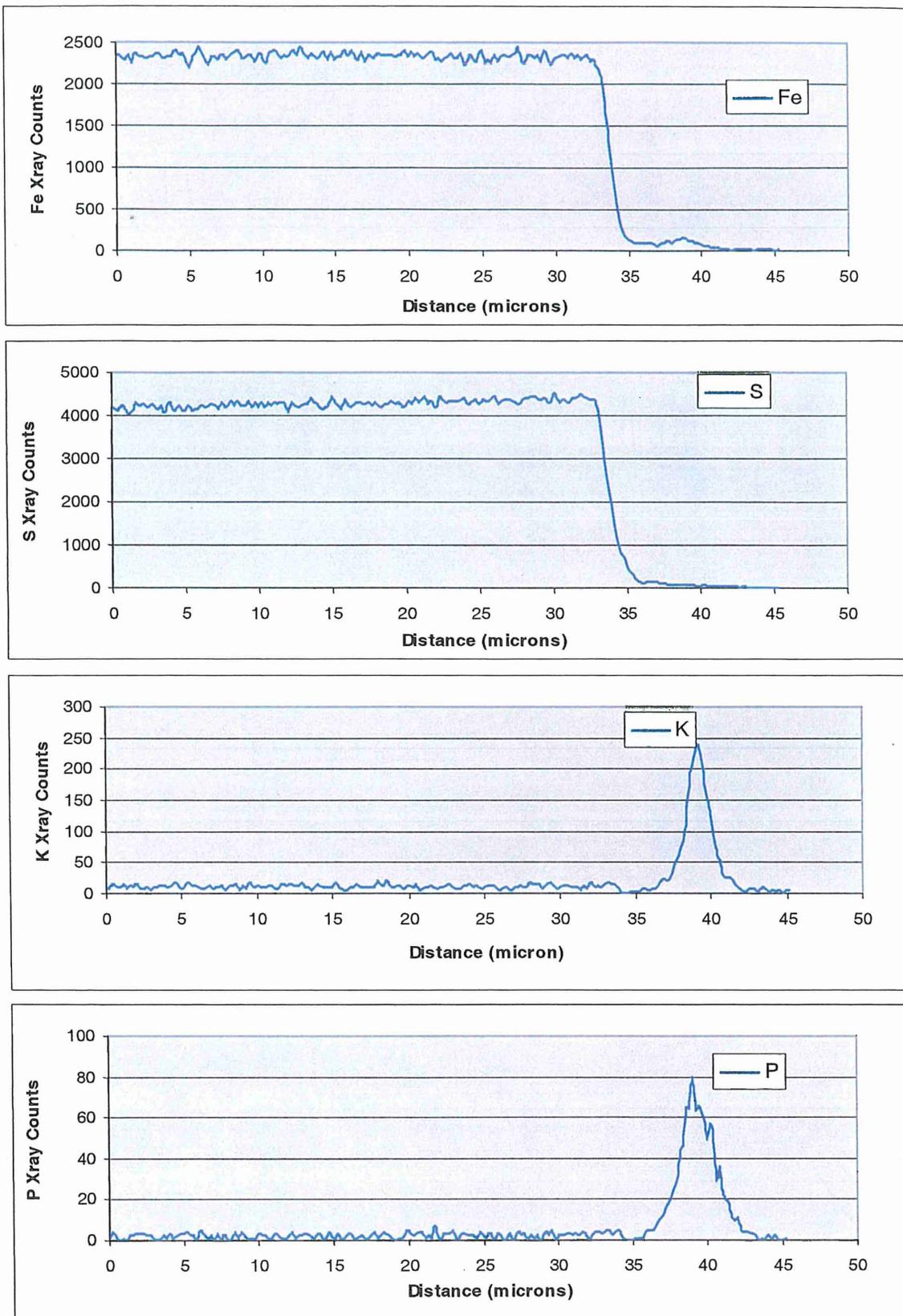


Figure 26. Microprobe results for pyrite from unleached Ecobond reactor.

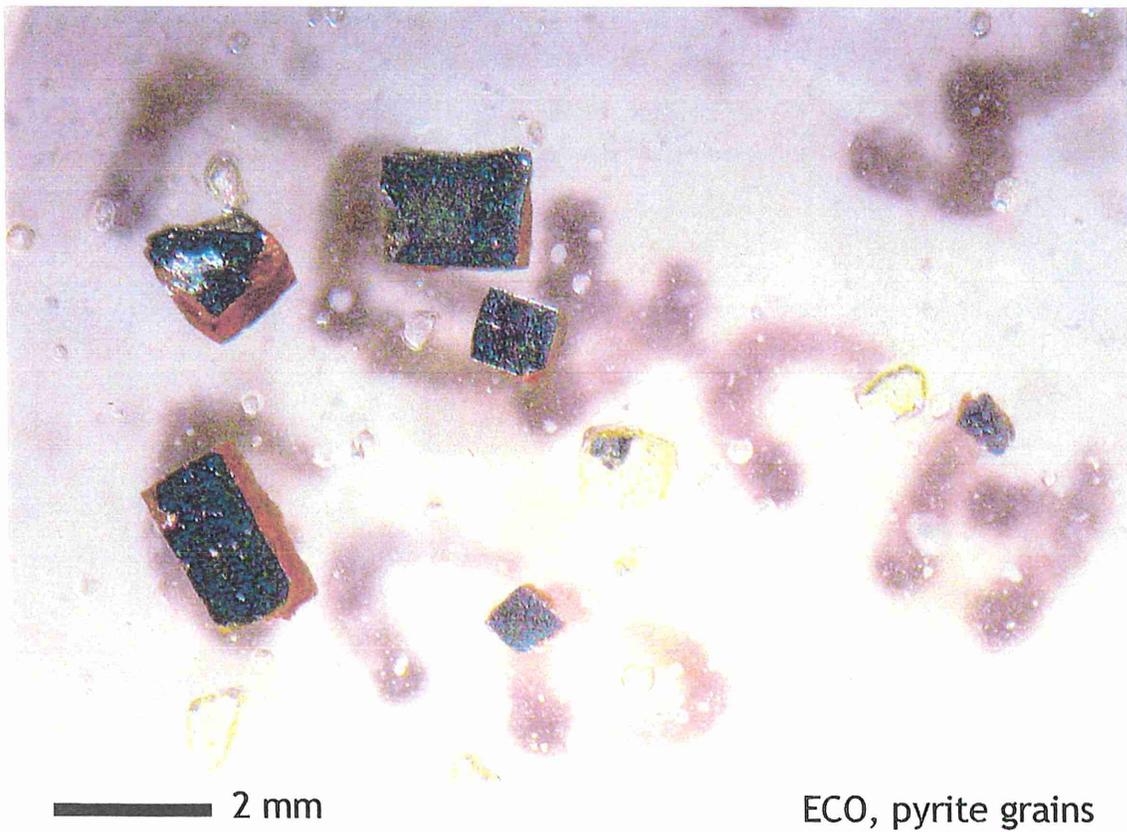


Figure 27. Pyrite cubes selected for analyses from leached Ecobond reactor.

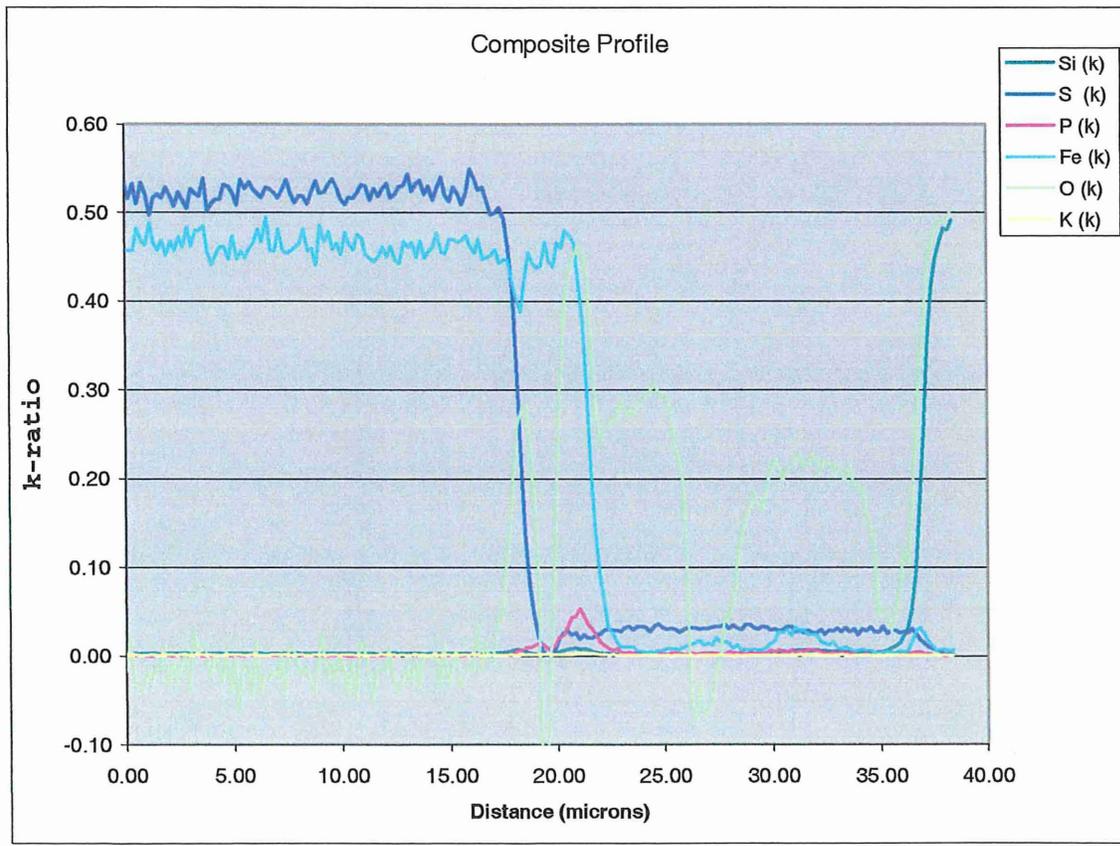
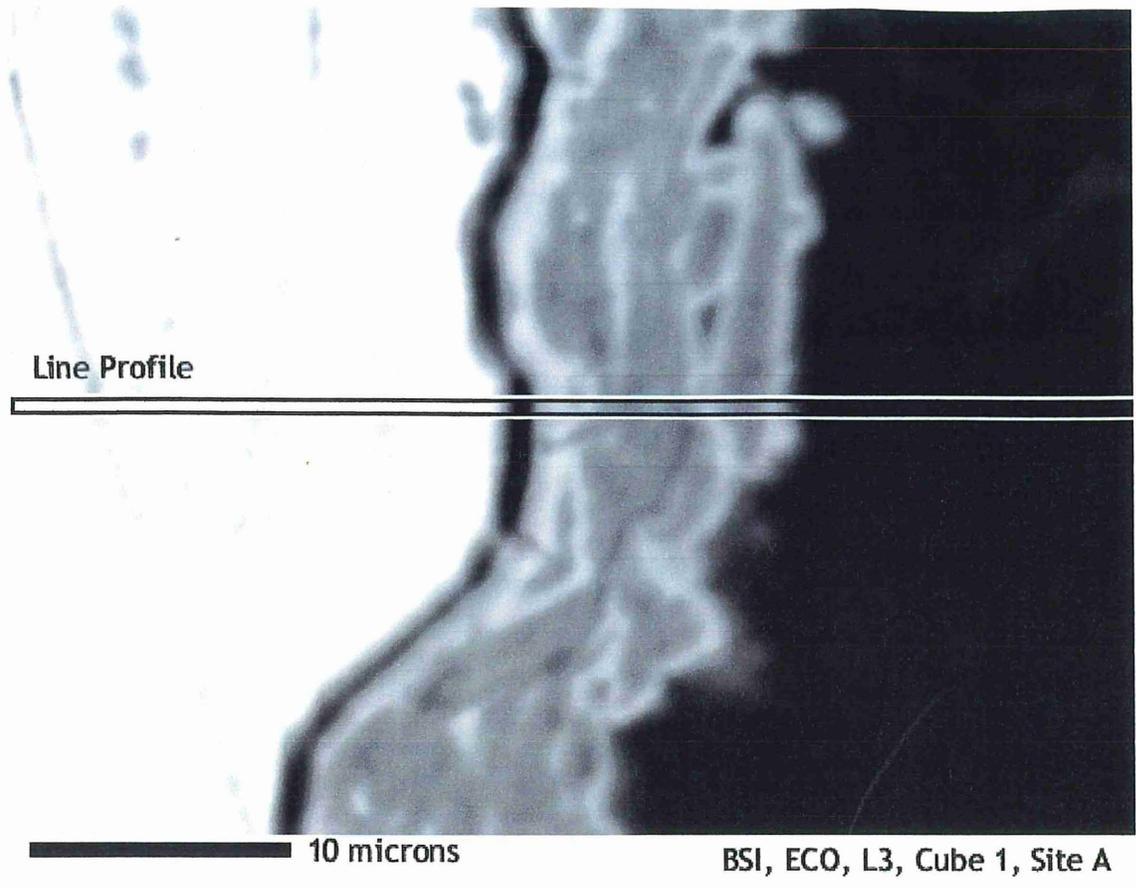


Figure 28. Microprobe results for pyrite cube 1 from leached Ecobond reactor.

Note: The Y-axis is the weight fraction of each element uncorrected for matrix effects

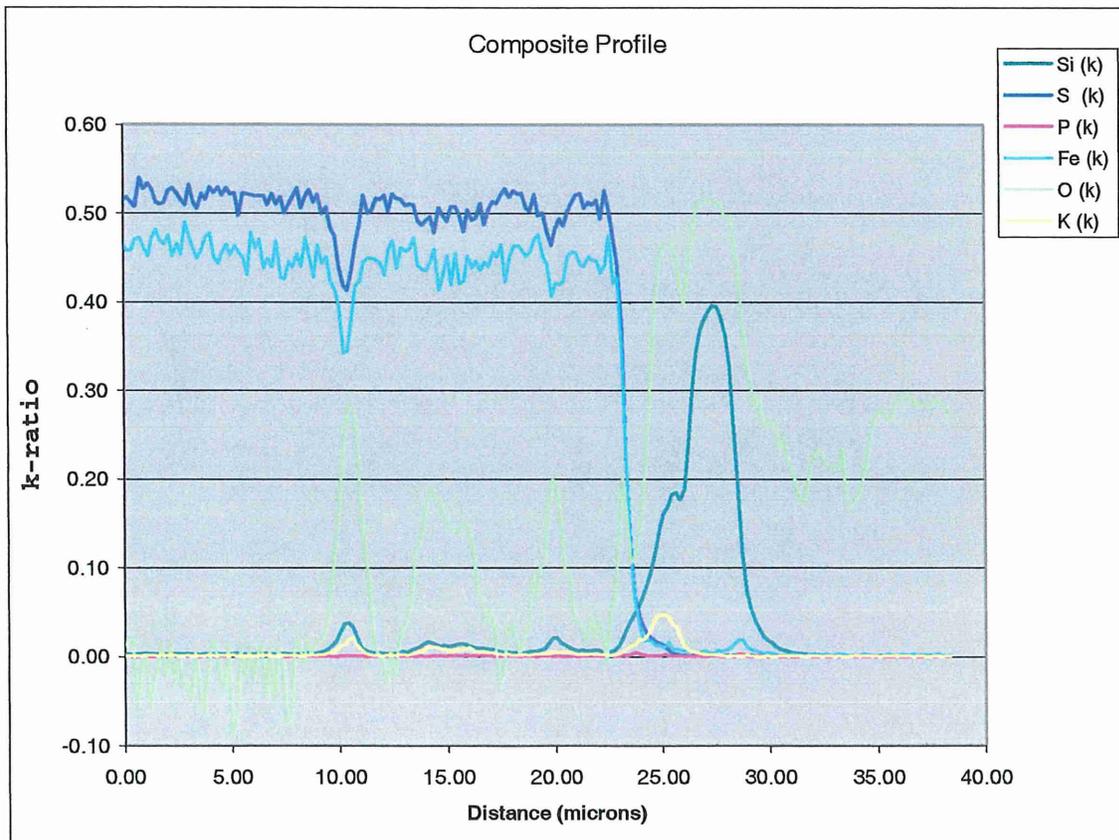
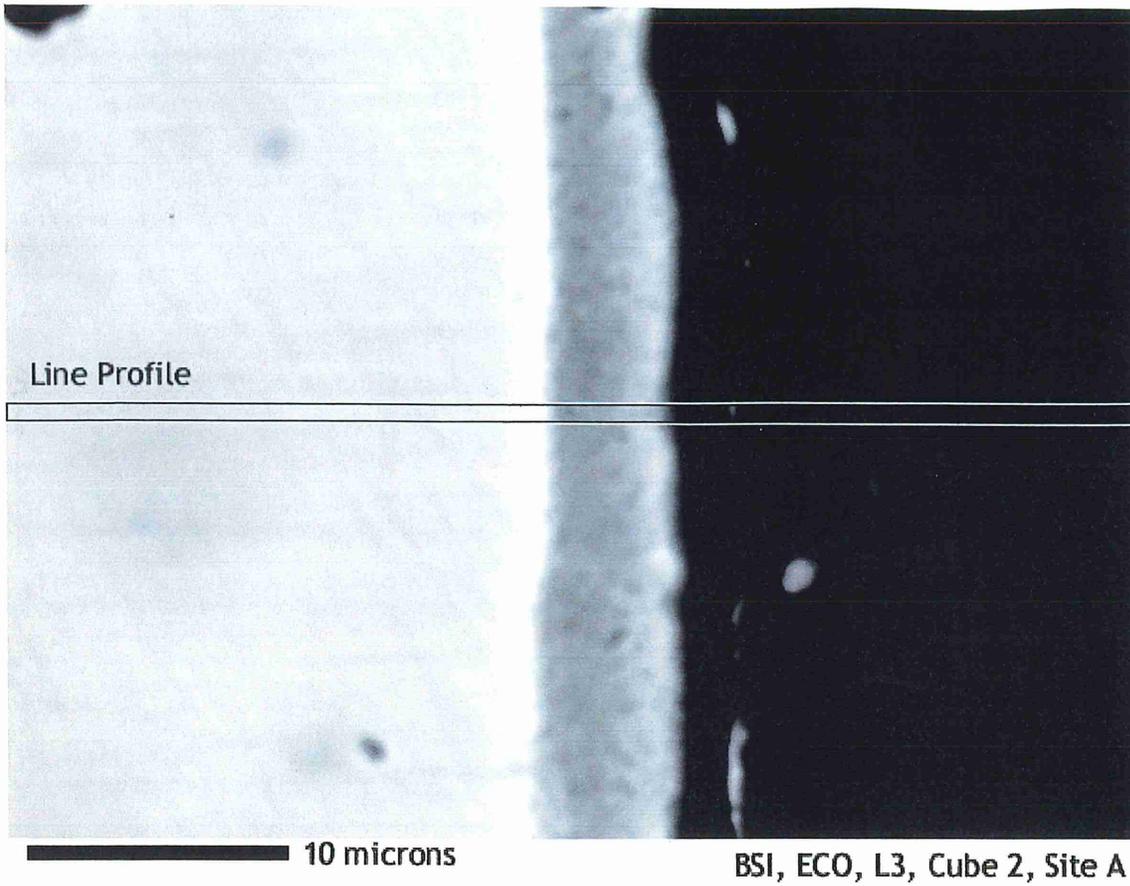


Figure 29. Microprobe results for pyrite cube 2 from leached Ecobond reactor.

Note: The Y-axis is the weight fraction of each element uncorrected for matrix effects.

Figure 30. Comparison of control cell with 1.5% solution Ecobond cell on 1/10/02 (top photo) and on 8/19/02 (bottom photo).

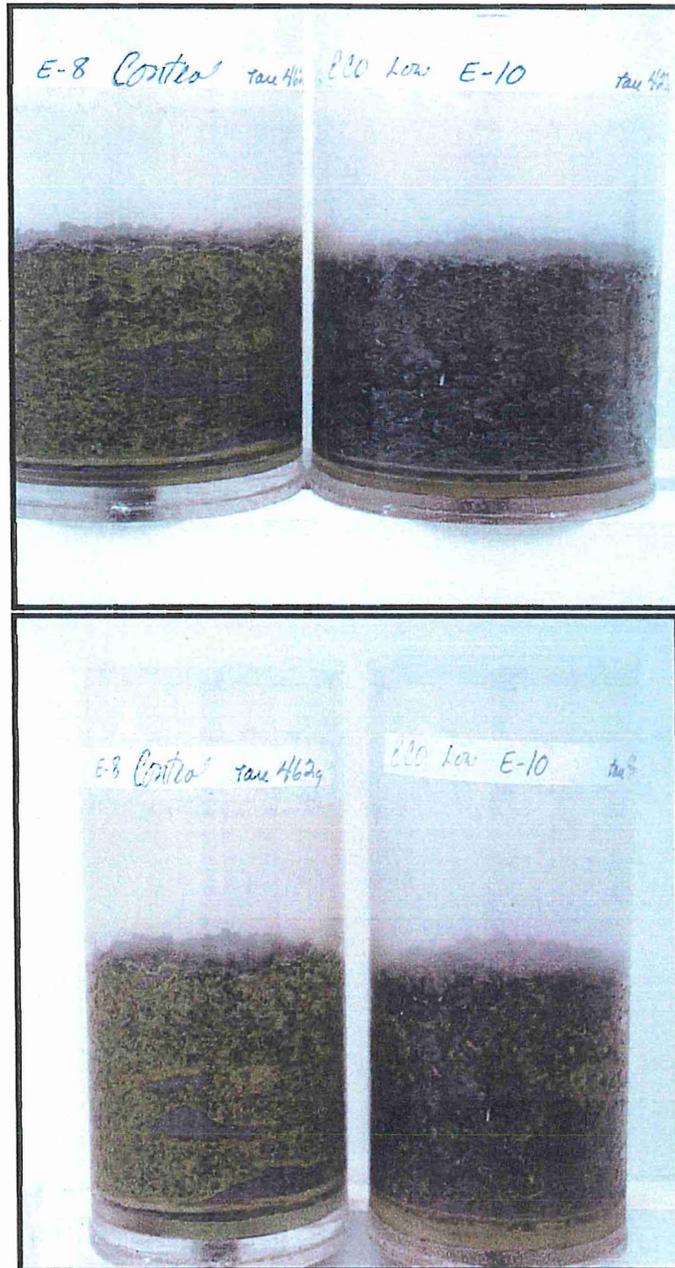


Figure 31. Comparison of control cell with 3% solution Ecobond cell on 1/10/02 (top photo) and on 8/19/02 (bottom photo).



Figure 32. Comparison of control cell with 4.5% solution Ecobond cell on 1/10/02 (top photo) and on 8/19/02 (bottom photo).



Figure 33. Comparison of control cell with 1% solution KEECO cell 1/10/02 (left photo), on 8/19/02 (middle photo), and on 8/9/04 (right photo).

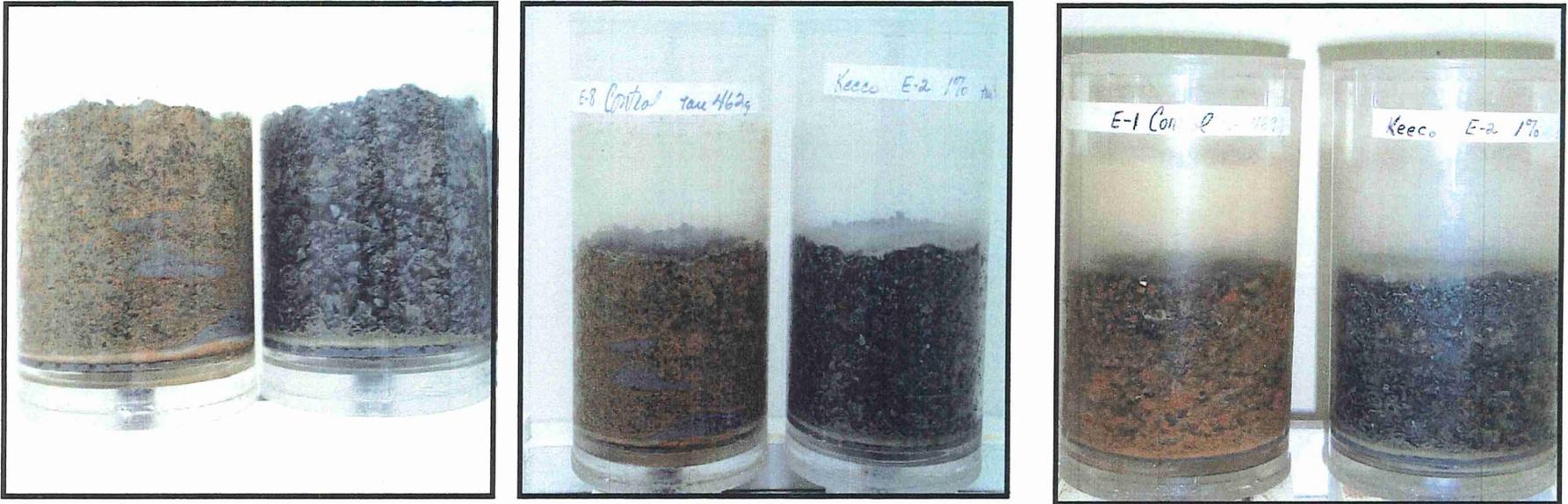


Figure 34. Comparison of control cell with 3% solution KEECO cell 1/10/02 (left), on 8/19/02 (middle), and on 8/9/04 (right).

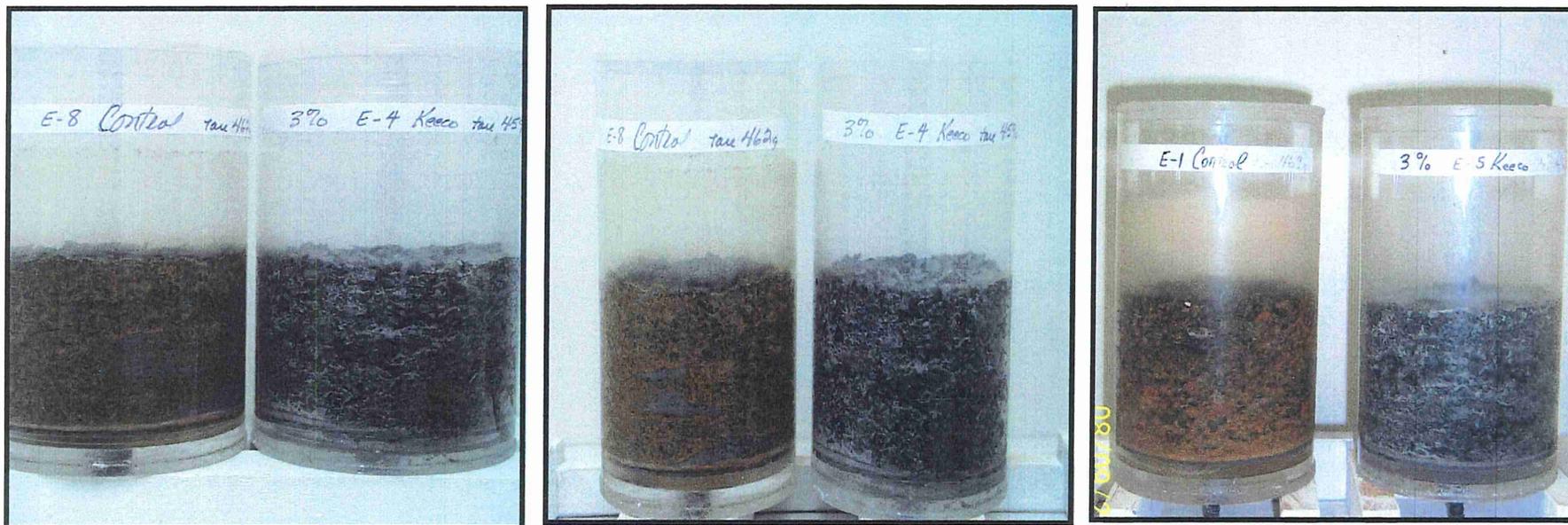


Figure 35. Comparison of control cells with 5% solutin KEECO cell on 1/10/02 (left photo), on 8/19/02 (middle photo), and on 8/9/04 (right photo).



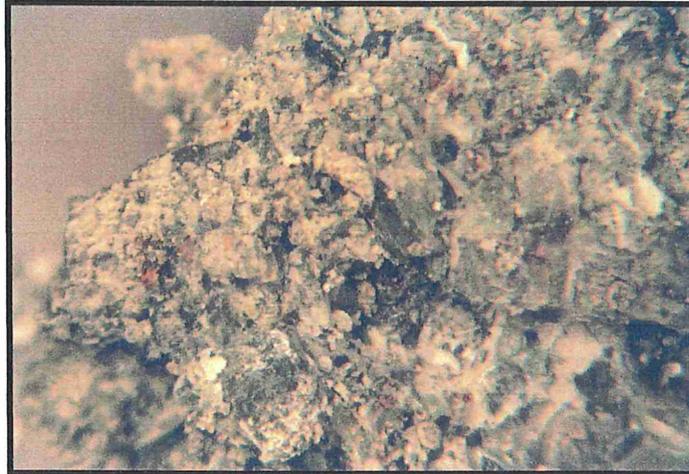
Figure 36. Close up of 1% and 5% KEECO reactors, 8/9/04.

Oxidation is more visible in the 1% (left) than in the 5% (right)

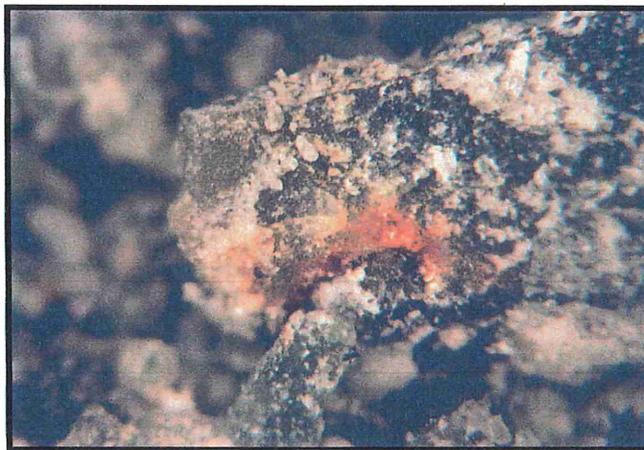


Figure 37. Material treated with 3% KB-SEA™. Images show oxidation has occurred despite visible coating.

This section is cemented but still has some oxidation. Magnification 0.7



This section shows an area with little cementation, finer grains, and oxidation despite visible coating. Magnification = 1.5.



This section shows a highly cemented area with coarser grains. Some oxidation has occurred despite the cementation. Magnification = 0.7.

