FINAL REPORT—BERKELEY PIT INNOVATIVE TECHNOLOGIES PROJECTS: GEO2 LIMITED DEMONSTRATION

MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 7

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Final Report—Berkeley Pit Innovative Technologies Projects: Geo2 Limited Demonstration

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Foreword

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

The National Risk Management Research Laboratory (NRMRL) of the EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis. This supports the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the U.S. Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc. (MSE), and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communication link between the researcher and the user community.

The objective of this demonstration was to remediate Berkeley Pit water to the extent that it could be safely used for agricultural applications, to demonstrate the suitability of the technology in allowing continuous online treatment that could be scaled up to match present inflows into the Berkeley Pit, and to evaluate the possible recovery of the economic minerals in the compacted precipitate.

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Executive Summary

The primary goal of this demonstration was to remediate Berkeley Pit water to the extent that it could be safely used for agricultural applications. Other goals were to demonstrate the suitability of the technology to a continuous online treatment that could be scaled up to match present inflows into the Berkeley Pit and to evaluate the possible recovery of the economic minerals in the compacted precipitate.

The Geo2 Limited (Geo2) technology arose from earlier studies on the formation of naturally occurring double cation hydroxy mineral compounds (e.g., pyroaurite, hydrotalcite, takovite, green rust, etc.) at or near earth surface conditions. It was theorized from the published composition of the deep Berkeley Pit water that the component dissolved metal values could, to a large extent, be made to react with each other under suitable conditions to form a precipitate similar to the minerals cited above.

In the three experiments conducted where limestone and lime were used as the pH modifying agents, the average concentration of heavy and toxic metals was significantly reduced, and the average pH of the treated water was less than 8, making it suitable for agricultural applications.

The flocculent nature of the products that possess the pyroaurite-type structure, and possibly the presence of some unreacted limestone, added to the ease of separating by filtering the residue from the treated supernatant water. The limestone-lime treatment was decreased from 1 hour to 34 minutes without decreasing the efficiency of the remediation. Moreover, the ease of dewatering gives a compact filter residue suitable for the economic recovery of the minerals therein.

The direct use of deep Berkeley Pit water without an initial oxidative stage also provides an advantage by allowing the water to be drawn directly from the subsurface layers and treated directly in a pipe reactor whose length can be varied to increase the reaction time if necessary. The presence of supersaturated calcium sulfate (gypsum) in the treated water presents no disadvantage for agricultural use, especially in alkaline soils to which gypsum is commonly added to improve the soil structure.

Since no organic reagents are involved in the process, there is no fear of increased mutagenicity following chlorination if the treated water approaches drinking standards. Even for other than potable applications, it is highly desirable to exclude adding any organic reagents that may degrade into environmentally unacceptable compounds.

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1. Introduction

The experiments conducted at Montana Tech of The University of Montana (Montana Tech) demonstrated the Green Precipitate process patented by Geo2 Limited (Geo2), a small Australian Company listed on the Australian Stock Exchange. The capitalization of the company's market as of August 20, 1996, was approximately \$24 million U.S. dollars. The company has approximately 1,500 shareholders and has been in operation for 10 years. Apart from the Green Precipitate process, Geo2 is active in several major research projects involving both internal and grant funding.

The demonstration at the Montana Tech campus strictly followed a quality assurance project plan (QAPP) that was prepared by Montana Tech and Geo2 and approved by the U. S. Environmental Protection Agency's (EPA) National Risk Management Research Laboratory (NRMRL). The demonstration was part of the Mine Waste Technology Program (MWTP) and the Berkeley Pit Innovative Technologies Project. Montana Tech personnel involved in the demonstration were Dr. Karl Burgher, Project Manager, Mine Waste Technology Program; Mr. Steve Anderson, Associate Project Manager, Mine Waste Technology Program and Berkeley Pit Innovative Technologies Project Manager; and Ms. Catherine Wassmann, Quality Assurance Manager and Project Engineer, Berkeley Pit Innovative Technologies Project.

The Green Precipitate process was devised by Dr. Reginald Taylor, a recently retired Chief Research Scientist in the Australian Commonwealth Scientific and Industrial Research Organization and an elected Fellow of the Australian Academy of Technological Sciences and Engineering. Dr. Taylor received his Docteur en Sciences Agronomiques from the University Louvain-La-Neuve, Belgium, as well as a B.S. in Physics and an M.S. in Soil Science at the University of Adelaide, South Australia. He has recently been conducting research on transdermal drug delivery.

Dr. Taylor had previously researched the formation conditions of naturally occurring and synthetic members of the pyroaurite ($Mg_6Fe(III)_2(OH)_{16}.CO_3$) group of minerals (Ref. 1, 2, and 3). In relation, Dr. Taylor theorized that by adjusting the environmental conditions, a large proportion of the metal cations found in Berkeley Pit water could be made to react with one another to form a crystalline precipitate of such a metal(II) metal(III) hydroxy compound where the metal(III) can comprise iron (III) [Fe(III)] and aluminum (III) [Al(III)] and the various divalent cations contributing to the metal(II) composition.

Using a sample of Berkeley Pit water stored in an high-density polyethylene (HDPE) flask, some initial experiments were conducted by Geo2 in the Australian Commonwealth Scientific and Industrial Research Organization Division of Soils laboratory in Adelaide, South Australia. Because storage in HDPE still allows oxygen to diffuse in and to partially oxidize the Fe(II) present, the solution as received did not represent the actual composition of the deep Berkeley Pit water. A sample of this oxidized water was filtered and allowed to react under conditions considered favorable to the formation of a pyroaurite-type compound, and the precipitate and filtrate were examined. Using inductively coupled argon plasma (ICP) analysis, the filtrate was found to contain very low [often less than 1 part per million (ppm)] metal concentrations compared with the original status of many hundreds of ppm. X-ray diffraction analysis of the filter residue confirmed that the major precipitate was a crystalline member of the pyroaurite group. The ease of synthesizing this type of compound endorses the comment of H.F.W. Taylor who stated that it is only necessary to bring together in solution appropriate amounts of a divalent and trivalent metal at the right pH and that these pyroaurite-type compounds form very readily (Ref. 4).

In later trial experiments in Adelaide, the composition of unoxidized Berkeley Pit water was simulated from a solution of selected metal salts, generally sulfates. Again, the metal concentrations in solution were markedly reduced after initiating the precipitation reaction, which was named Induced Hydrolysis.

2. Process Description

The Geo2 bench-scale project demonstrated the removal of metal ions from Berkeley Pit water using mixed cation hydroxy salts.

2.1 General Overview

The project addressed the issue of remediating the acid mine drainage waters from the Berkeley Pit. Double or mixed cation hydroxy salts having a pyroaurite-like structure, such as the species commonly known as green rust, were precipitated from polluted waters. The hydroxy salts have the capacity to entrain foreign heavy metal cations, and because of their characteristic course, platey morphology, the sludge can easily be separated from the remediated water.

This demonstration was proposed to provide a batch bench-scale visualization of the induced selective precipitation (ISP) process. Fresh samples of Berkeley Pit water were used to optimize the process operating parameters and to reduce concentrations of reduced species in the water.

The data obtained from this demonstration may, in the future, be used to design a 3,500 gallon per minute (gpm) remediation reactor. The input stream of this reactor would be comprised of Berkeley Pit water, and the output streams would be comprised of heavy metal sludge and a remediated water stream that would meet Montana drinking water standards and National Secondary Drinking Water Regulations.

2.1.1 The Process

A schematic process description for the proposed batch ISP reactor is provided in Figure 2-1.

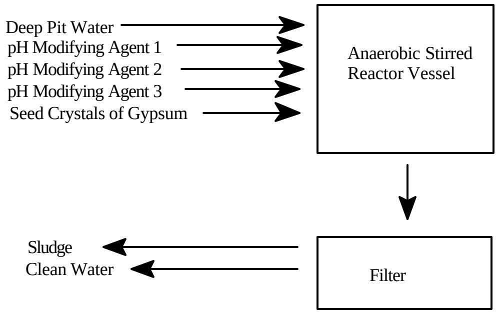

Figure 2-1. Process description of the proposed ISP reactor.

The seed crystals of gypsum were added to facilitate the precipitation of sulfate ions present in Berkeley Pit water. The three pH modifying agents (1, 2, and 3) used were limestone ($CaCO_3$), lime (CaO), and alkaline tailings. The process requires the sequential addition of pH modifying agents at various stages, and it may be possible, for example, that pH modifying agents 1 and 2 are both $CaCO_3$ but yet are delivered at different times. The goal is to find the best combination for removing heavy metals and sulfate.

The volume of the batch reactor was 500 milliliters (mL), and 400 mL of Berkeley Pit water taken from a depth of 200 feet were used in each experiment. The key features are given below.

1. Use of a combination of minor quantities of oxidized Berkeley Pit water taken from the surface with major quantities of Berkeley Pit water taken from a depth of 200 feet. The water was placed in a nonoxidizing controlled atmosphere precipitation vessel.

2. Use of a pH ramp starting from a pH of 3 (initial condition of Berkeley Pit water) and ending at a pH of 8.5 to 9 (final pH of remediated Berkeley Pit water).

3. Possible use of nucleating agents to encourage the precipitation of gypsum. Nucleating agents are small, pre-formed crystals, upon whose surfaces further precipitation can occur. By providing these starter surfaces, further crystallization can be better controlled than if no nucleating agent is present. The nucleating agents were a slurry of gypsum crystals, but various crystal sizes were tried. Nucleating agents were added in concentrations of 0.1 to 0.5%.

While initial experiments used a soluble pH modifying agent [sodium carbonate (Na_2CO_3)], further optimization work focused on the timed, multi-step addition of fine particulate pH modifying agents (e.g., $CaCO_3$ and CaO). These modifying agents were added in concentrations of 0.5 to 2%. At the conclusion of the batch reaction, the precipitate was filtered from the remediated water. The remediated water was analyzed by ICP.

2.1.2 Statement of Project Objectives

The primary project objective was to remove dissolved species in Berkeley Pit water.
The success of the process was evaluated by measuring the concentrations of copper (Cu), zinc (Zn), cadmium (Cd), arsenic (As), selenium (Se), chromium (Cr), aluminum (Al), iron (Fe), manganese (Mn), and sulfate (SO_4) and also by determining the pH before and after the Berkeley Pit water was treated. All concentrations were expected to be at or below the target levels specified in Table 3-1.

2.2 Experimental Design

For each trial run of the batch Green Precipitate process, the following measurements were taken:

Critical Measurements:

- pH of reaction vessel contents on a continuing basis; and
- concentrations of residual species in remediated water determined by ICP.

Noncritical Measurements:

- room temperature;
- calibration of pH electrodes at room temperature with two standard buffers;
- volume of Berkeley Pit water (taken from a depth of 200 feet) transferred to reactor;
- timing and volume of multi-stage addition of pH modifying agents and nucleating agents;
- time to end of reaction; and
- volume of filtrate/sludge.

The critical measurements were used to choose optimal process control values and to establish reproducibility parameters.

The batch Green Precipitate reactor was operated under various conditions of timed, multi-stage additions of pH modifying agents and nucleating agents.

One 400-mL sample of Berkeley Pit water taken from a depth of 200 feet was used for each trial experiment of the Green Precipitate process. Three of these trial experiments were replicates run under optimum process conditions.

3. Experimental Details

A series of six tests were carried out, and the methodology used in each experiment is described below. The aims of the respective tests are discussed in Section 4.

3.1 Test 1—August 12, 1996

3.1.1 Sample

A 3-liter flask of unoxidized Berkeley Pit water that was collected on August 1, 1996, from a depth of 200 feet was opened, and three subsamples were taken and used to completely fill three 500-mL autoclave bottles. Using subsamples taken from the original water sample ensured that similarly treated water was used in each of the three experiments. For each experiment, 400 mL of Berkeley Pit water were used.

3.1.2 Reagent Preparation

The pH modifying agents used were 0.1 gram (g) per milliliter (g/mL) of $CaCO_3$ and 0.1 g/mL of CaO, both in suspension. (3 g were dispersed in 30 mL of distilled water in each case.) The CaO was taken from the lower part of the bottle to minimize the risk of having CaO that might have been partially converted to carbonate.

3.1.3 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere. From the data obtained from experiment RMTMT6, it was calculated that approximately 20 mL of the $CaCO_3$ suspension were needed to quickly raise the pH to around 5.3 to 5.4. After raising the pH, aliquots of the CaO suspension, calculated from the same data obtained from experiment RMTMT6, were added at various specific times to adjust to the required pH value. The changes in pH and color resulting from these additions are noted in Table 3-1.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-mL volumetric flask; 250 mL of the filtrate were refrigerated before preparation and dispatch to Colorado. The solution was filtered through a 0.45-micrometer (µm) filter and used to make 60-, 50-, and 120-mL samples, each labeled GEO2RMT1 AUG12. The samples were coded as Geo 1-1 for analysis in Colorado.

The remainder of the solution was added to a 500-mL beaker, and 10 volts of alternating current were then applied between two graphite electrodes that had been inserted into the clear solution from 11:30 a.m. on August 13, 1996, to 9:00 a.m. on August 14, 1996. The solution was then bubbled with carbon dioxide (CO_2) for 2 hours, filtered through a #41 paper, and refrigerated before being further filtered through a 0.45-µm filter, labeled as GEO2RMT1A AUG12. The samples were coded as Geo 2-1 for analysis in Colorado.

3.2 Test 2—August 13, 1996

This experiment was a repeat of experiment GEO2RMT1. A bottle of stored Berkeley Pit water that was taken from the original 3L flask collected on August 1, 1996, was used.

3.2.1 Sample

The sample consisted of 400 mL of Berkeley Pit water that were collected August 1, 1996, and separated into subsample on August 12, 1996.

3.2.2 Reagent Preparation

pH modifying agents were 0.1 g/mL $CaCO_3$ and 0.1 g/mL CaO, both in suspension. (3 g were dispersed in 30 mL of distilled water in each case.) The CaO was taken from the lower part of the bottle to minimize the risk of having CaO that might have been partially converted to carbonate.

3.2.3 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere. The data obtained from experiment GEO2RMT1 was used to determine the amounts of $CaCO_3$ and CaO suspensions required to quickly raise the pH to around 5.3 to 5.4 and also to a pH of 7.6. The changes in pH and color resulting from these additions are noted in Table 3-4.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-mL volumetric flask; 250 mL of filtrate were refrigerated before preparation and dispatch to Colorado. The solution was filtered through a 0.45-µm filter and used to make 60-, 50-, and 120-mL samples labeled GEO2RMT2 AUG13. The samples were coded as Geo 1-2 for the Colorado analysis.

The remainder of the solution was added to a 500-mL beaker, and 10 volts of alternating current was then applied between two graphite electrodes that had been inserted into the clear solution from 11:00 a.m. on August 14, 1996, to 9:00 a.m. on August 15, 1996. The solution was bubbled with CO_2 for 2 hours, filtered through a #5 paper, and refrigerated before being further filtered through a 0.45-µm filter and labeled as GEO2RMT2A AUG12. The samples were designated as Geo 2-2 for the Colorado analysis.

3.3 Test 3—August 14, 1996

This experiment was a repeat of experiments GEO2RMT1 and GEO2RMT2. A bottle of stored Berkeley Pit water taken from the original 3L flask that was collected on August 1, 1996, was used.

3.3.1 Sample

The sample consisted of 400 mL of Berkeley Pit water that was collected on August 1, 1996, and separated into subsamples on August 12, 1996.

3.3.2 Reagent Preparation

pH modifying agents were 0.1 g/mL $CaCO_3$ and 0.1 g/mL CaO, both in suspension. (3 g were dispersed in 30 mL of distilled water in each case.) The CaO was taken from the lower part of the bottle to minimize the risk of having CaO that might have been partially converted to carbonate.

3.3.3 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere. The data obtained from experiment GEO2RMT1 was used to determine the amounts of $CaCO_3$ and CaO suspensions required to quickly raise the pH to around 5.3 to 5.4 and also to a pH of 7.6. The changes in pH and color resulting from these additions are noted in Table 3-7.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-mL volumetric flask; 250 mL of the filtrate were refrigerated before preparation and dispatch to Colorado. The solution was filtered through a 0.45-µm filter and used to make 60-, 50-, and 120-mL samples labeled GEO2RMT3 AUG14. The samples were coded as Geo 1-3 for the Colorado analysis.

The remainder of the solution was added to a 500-mL beaker, and 10 volts of alternating current were then applied between two graphite electrodes that had been inserted into the clear solution from 11:00 a.m. on August 15, 1996, to 9:00 a.m. on August 16, 1996. A much heavier than normal precipitation of gypsum was present on the electrodes and in the beaker. As a result, the suspension was filtered through a #5 filter before bubbling the filtrate solution with CO_2 for 2 hours. No additional filtering was performed before the filtrate was filtered through a 0.45-µm filter and sent to Colorado for analysis. The solution was labeled as GEO2RMT3A AUG12 and coded as Geo 2-3.

3.4 Test 4—August 12, 1996

This experiment was the first of three experiments where an alkali was used to raise the pH of the water to the levels required to remediate heavy and toxic metal concentrations. The use of alkali in remediating Berkeley Pit water was prescribed in the QAPP for the Geo2 demonstration.

In these experiments, a Metrohm Titrino unit was used to either raise the pH to a pre-set level or to carry out a reaction at a constant pH. For example, where hydrolysis of a metal species is occurring, the pH will tend to drop; therefore, the alkali must be added to restore and maintain the pre-set pH. A 1 molar (M) Na_2CO_3 solution was used, and the Metrohm Titrino unit was pre-programmed to carry out the required pH adjustments.

In the three experiments, the titration parameters, as required in the QAPP, were altered slightly to gain more information. Although the alterations could have resulted in varied residual metal concentrations in the treated water, it was determined that using an alkali to modify the pH served no useful purpose other than to repeat the experiments carried out in Australia and to demonstrate the efficacy of the technology. The use of a sodium alkali salt, such as $Na2CO_3$, to raise the pH leaves a high sodium concentration in the remediated water, which could prove deleterious to soils if the treated water was used for agricultural purposes.

3.4.1 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-mL volumetric flask; 250 mL of filtrate were refrigerated on August 16, 1996. The solution was filtered through a 0.45-µm filter to obtain 60-, 50-, and 120-mL aliquots. These samples (GEO2RMT4 AUG12) were coded as Geo 3-1 for the Colorado analysis.

3.5 Test 5—August 15, 1996

This experiment was a repeat of experiment GEO2RMT4 except a different program was used to alter the pH levels at different times.

3.5.1 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere.

In this experiment, three programs were used from the pre-programmed Metrohm unit. The programs were:

- set pH 5.3;
- pH 7.3 stat; and
- set pH 9.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-ml volumetric flask; 250 mL of filtrate were refrigerated. On August 16, 1996, the solution was filtered through a 0.45-µm filter to obtain 60-, 50-, and 120-mL aliquots. These samples (GEO2RMT5 AUG15) were coded as Geo 3-2 for the Colorado analysis.

3.6 Test 6—August 16, 1996

This experiment was a repeat of experiments GEO2RMT4 and GEO2RMT5 except different programs were used to alter the pH levels at different times.

3.6.1 Procedure

The 400 mL of Berkeley Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen was passed into the vessel above the liquid surface to create an inert atmosphere.

In this experiment, a combined program (TIP) called SUS BASE was used. This program involved five operations, which included:

- set pH to 5.3;
- set pH to 7.3;
- add 1 mL 1M $Na2CO_3$ solution;
- pause for 60 minutes; and
- pH 8.8 stat.

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel. The filtrate and washings were made up to volume in a 500-mL volumetric flask; 250 mL of filtrate were refrigerated. On August 16, 1996, the solution was filtered through a
0.45-µm filter to obtain 60-, 50-, and 120-mL aliquots. These samples (GEO2RMT6 AUG12) were coded as Geo 3-3 for the Colorado analysis.

Table 3-1. Test 1 details.

Time	**mL of $CaCO_3$ Suspension Added**	**Cumulative $CaCO_3$ Addition (mL)**	**pH Observed Trend**	**Color**
09:40			2.86	clear solution
09:40	20 mL added in 5-mL lots	20		
09:42		20	4.59	pale lemon precipitate
09:44		20	5.25	
	mL of CaO Suspension Added	**Cumulative CaO Addition (mL)**		
09:44	10	10	6.17 6 6.77	yellow olive green
09:45	1	11	6.93 6	olive green
09:46	1	12	7.09 6	olive green
09:48	1	13	7.51 67.64	olive green forming large floccules
09:49		13	7.7	
09:53		13	7.9	Going darker less dark but with brownish tinge.
10:00	$*N_2$ off air in	13	8.05	
10:00	1	14	8.94 6 9.027	
10:07			8.90 78.87	
10:10	0.5	14.5	9.42 6 7	
10:25	fast stirring	14.5	8.81 7	Getting brown
10:30	TERMINATED	14.5	8.72	
* Nitrogen				

Table 3-2. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
GEO2 RMT1	*U	U	1.1	5.09	0.09	U	0.07	U	U	2,700
GEO2 RMT1A	U	U	1.1	5.17	0.09	U	0.17	U	U	3.200
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	4,000

* The element being determined is below the limit of detection.

Table 3-3. Results allowing for dilution.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT1C	*U	U	1.32	6.36	0.11	U	0.08	U	U	3,375
GEO2 RMT1AC	U	U	1.37	6.46	0.11	U	0.21	U	U	4,000
Pit Water	U	0.001	288	209	1,070	U	572	189	1.96	9,500

*The element being determined is below the limit of detection.
RMT1 pH 8.0; RMT1A pH 5.9
GEO2RMT1C refers to the converted value after allowing for the 400-mL to 500-mL dilution.
pH of Berkeley Pit water 2.9

Table 3-4. Test 2 details.

Time	mL of $CaCO_3$ Suspension Added	Cumulative $CaCO_3$ Addition (mL)	pH Observed Trend	Color
09:40			2.9	clear solution
09:40	20 mL added in 5-mL lots			
09:42		20	5.18	pale lemon precipitate
09:44			5.41	pale lemon precipitate
	mL of CaO Suspension Added	**Cumulative CaO Addition (mL)**		
09:45	10	10	5.81 6	yellow olive green
09:48		10	7.09 6	olive green
09:48	1	11	7.73 6	olive green forming large floccules
09:54		11	8.40 6	olive green
09:56		11	8.65	
10:00		11	8.83	Going darker less dark but with brownish tinge.
10:02	*N_2 off air in	11	8.84	
10:00	fast stirring	11	8.94 6 9.027	
10:05	0.5	11.5	9.60 7	
10:14		11.5	8.94 7	
10:20		11.5	8.84	Getting brown.

10:33		11.5	8.76	
10:35		11.5	8.75 7	
10:38	TERMINATED	11.5	8.72	
*Nitrogen				

Table 3-5. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT2	*U	U	0.09	4.08	U	U	U	U	U	2,400
GEO2 RMT2A	U	U	1.0	4.0	U	U	0.07	U	U	2,800
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	4,000
*The element being determined is below the limit of detection.										

Table 3-6. Results allowing for dilution.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT2C	*U	U	0.11	5.10	U	U	U	U	U	3,000
GEO2 RMT2AC	U	U	1.25	5.0	U	U	0.08	U	U	3,500
Pit Water	U	0.001	288	209	1,070	U	572	189	1.96	10,600
*The element being determined is below the limit of detection RMT2 pH 7.9; RMT2A pH 5.6 GEO2RMT1C refers to the converted value after allowing for the 400-mL to 500-mL dilution. pH of Berkeley Pit water 2.9										

Table 3-7. Test 3 details.

Time	mL of CaCO3 suspension added	Cumulative CaCO3 addition (mL)	pH Observed trend	Color
10:43			2.91	clear solution
10:43	20 mL added in 5- mL lots	20	4.41 66	pale lemon
10:47		20	5.30	pale lemon precipitate
	mL of CaO suspension added	**Cumulative CaO addition (mL)**		
10:47	10	10	6.26 6	yellow olive green olive green brownish tinge
10:52	*N2 off air in	10	9.43 7	
11:04		10	8.95 7	
11:13		10	8.76 7	
11:17	TERMINATED	10	8.73	
*Nitrogen				

Table 3-8. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate.

Sample	**As ppm**	**Se ppm**	**Al ppm**	**Mn ppm**	**Fe ppm**	**Cr ppm**	**Zn ppm**	**Cu ppm**	**Cd ppm**	**SO4 ppm**
GEO2 RMT3	*U	U	1.0	4.11	U	U	U	U	U	2,600
GEO2 RMT3A	U	0.001	0.9	4.47	U		0.13	U	U	2,800
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	4,000
*The element being determined is below the limit of detection.										

Table 3-9. Results allowing for dilution

Sample	**As** **ppm**	**Se** **ppm**	**Al** **ppm**	**Mn** **ppm**	**Fe** **ppm**	**Cr** **ppm**	**Zn** **ppm**	**Cu** **ppm**	**Cd** **ppm**	**SO4** **ppm**
GEO2 RMT3C	*U	U	1.25	5.14	U	U	U	U	U	3,250
GEO2 RMT3AC	U	0.001	1.025	5.59	U	U	0.157	U	U	3,500
Pit Water	U	0.001	288	209	1,070	U	572	189	1.96	9,500
RMTGEO3 pH 8.0; GEO2RMT3A pH 5.3 GEO2RMT1C refers to the converted value after allowing for the 400-mL to 500-mL dilution. pH of Berkeley Pit water 2.9 *The element being determined is below the limit of detection										

Table 3-10. Test 4 details.

Time	**Action**	**Observations**
14:00	Set pH to 5.3.	Solution went from a colorless solution to a yellow brown suspension.
14:15	Program pH 7.35 stat commenced.	During this stage, the suspension acquired a green color.
14:45	Program pH 8.8 stat commenced.	Suspension became a darker green. Program stopped before pH 8.8 had been reached due to a time cutout function and was restarted. During this stage, the *N_2 was turned off and air passed in to allow some oxidation.
15:15	TERMINATED	
*Nitrogen		

Table 3-11. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate

Sample	**As** **ppm**	**Se** **ppm**	**Al** **ppm**	**Mn** **ppm**	**Fe** **ppm**	**Cr** **ppm**	**Zn** **ppm**	**Cu** **ppm**	**Cd** **ppm**	**SO4** **ppm**
GEO2 RMT4	*U	0.001	0.3	0.1	0.1	U	U	U	U	6,000
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	4,000
*The element being determined is below the limit of detection										

Table 3-12. Results allowing for dilution.

Sample	**As** **ppm**	**Se** **ppm**	**Al** **ppm**	**Mn** **ppm**	**Fe** **ppm**	**Cr** **ppm**	**Zn** **ppm**	**Cu** **ppm**	**Cd** **ppm**	**SO4** **ppm**
GEO2 RMT4C	*U	0.001	0.375	0.125	0.125	U	U	U	U	7,500
Pit Water	U	U	278	210	1,080	U	589	181	2.0	9,700
*The element being determined is below the limit of detection pH treated water 8.6 GEO2RMT1C refers to the converted value after allowing for the 400-mL to 500-mL dilution. pH of Berkeley Pit water 2.9										

Table 3-13. Record of the pH values, base consumption, and observations.

Time	Action	Observations
08:30	Stirring speed 3.	Original pH of 2.9.
08:30	Started program set pH 5.3. Required 9.609 mL 1M Na2CO3 solution to achieve pH. Time was 6 minutes.	Solution went from a colorless solution to a yellow brown with a slight greenish tinge.
08:38	second stage pH to 7.3 stat commenced.	At pH 5.6 the suspension started to acquire a green tinge.
09:08	Stirring speed increased to 4.	At pH 6.49 the color was olive green.
09:16	Stirring speed increased to 6.	
09:17	With a base consumption of 12.978 mL the pH of 7.31 was reached.	
09:18	1 mL of base injected and the solution stirred for a further hour. Then *N2 off and air admitted. pH was 7.2.	
10:18	pH 8.8 stat commenced and left stirring with the following observations.	
10:30		Going browner.
10:34	pH dropping to 8.72.	
10:38	pH down to 8.66.	Very flocculent green-brown precipitate.
10:38	TERMINATED pH was now 8.65.	
*Nitrogen		

Table 3-14. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT5	*U	0.001	U	1.39	U	U	0.06	U	U	6,200
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	
*The element being determined is below the limit of detection.										

Table 3-15. Results allowing for dilution.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT5C	*U	0.001	U	1.74	U	U	0.075	U	U	7,750
Pit Water	U	U	278	210	1,080	U	589	181	2.0	9,700
* The element being determined is below the limit of detection pH of treated water 8.8 GEO2RMT1C refers to the converted value after allowing for the 400-mL to 500-mL dilution. pH of Berkeley Pit water 2.9										

Table 3-16. Record of the pH values, base consumption, and observations.

Time	Action	Observations
08:56	Stirring speed 3.	Original pH of 2.9.
08:56	Started combined program. Required 8.24 mL of alkali to bring the pH to the first value of 5.3 and this took 9 minutes.	Solution went from a colorless solution to a yellow brown suspension at about pH 4.
09:05	Second stage set pH to 7.3 started.	At pH 5.6 the suspension started to acquire a green tinge.
09:08	Stirring speed increased to 4.	At pH 6.49 the color was olive green.
09:16	Stirring speed increased to 6.	
09:17	With a base consumption of 12.978 mL the pH of 7.31 was reached.	
09:18	1 mL of base injected and the solution stirred for a further hour. Then *N2 off and air admitted. pH was 7.2	
10:18	pH 8.8 stat commenced and left stirring with the following observations.	
10:30		Going browner.
10:34	pH dropping to 8.72.	
10:38	pH down to 8.66.	Very flocculent green-brown precipitate
10:38	TERMINATED pH was now 8.65.	

*Nitrogen

Table 3-17. Results of ICP analysis for the 400-mL diluted to 500-mL filtrate.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4\ ppm
GEO2 RMT6	U	0.002	0.2	13.8	U	U	0.13	U	U	6,500
Target	0.1	0.2	2.0	7.0	0.3	0.05	5.0	1.0	0.01	4,000

Table 3-18. Results allowing for dilution.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm
GEO2 RMT6C	*U	0.0025	0.25	17.25	U	U	0.162	U	U	8,125
Pit Water	U	U	278	210	1,080	U	589	181	2.0	9,700

*The element being determined is below the limit of detection
pH of treated water 8.1
GEO2RMT6C refers to the converted value after allowing for the 400-mL to 500-mL dilution.
pH of Berkeley Pit water 2.9

4. Results and Discussion

Although six experiments were described in Section 3, nine results were actually obtained from ACZ Laboratories in Steamboat Springs, Colorado. The additional results were received because the filtrate obtained from Tests 1, 2, and 3 were divided into two parts: one part was analyzed by ICP, Ion Chromatography, and for electrometric pH determination while the remainder of the solution was further treated by a form of gypsum seeding followed by bubbling in of CO_2. In Table 4-1, the second series of three samples, designated MT1A, MT2A, and MT3A, represent the further treatment of samples 1, 2, and 3.

The third series of experiments, MT4, MT5, and MT6, were performed only as a replication of the earlier trial tests carried out in Adelaide. A 1M Na_2CO_3 solution was used for the pH modification, and reactions at a pH of 7.3 and 8.6 were carried out under pH stat conditions. The methods and times of the pH modifications in the three experiments were varied; however, this remediation method did not warrant repeating the three experiments. The decision not to repeat the experiments was made because any marked increase in the sodium level of the effluent water would make the effluent unsuitable for application to soils by reducing both its structure and fertility.

In all of the experiments conducted throughout this demonstration, 400 mL of Berkeley Pit water after treatment were made to 500-mL volume for analysis. The results given in Table 4-1 have been corrected for this dilution by multiplying the determined concentrations by 1.25.

In Table 4-1, "U" denotes that the element being determined is below the limit of detection for the standard method being used. These detection limits (in ppm) for the various elements cited are: As 0.02; Se 0.04; Al 0.03; Fe 0.01; Cr 0.01; Zn 0.05; and Cd 0.003.

As is evident in Table 4-1, the environmentally unacceptable concentration of most of the heavy and toxic metals has been markedly reduced to levels that would be acceptable for agricultural applications. The residual high concentration of sulfate is due to the super-saturation of the water with gypsum, which, for certain soils, is an added advantage. The metal concentration levels for the first six samples are at or below the modified target values specified in the QAPP. Some of the analytical results raise questions that need to be considered. For example, in sample MT2, the Al concentration is listed as 0.11 ppm; whereas, in sample MT2A, which was the same solution further treated to remove gypsum and excess Ca, the level is increased to 1.25 ppm. Similar anomalies arise from the variation in the Zn levels, which are, however, below the target value. One contributing factor could have been the dilution factor correction applied to the A group samples. During the 20-hour gypsum seeding, some evaporation occurred; however, the full dilution factor was applied.

By comparing the first two groups of three samples (i.e., 1 with 1A, etc.), it is seen that the further treatment did not reduce the sulfate concentration reflecting the gypsum content in solution. However, the pH was reduced, which was probably due to the bubbling in of CO_2 into the final effluent. The CO_2 liberated in the first pH modification treatment with CaO could be fed into this later process stage to modify the final pH.

The green precipitate described in each of the experiments dried out readily when exposed to air and turned to a yellow or yellow-brown powder. The three precipitates from the alkali-treated samples, however, were less friable.

In the Appendices, four of the preliminary experiments (RMTMT2, RMTMT4, RMTMT5, and RMTMT6), which were conducted at Montana Tech, are described. The presumed optimum conditions were chosen from these experiments. In experiment RMTMT5, powdered calcium carbonate and CaO were added as the pH modifiers rather than adding these compounds in suspension. The analytical results from this experiment, obtained from the analytical facilities at Montana Tech, show that there was little loss of efficiency in using the powder rather than the suspension by comparison with RMTMT6.

Experiment RMTMT2 was conducted using only CaO rather than $CaCO_3$ and CaO. The analytical results for this experiment show that the remediation of the Berkeley Pit water was equally efficient as with those experiments done with both $CaCO_3$ and CaO.

Assuming a similar efficiency with an upscaling of this methodology and assuming a treatment rate of 3,500 gallons (imperial)/minute for 24 hours a day and 7 days per week, there would be a consumption of approximately 40,500 tons of $CaCO_3$ and 20,200 tons of CaO per annum for the processing of around 1.5 billion gallons of water.

Table 4-1. Results of analyses using variations of the Green Precipitate Process.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO4 ppm	pH
RMT1	*U	U	1.325	6.36	0.112	U	0.087	U	U	3,375	8.0
RMT2	U	U	0.11	5.1	U	U	U	U	U	3,000	7.9
RMT3	U	U	1.25	5.14	U	U	U	U	U	3,250	8.0
RMT1A	U	U	1.35	6.46	0.112	U	0.212	U	U	4,000	5.9
RMT2A	U	U	1.25	5.0	U	U	0.087	U	U	3,500	5.6
RMT3A	U	0.001	1.025	5.59	U	U	0.157	U	U	3,500	5.3
RMT4	U	0.001	0.375	0.125	0.125	U	U	U	U	7,500	8.6
RMT5	U	0.001	U	1.74	U	U	0.075	U	U	7,750	8.8
RMT6	U	0.002	0.25	17.25	U	U	0.1625	U	U	8,125	8.1
PIT WATER	U	0.001	288	209	1070	U	572	189	1.96	9,500-10,600	2.9

*The element being determined is below the limit of detection

5. References

1. Taylor, R.M., “Formation and Properties of Fe(II) Fe(III) Hydroxy-Carbonate and Its Possible Significance in Soil Formation, *Clay Mineral, 15*, 369-382, 1980.
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3. Taylor, R.M., Schwertmann, U., and Fechter, H., “A Rapid Method for the Formation of Fe(II) Fe(III) Hydroxy- Carbonate, *Clay Mineral, 20*, 147-151, 1985.
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Appendix A

Data Validation

Appendix B

Results Obtained from Montana Tech

Sample RMTMT2AUG1

Material Used: Fresh Pit water collected August 1 in 3-liter glass containers that were filled completely, stoppered, and covered with parafilm.

Reagent Preparation: pH modifying agent is 0.731M CaO suspension (3.2 g dispersed in 80 mL of distilled water).

Material Preparation: 400 mL of the freshly gathered Pit water. The residual Pit water in the glass bottle was also bubbled with the natural gas for about 10 seconds before being closed in an effort to minimize oxidation.

Procedure: The 400 mL of Pit water was added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of natural gas as an inert atmosphere was passed into the vessel above the liquid surface. Samples of the prepared CaO suspension being constantly stirred magnetically were taken using a dispensing pipette and added to the solution at noted times. From the earlier results of RMTMT1JUL31, larger amounts of suspension could be added without overshooting the pH values required at the various stages of the experiment. The resultant changes in pH and color resulting from these additions were noted in the table below.

Time	mL of CaO suspension added	Cumulative addition (mL)	pH Observed Trend	Color
11.30			3.03	clear solution
11.30	5	5	3.81	
11.35	8	13	4.59	pale lime green
11.38	8	21	5.13 6	slightly darker
11.40	8	29	5.87 6 5.96	dark olive green
11.42	1	30	6.04 6 6.05	
11.43	1	31	6.12 6 6.16	
11.44	5	36	6.59	going darker
11.47	6	42	7.52 67.607	
			7.51 67.70	
11.58	5	47	9.53 7	
12.07		47	9.05	a brown tinge
12.21		47	8.99	lighter brown/green
13.17		47	8.82	going y/brown
13.20		47	8.81	
13.30	TERMINATED	47	8.79	

The dark green-brown suspension had been diluted to 559 mL, and 250 mL were taken and bottled for ICP analysis and labeled as RMTMT2AUG1.

The remainder of the solution was added to a 500-mL beaker, and 10 volts of alternating current were applied between two graphite electrodes inserted into the clear solution (14.00 hours). At 9.00 hours on August 2, the electrodes were removed, and a small amount of sodium carbonate was added to the clear solution. There was an immediate flocculent white ppte, presumably $CaCO_3$, which was easily filtered off. The filtrate was labeled RMTMT2AAUG1 and sent for ICP analysis. The residue from the first filtration was labeled as such with the code RMTMT2AUG1 and, after drying, consisted of a yellow-brown powder as expected.

A 400-mL sample of the fresh Pit water was made up to 500 mL and sent with the other samples for analysis to obtain an estimation of the effectiveness of the technique.

The values obtained for analysis of the solutions RMTMT2AUG1 and RMTMT2AAUG1 by ICP were:

SAMPLE	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Mg ppm	Ca ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT2	BDL	BDL		3.151	BDL	0.009		702.4	0.013	0.029	0.0067	2309
RMTMT2A	BDL	BDL		BDL	BDL	0.029		2.884	BDL	0.021	0.0024	2878

Analysis of the same samples by Bill Chattam gave the following results:

SAMPLE	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Mg ppm	Ca ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT2		0.054	0.140	3.289	BDL	BDL	67.9	601	0.028	0.031	0.0089	2309
RMTMT2A		0.024	0.014	0.038	0.004	0.029	46.79	3.554	0.022	0.057	0.0022	2878

After correction for dilution of the solutions the values were :

SAMPLE	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Mg ppm	Ca ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT2	BDL	BDL		4.39	BDL	0.012		979	0.018	0.041	0.0094	3321
RMTMT2A	BDL	BDL		BDL	BDL	0.041		3.982	BDL	0.029	0.0034	4014

This suggests that purging with CO_2 after gypsum has precipitated will reduce the Ca level following the extensive use of CaO and $CaCO_3$ to modify the pH.

August 5, 1996

Sample RMTMT4AUG5

Sample: 400-mL fresh Pit water collected August 1 in 3-liter glass containers that were filled completely, stoppered, and covered with parafilm.

Reagent Preparation: pH modifying agents were 0.1 g/mL 1 micron $CaCO_3$ suspension and 0.1 g/mL CaO suspension (3 g dispersed in 30-mL distilled water in each case).

Procedure: The 400 mL of Pit water was added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of natural gas as an inert atmosphere was passed into the vessel above the liquid surface. From the data of experiment RMTMT3, it was calculated that about 17 mL of the $CaCO_3$ suspension was needed to quickly raise the pH to around 5.3 to 5.4. After that value, aliquots of the CaO suspension, calculated from the data of RMTMT3, were added at the various times to adjust to the required pH value. The resultant changes in pH and color resulting from these additions are noted in the table below.

	mL of CaCO3	Cumulative CaCO3	pH Observed - trend	Color
10.06			2.97	clear solution
10.06	17	17	4.88 6	pale lemon suspension
10.08	1	18	5.00 6	
10.08	2	20	5.12 6	pale yellow ppte
	mL of CaO	Cumulative CaO		
10.13	14	14	7.2967.68	olive green
10.17		14	7.68	
10.23		14	7.77	
10.30		14	7.91	
10.50 air in		14	8.30	dark green
11.12		14	8.40	
11.12	2	16	9.917	
11.19		16	8.767	
11.19	1	17	9.557	lighter green
11.43		17	8.59	
11.43	0.5	17.5	9.15	brownish tinge
11.58		18	8.67	
12.34		18	8.48	
12.35	0.5	18	9.26	yellow brown
12.43		18	8.87	
		18		
10.45	TERMINATED	18	8.82	

The dark green-brown suspension was filtered, and the filtrate and washings were made up to volume in a 500-mL volumetric flask. A total of 250 mL were taken and bottled for ICP analysis and labeled as RMTMT4AUG5. The sample was then refiltered through a 0.45-µm filter.

The remainder of the solution was added to a 500-mL beaker, and 10 volts of alternating current were applied between two graphite electrodes inserted into the clear solution until 10.00 on August 6. There was no visible precipitate. The solution was then stirred magnetically for 2 additional hours; powdered gypsum from the filtered MT3A3 was then added as seed crystals. This was stirred for an additional hour before filtering first through a #42 paper to retain the seed material and then through a 0.45-µm filter. The sample was sent for analysis labeled as RMTMT4A.

Results of ICP analysis for the 400-mL diluted to 500-mL filtrate was:

Sample	As	Se	Mn	Fe	Cr	Ca	Zn	Cu	Cd	SO_4
RMTMT4	BDL	0.125	1.535	BDL	0.046	260	0.015	0.012	0.006	2236
MT4A	BDL	BDL	1.77	BDL	BDL	182	0.053	0.006	BDL	?
Target	0.1	0.2	0.05	0.3	0.05		5.0	1.0	0.01	

When converted to the original volume, the concentrations in the treated Pit water can be compared to the Pit water as sampled on August 1. RMTMT4C refers to the converted value.

Sample	As	Se	Mn	Fe	Cr	Ca	Zn	Cu	Cd	SO_4
RMTMT4C	BDL	0.16	1.92	BDL	0.058	325	0.02	0.015	0.08	2795
MT4AC	BDL	BDL	1.21	BDL	BDL	227	0.06	0.008	BDL	?
Pit Water - No Values										

August 7, 1996

Sample RMTMT5AUG7

This experiment was based on the data of RMTMT4 of August 5; however, the limestone and lime were added as a solid powder rather than as measured volumes of a known density suspension. Because there may not have been an adequate dispersion on addition of the powder, a greater amount of limestone than necessary may have been used.

Sample: The 400 mL of fresh Pit water collected on August 1, which had been subsamples and stored in 500-mL autoclave bottles, were completely filled and stoppered.

Reagent Preparation: pH modifying agents were powdered 1 micron $CaCO_3$ and AR grade CaO. It is not known whether there had been any transformation of the lime to $CaCO_3$.

Procedure: The 400 mL of Pit water were added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of CO_2 was used as a nonoxidizing atmosphere. However as soon as CaO was being added, it was realized that the CO_2 could react and precipitate the CaO as limestone without modifying the pH to the extent it should. At this stage, shown in the time table below, natural gas was introduced instead. The resultant changes in pH and color resulting from additions of powdered limestone and lime are noted in the table below.

Time	grams of CaCO3 added	Cumulative CaCO3 addition (grams)	pH Observed - trend	Color
09.30			2.88	clear solution
09.30	2	2	3.7 6 slowly	pale lemon suspension
09.32		2	4.00 6	
09.33		2	4.83 6	pale yellow ppte
09.45		2	5.21 6	
	grams of CaO added	Cumulative CaO addition (grams)		
09.45	1	1	5.55	greenish tinge
09.48		1	5.64	yellow-olive color
09.54	Air6 natural gas	1	5.88	
09.55-10.00	1.0	2		yellow/olive green
10.03		2	6.936	becoming greener
10.04		2	7.066	
10.06		2	7.106	olive green
10.10		2	7.186	getting darker
10.13		2	7.576	
10.17		2	8.096	
10.30		2	9.287	gas off air in
10.38		2	9.147	getting brown tinge
10.46		2	9.03	
10.50	Terminated	2	9.00	yellow brown

The dark green-brown suspension was filtered, and the filtrate and washings were made up to a volume of a 564-mL volumetric flask. A total of 250 mL were taken and bottled for ICP analysis and labeled as RMTMT5AUG7. This was stored in the refrigerator and was refiltered through a 0.45-µm filter for analysis.

The remainder of the solution was added to a 500-mL beaker and stirred for 5 hours. It was then subjected to a 10-volt ac electrolysis using graphite electrodes inserted into the clear solution at 16.15. After 17 hours (09.15 Aug. 8), the electrolysis was stopped, and it was noted that there had been a good yield of gibbsite. The suspension was filtered through a #42 paper, and CO_2 was passed through the filtrate for 2 hours. The solution was then filtered through a 0.45-µm filter for analysis. This sample was labeled as RMTMT5AAUG7.

Results of ICP analysis for the 400-mL diluted to 500-mL filtrate were:

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT5	BDL	2.87	1.28	0.73	BDL	BDL	0.001	BDL	0.006	
MT5A	BDL	2.16	1.27	0.68	BDL	BDL	0.036	0.059	0.006	
Target	0.1	0.2	0.15	0.05	0.3	0.05	5.0	1.0	0.01	

When allowance is made for the dilution from 400 to 564 mL, the concentration values are modified as below. The C designation refers to the adjusted value.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO$_4$ ppm
RMTMTC	BDL	4.05	1.81	1.03	BDL	BDL	0.002	BDL	0.008	
MT5AC	BDL	3.05	1.80	0.95	BDL	BDL	0.052	0.08	0.009	
Pit Water - No Values										

Note that in this experiment, 2 g of limestone and 2 g lime were used for the 400 mL. I don't believe the limestone was used efficiently. The high Se concentration in both samples seems unreasonable in view of all the previous results.

August 8, 1996

Sample RMTMT6AUG8

Sample: The 400 mL of Pit water was collected August 1, was subsampled, and was stored in a 500-mL stoppered autoclave.

Reagent Preparation: pH modifying agents were 0.1 g/mL 1 micron $CaCO_3$ suspension and 0.1 g/mL CaO suspension (3 g dispersed in 30-mL of distilled water in each case). The CaO was taken from the lower part of the bottle to minimize the risk of having CaO that might have been partially converted to the carbonate.

Procedure: The 400 mL of Pit water was added to a Metrohm reaction vessel, and a calibrated pH probe was inserted. A small flow of nitrogen as an inert atmosphere was passed into the vessel above the liquid surface. From the data of experiment RMTMT4, it was calculated that about 17-20 mL of the $CaCO_3$ suspension was needed to quickly raise the pH to around 5.3 to 5.4. After that value, aliquots of the CaO suspension, calculated from the data of experiment, were added at the various times to adjust to the required pH value. The resultant changes in pH and color resulting from these additions were noted in the table below.

Time	mL of CaCO3 suspension added	Cumulative CaCO3 addition (mL)	pH 0bserved - trend	Color
10.30			2.88	clear solution
10.40-10.44	20 mL added in 5-mL lots	20	4.81 6 5.38	pale lemon suspension
10.44	2.0	20	5.12 6	pale yellow ppte
	mL of CaO suspension added	Cumulative CaO addition (mL)		
10,44-10,47	12	12	5.12 6	
10.48		12	7.64 6	olive green
10.50		12	7.94 6	
10.52		12	8.20 6	dark green
10.55		12	8.67 6	dark green
11.00		12	8.92 6	
11.00	0.2	12.2	9.31 7	less dark but with brownish tinge
11.13	N2 off air in	12.2	9.10	
11.3	TERMINATED	12.2	9.27	still very green

The dark green-brown suspension was filtered through a #41 paper using a Buchner funnel, and the filtrate and washings were made up to volume in a 500-mL volumetric flask. A total of 250 mL were taken, and after filtering through a 0.45-µm filter, were bottled for ICP analysis, labeled, and stored in the refrigerator.

The remainder of the solution was added to a 500-mL beaker, and gypsum seeds harvested from the earlier work were added; 10 volts of alternating current were then applied between two graphite electrodes inserted into the clear solution for 4 hours with magnetic stirring. The suspension was then filtered through a #41 paper and bubbled with CO_2 for 15 minutes before further filtering through a 0.45-µm filter. The solution was then labeled as RMTMT6AAug8 and sent for analysis.

Results of ICP analysis for the 400-mL diluted to 500-mL filtrate were:

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Zn ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT6	BDL	BDL	0.156	0.876	BDL	BDL	0.064	0.04	0.123	
MT6A	BDL	BDL	0.284	1.092	BDL	BDL	BDL	0.05	0.01	
Target	0.1	0.2	0.15	0.05	0.3	0.05	5.0	1.0	0.01	

RMTMT6C refers to the converted value after allowing for the dilution.

Sample	As ppm	Se ppm	Al ppm	Mn ppm	Fe ppm	Cr ppm	Mg ppm	Cu ppm	Cd ppm	SO_4 ppm
RMTMT6C	BDL	BDL	0.195	1.09	BDL	BDL	103	0.04	0.016	
MT6AC	BDL	BDL	0.355	1.36	BDL	BDL	120	0.06	0.012	
Pit Water - No Values										

The increase in the concentration of some elements in the A sample does not seem feasible since it should be at least as low as the original treated filtrate from treatment.