Maxi-Acid (TM): In-Situ Amelioration of Acid Mine Drainage Problems

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EXECUTIVE SUMMARY

The development of technologies to ameliorate acid mine drainage problems has had few successes. Most often, once acid mine drainage exists, the company responsible develops treatment programs to make sure that water resources and land are not contaminated by the acid mine drainage. These treatments usually result in significant costs and do not result in a cure to the problem.

Much effort and money has been spent on the problems associated with acid mine drainage. However, it appears that most of the meaningful breakthroughs have come in the area of treatment of the results of the problem (i.e. water treatment). There have been few breakthroughs in the prevention of acid formation. Most of the work associated with the prevention of acid formation has dealt with the prevention of oxidation using grouting to seal mines, removing oxygen from the system or preventing water flow into the mines, using bactericides to eliminate the catalytic effect of *Thiobacillus ferrooxidans*, and modifying the mining methods. The Maxi-Acid™ technology takes a different approach to the problem. A site treated using Maxi-Acid won't be expected to generate acid mine drainage for a number of years, if ever. The application of Maxi-Acid is expected to eliminate continuous treatment of acid waters discharged from applicable mine sites.

The work accomplished to date includes characterization of overburden materials that contain large quantities of potential acidity, and preliminary evaluations of the acid-generating capabilities of materials containing high levels of potential acidity (pyritic materials) using humidity cells

This research effort is in the preliminary stages. To date, a number of interesting findings have been made that could be used to contribute to the elimination of acid mine drainage. However, the concepts that are expected to have the most significant impact on the formation of acid mine drainage have not yet been substantiated.

INTRODUCTION

Problem and Significance

Presently, millions of hectares of land are influenced by acid mine drainage problems. Current estimates for the treatment of acid mine drainage from active mine sites are in the hundreds of millions of dollars on an annual basis. A recent article by Dr. Paul Ziemkiewicz, the director of the National Mine Land Reclamation Center, indicated that the coal industry in West Virginia alone spends roughly \$1 million per day treating acid mine drainage. The total cost is substantially higher since it is often necessary to treat acid mine drainage from mines and refuse piles for decades following coal extraction and/or cleaning. A major part of the cleanup of abandoned mine sites is also associated with acid mine drainage problems. It is estimated that the cleanup of the half-million abandoned mine sites currently thought to exist could cost up to \$71 billion. It is obvious that the problem is immense and becoming more significant each day. Over the past four or five decades, volumes of information have been gathered relative to the environmental and socioeconomic impacts of acid mine drainage. However, new ideas and approaches to ameliorate the problem are needed.

Background

A considerable amount of research has been done on acid mine drainage issues over the past forty or fifty years. Much of the work has been associated with the mechanisms responsible for the formation of the acid waters and the treatment of acid waters discharging from reaction sites. These areas are still the topics of major research programs. At the present time, considerable effort is being expended to develop technologies to prevent acid mine drainage from developing. Such procedures as mixing fly ash from power plants and kilns with spoil that contains significant amounts of potential acidity have been used successfully to prevent the generation of acid.

Most of the work associated with the amelioration of acid mine drainage problems has dealt with the prevention of pyrite oxidation by sealing mines and using bactericides to eliminate the catalytic effect of *Thiobacillus ferrooxidans*. In addition, neutralization of the acid using lime products and other materials, such as apatite, that react with the reaction products of the acid generation have also been used with some success. However, the fact is that most of the technologies developed have not greatly reduced the acid mine drainage problem.

The Formation of Acid Mine Drainage

Acid mine drainages typically have pH values below 2.3, acidities near 5000 mg/L, and anionic concentrations (mostly sulfate) exceeding 10,000 mg/L (Caruccio et al., 1981). Iron disulfides in the

form of pyrite and marcasite are the predominate contributors to the production of acid mine drainage. The following reactions occur during the oxidation of the disulfides as described by Stumm and Morgan (1970):

The stoichiometry of equation (1) shows that for every mole of pyrite oxidized to Fe^{2+} , there are two moles of acidity generated as H^+ . Subsequently, the Fe^{2+} is oxidized to Fe^{3+} via reaction (2). This reaction proceeds quite slowly; in fact Stumm and Morgan (1970) observed half-times for Fe^{2+} oxidation on the order of 1000 days. Once the Fe^{3+} is formed, it combines with H_2O to form insoluble $\text{Fe}(\text{OH})_3$ as shown in equation (3). Therefore, the dissolution of each mole of pyrite results in the release of four equivalents of acidity. As the Fe^{3+} concentrations increase with increased acidity, the Fe^{3+} becomes important as an oxidizing agent. Several research efforts have shown that pyrite is rapidly oxidized by Fe^{3+} in the absence of oxygen and at low pH values (Garrels and Thompson, 1960; Smith et al., 1968). This reaction is shown above as (4). Fe^{3+} becomes the only important oxidizing agent when pH values are in the 3 or below range (Singer and Stumm, 1969). These researchers also found that the presence of O_2 did not influence the kinetics of the reaction. Since pyrite can reduce Fe^{3+} to Fe^{2+} faster than Fe^{2+} can be regenerated into Fe^{3+} by O_2 , the pyrite will reduce all the Fe^{3+} and the reaction will stop. Thus, the Fe^{2+} to Fe^{3+} oxidation is considered to be the rate-limiting step in the production of acid. A major catalyst of this reaction is the bacterium *Thiobacillus ferrooxidans*, which is known to increase the Fe^{2+} oxidation rate by six orders of magnitude (Singer and Stumm, 1970; Nordstrom, 1976). This reaction makes Fe^{3+} readily available for pyrite oxidation.

The amount of acid generated from pyritic materials can be reduced or eliminated by inhibition of the iron-oxidizing bacteria and the reduction in the solubility of Fe^{2+} and Fe^{3+} , with increased pH resulting from the production of alkalinity. In fact, Caruccio (1968) showed that the amount of acidity of mine drainages in western Pennsylvania was a function of (1) the pH of the groundwater, (2) the presence of calcareous materials such as CaCO_3 within the strata, (3) the mode of occurrence of the iron disulfides, and (4) the neutralizing capacity of the ground water. Similar results were obtained in studies in eastern Kentucky (Caruccio et al., 1976; Caruccio and Geidel, 1978; and Caruccio et al., 1977). From this brief discussion, it is apparent that materials such as CaCO_3 and CaO that possess neutralization potential can be used with favorable results to reduce acid mine

drainage problems. In fact, many studies have shown that limestone materials were effective in neutralizing acid in acid mine drainage applications (Mihok and Chamberlain, 1968; Pearson and McDonnel, 1975; Barton and Vatanatham, 1976; Geidel and Caruccio, 1982). In addition, fly ash materials that possess neutralization potential have been used as amendments to surface "soils" to ameliorate acid conditions with some success. Thus, it is apparent that clean coal technology waste grouts with significant neutralization potential would influence the development of acid mine drainage from grouted underground mines.

The Treatment of Acid Mine Drainage

Many attempts have been made to treat the acid mine drainage problem. Surface materials have been removed, and lime has been applied to the surface areas to increase the alkalinity of groundwater recharge waters, which would neutralize the acidity of the discharge water. Materials such as kiln dust and fly ash from coal combustion have been mixed with acid-forming materials, resulting in waters that meet discharge requirements. Cropping techniques such as growing alfalfa in the recharge areas have also been used to reduce the amount of recharge available to the affected aquifer. Wetland sites have been constructed to provide passive treatment systems for the cleanup of acid waters. Many of these techniques, if properly implemented during a mining or reclamation operation, may result in a post-mining condition that does not produce acid mine drainage, at least in the short run. However, research in the containment or elimination of acid mine drainage from sites that are currently producing acid has shown limited success. Attempts to eliminate the continued formation of acid have included the use of bactericides and the use of grouting and other techniques, such as modification of mining plans, to prevent oxygen and/or water from reaching the reaction zone. It is anticipated that Maxi-AcidTM could become an important treatment process for a large number of acid mine drainage sites.

TECHNICAL APPROACH

The objective of this project is to develop Maxi-Acid, a process for the in-situ treatment of acid mine drainage problems.

Laboratory Simulation and Method Development

The overburden material that contains the acid-forming material is placed in flexible-wall permeameters and/or rigid-wall columns and leaching pads for testing purposes. The materials are subjected to different environmental conditions that may influence the production of acidity and alkalinity.

Elimination of the Oxidation Process

The system is affected with amendments, such as lime slurries, phosphate solutions, and bactericides (Promac), that will reduce and possibly eliminate the production of acid. Leachates will be sampled and analyzed for pH and elements such as Fe, Al, and Mn.

Treatment System for an Underground Mining Situation

A simulated underground mine will be established in the laboratory using a set of columns. The columns will contain acid-forming materials that are actively generating acid due to the oxidation of pyritic materials. The treatments will be incorporated into the system with a peristaltic pump at a rate that seems to simulate water movement through an underground mine. Appropriate analysis will be made of the water exiting the columns as the experiments progress.

Treatment System for a Surface Mining Application

A simulated surface mining operation will be established in the laboratory using a leaching pad. Various methods of treatment application will be tested, including surface applications and injection at specific depths. The chemicals used in this type of treatment will be critical to the success of the process. A significant effort will be made to use materials that result in an environmentally sound treatment. Following the treatment, additional leaching of the treated materials with water will provide an evaluation of the importance of "elemental bleeding" following the treatment.

Retrieval of Waters from the Treated System

Following the injection of treatment materials into the reaction zone of the mine system, unreacted treatment solutions and reaction products must be removed, treated and disposed of. Several methods will be evaluated to remove the reaction products from the reaction zone, including a pump and treat system. Other possibilities will include horizontal and vertical wells and weeping well collection systems.

RESULTS AND DISCUSSION

The work accomplished to date includes characterization of overburden materials that contain large quantities of potential acidity and preliminary evaluations of the acid-generating capabilities of materials containing high levels of potential acidity (pyritic materials) using humidity cells.

Characterization of the Overburden Materials Used in the Study

The materials used for this work were collected from the lignite mining area of southeastern Texas. This overburden was selected as a typical material containing high amounts of potential acidity. The origin of the material is the reduced overburden collected from the Wilcox Group. These materials usually contain pyritic materials in various morphological forms such as framboids, polyframboids, and larger sand and silt size particles. The materials typically have from 0.1% to 1.5% pyritic sulfur content prior to oxidation. The materials collected consisted of reduced overburden material that had been influenced by air oxidation for a considerable period of time and a reduced material that had recently been extracted from the overburden formation. Chemical evaluations with respect to acid/base potential are shown in Table 1. The oxidizing overburden had a pH of 2.8 and an acid/base potential of -30.4 Kg CaCO₃/1000 Kg of overburden material, and the reduced material had a pH of 4.1 and an acid/base potential of -58.3 Kg CaCO₃/1000 Kg of overburden material. The oxidized material contains significant salt levels (electrical conductivity = 9.5) compared to the unoxidized material (electrical conductivity = 2.6). This difference would be expected as a result of pyrite oxidation and the subsequent release of salts.

Table 1. Potential Acidity Evaluations of the Reduced Overburden Materials

Characteristic	Reduced Overburden (No Oxidation)	Reduced Overburden (Oxidizing)
pH	4.1	2.8
EC (mS/cm)	2.6	9.5
Total Sulfur(%)	1.86	0.78
Total S Potential Acidity (Kg/1000Kg)	58.1	24.4
Neutralization Potential (Kg/1000Kg)	-0.19	-6.06
Total S Acid/Base Potential (Kg/1000Kg)	-58.3	-30.4
Sulfate S (%)	0.27	0.35
Pyritic S (%)	1.47	0.37
Organic S (%)	0.12	0.06
Pyritic S Potential Acidity (Kg/1000Kg)	45.9	11.6
Pyritic S Acid-Base Potential (Kg/1000Kg)	-46.1	-17.6
Acidity (meq/100g)	6.06	7.03

Long-Term Acid-Generating Capacity of Acid-Forming Overburden

The acid-generating capacity of the acid-forming materials was evaluated using a humidity cell technique. The intention of this work is to provide a baseline for our continued effort with Maxi-Acid and to determine if the treatment can result in the reduction of acid formation. The humidity cell oxidation process was run for 336 days, with the pH and electrical conductivity (EC) data presented in Figures 1 and 2, respectively. The acid-forming materials used in this study had an initial pH of 3.44 and an EC of 3.88 mS/cm. As the humidity cell oxidation progressed, the pH decreased to about 2.75 after 7 days and tended to slowly decrease to about 2.46 after 70 days. From 70 days to 336 days, the pH fluctuated between 2.6 and 2.8 (Figure 1). These data indicate that the acid-forming process is initially accelerated to a level that is dictated by the mineralogy of the system.

The EC data shown in Figure 2 provide similar indications. The initial increase in EC from 3.88 to about 9.16 is due to the large amount of reaction products generated by the accelerated acid-forming reactions. The EC values decreased from day 7 to day 336 as the oxidation processes continued. This substantial reduction in EC values is due to the use of leaching as part of the weekly operation of the humidity cell, resulting in the removal of reaction products from the system. In addition, the kinetics of the reactions causing the reduction of pyritic materials may be slowing.

Figure 1. The Influence of Humidity Cell Treatment on the pH of the Acid-Forming Overburden with Time

Figure 2. The Influence of Humidity Cell Treatment on the EC of the Acid-Forming Overburden with Time

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