LABORATORY STUDY OF THE COATING METHOD TO CONTROL ARD GENERATION

by

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ABSTRACT

This study proposed a new approach in preventing ARD generation by coating rock surfaces to exclude moisture and oxygen. Four market-available materials, two of them epoxy based, one aromatic based, and the other silicon based, were tested with five different test conditions and techniques.

Six ARD generation tests were carried out to study the characteristics of the rock samples. The rock samples showed a strong ARD generating potential. The pH value and metal concentrations of the rock samples were near these observed in field measurements. The water to rock ratio influenced ARD generation significantly. The higher the rock to water ratio, the lower the pH value, and the higher the metal concentrations.

Five testing methods and techniques were carried out to study the coating material's ability to prevent ARD generation. In the coating capacity test, coating materials, epoxy-41, epoxy-43, and aromatic-W were tested with the agitation of water circulation. There was no significant difference amongst the three samples in pH and metal concentration.

The freezing and thawing test was designed to study the performance of materials during and after freezing and thawing cycles, the heating and cooling test for heating and cooling cycles. No significant alterations were identified on the surface of the coating materials during the tests. The freezing and thawing, and heating and cooling had no influence on the material capacity tests. However, silicone-S showed a much greater value of metal concentrations and much lower values of pH than the other three.

The bonding capacity test was designed to study a material's ability to adhere to the rock

surface and hold adjacent rocks together. All three materials, epoxy-41, epoxy-43, and acetone-W, showed a high performance, in which acetone-W was the best.

The thin section technique was used to visually observe the coating layers on the rock surface. Ten thin section samples coated with all four coating materials (epoxy-41, epoxy-43, acetone-W, silicone-S) under different test conditions (coating capacity test, freezing and thawing test, and heating and cooling test) were observed. No significant difference among the coating materials was found.

Through the above-mentioned tests and analysis, this preliminary study evaluated the performance of coating materials in preventing ARD generation using the coating method. The recommended coating materials in order of performance were acetone-W > epoxy-43 > epoxy-41. Silicone-S was not an appropriate material for the coating method.

CHAPTER 1

INTRODUCTION

1.1   STATEMENT OF THE PROBLEM

Acid Rock Drainage (ARD) commonly refers to drainage with low pH and rich in dissolved metal ions, which comes from cracked or piled sulfide-rich rocks. ARD is the result of chemical and biochemical reactions between exposed sulfide minerals, water, and air. During the reactions, sulfide minerals are oxidized to sulphuric acid, which dissolves metal ions. Hence, ARD is usually characterized by strong acidity with high metal concentration. The pH value of most ARD ranges from 2.5 to 5.0, and contains more than 30 metals, including heavy metals such as lead, zinc, copper, nickel, manganese, cesium, cobalt, etc. Since the early concern of ARD was from mine activity, ARD is also called Acid Mine Drainage (AMD).

Acidity of water flow can cause discoloration and turbidity in receiving waters, and loading metal ions can cause a decrease in aquatic flora and fauna, bioaccumulation of metals, and reduction in the quality of groundwater. For example, the most appropriate pH for the fishery is between 5.5 and 9, which is much higher than that of most ARD. Direct ARD flow will contaminate and damage aquatic life. Heavy metals are harmful to living creatures, including human beings. Therefore, ARD is a serious environmental issue, and arouses a great awareness in the mining industry, and the fishery and environmental agencies. Millions of dollars are spent annually in maintenance and treatment of ARD drainage.

ARD is generated by the oxidation of sulfide minerals though complex chemical and biochemical reactions. Primary ingredients of ARD generation are, 1) sulfide minerals, 2) water or a humid atmosphere, and 3) an oxidant, particularly oxygen from the atmosphere or from chemical sources (Ferguson, 1987). Pyrite (FeS_2), the most common iron sulfide, is a typical example of minerals for ARD generation. First, pyrite is oxidized by oxygen and water to ferrous (Fe^{2+}), and then Fe^{2+} is oxidized to ferric (Fe^{3+}). When the concentration of Fe^{3+} increases, Fe^{3+} acts as an oxidant itself to oxidize pyrite into Fe^{2+} at a rate faster than that of oxygen. When the pH value of ARD ranges from 2.5 to 3.5, bacteria accelerate sulfate oxidation and speed up the oxidation (Evangelou, 1995).

The demand for coal in the late 1900s, much of it high sulfide (pyrite) coal, triggered the activity of the mining industry, and greatly speeded up ARD generation. Large amounts of ARD flowed into adjacent water bodies, heavily contaminating water and causing damage to aquatic life, with a potential impact on human health. The ARD impact on the environment has become a serious mine-related environmental issue of worldwide concern.

For example, there were over 3 million acres affected by mining activities in the USA in 1980 (Paine, 1978), and about 450 abandoned mine tailings that may produce ARD in Japan (MMAG, 2003). About 3.6 billions tons of mine-related wastewater is produced in China with different degrees of acidity, only 30% of which is treated before flowing into rivers (CIGEM, 2003). According to the survey by Feasby et al (1994), 155 mines have been identified to be generating ARD across Canada. Twelve historical mines, nine recently closed sites, and five operating mines are known as acid-generating mines in B.C alone.

In recent years, new problems relating to ARD other than from the traditional mine industry have been identified as a concern as well. ARD generated at slopes of sulfuric bearing rock along highway corridors is becoming a recognized problem.

Historically, mine activities can be traced to ancient times; e.g. coal has been used in China since 1100 BC, and silver mines were operated in southern Spain by 950 BC. However, the environmental impact of those activities was negligible due to the extremely low productivity of the activity (Paine 1978).

During the past half century, many ARD preventing and controlling methods have been studied. Robertson and Barton-Bridge (1988) summarized those methods in three categories: 1) control of acid generation, 2) control of ARD migration, and 3) collection and treatment of ARD. Those three categories also indicate control levels of ARD in the aspect of effectiveness and cost. The most preferable method is controlling ARD generation, while the most common available method is collection and treatment.

Guideline 1998 summarized available methods as, 1) underwater storage, 2) chemical treatment, 3) blending and covers, and 4) waste segregation. The most applicable abatement measures are wet cover (e.g. covered by water) and dry cover (e.g. covered by clay) (Barton-Bridge, et al. 1989, Guideline, 1998). The wet cover method is considered as a long-term durable method based on currently available technology, while the dry cover is strictly limited due to the uncertainty of long-term durability and the insufficiency of research data (Guidelines, 1998).

Chemical neutralization methods have been used in Canada, the US, and England in recent years. Smith (2000) discussed a set of ARD leachate treatment plants for surface and ground leachate in order to meet discharge standards in the US. Those plants include, 1) active system, e.g. chemical treatment plant, and 2) passive system, e.g. treatment by wetland (Barton-Bridges, 1989).

Possy (2001) summarized some new methods, which are actually being researched, e.g.

Permeable Reactive Barrier (PRB), Deep Aquifer Remediation Tools (DARTS), etc. Evanglou (1995) proposed an idea of coating rock samples with potassium permanganate and silicate in a laboratory study. However, this was only studied in a small-scale indoor test.

So far, limited work has been done on rock coating to prevent ARD generation from exposed sulfide materials. This research presents a preliminary study of the coating method, which uses coating materials to exclude water and air from the rock, in order to avoid oxidation of sulfide minerals, and eventually to reduce and prevent the ARD generation.

Pennask Project

Pennask project is located at Pennask Creek along Highway 97C in the Thompson-Okanagan region (Figure 1.1). The highway was opened in 1991, and reported an ARD problem in 1997. Either side of Highway 97 is producing acidified runoff from both cut rock surfaces and fractured ditches, water from which eventually enters Pennask Creek, the largest spawning resource of Rainbow Trout in British Columbia (B.C). The ARD and metal leaching (ML) problem is of serious concern to Environment Canada, B.C, to the Ministry of Water, Air and Protection B.C, and to the Ministry of Transportation and Highways (MoTH).

Several studies have been undertaken to identify the ARD generation, and remedial methods have been studied. Minesite Drainage Assessment Group (Kevin A. Morin at al, 2003) reviewed existing studies, analyzed extensive water samples from the project area, and suggested several treatment methods, e.g. building chemical plants, relocating rock slopes, etc.

An extensive site investigation of the cut surface and sub rock layer was conducted by MoTH (2001), including a geological, geophysical, and geochemical survey, water sampling, and pH

and metal concentration analysis.
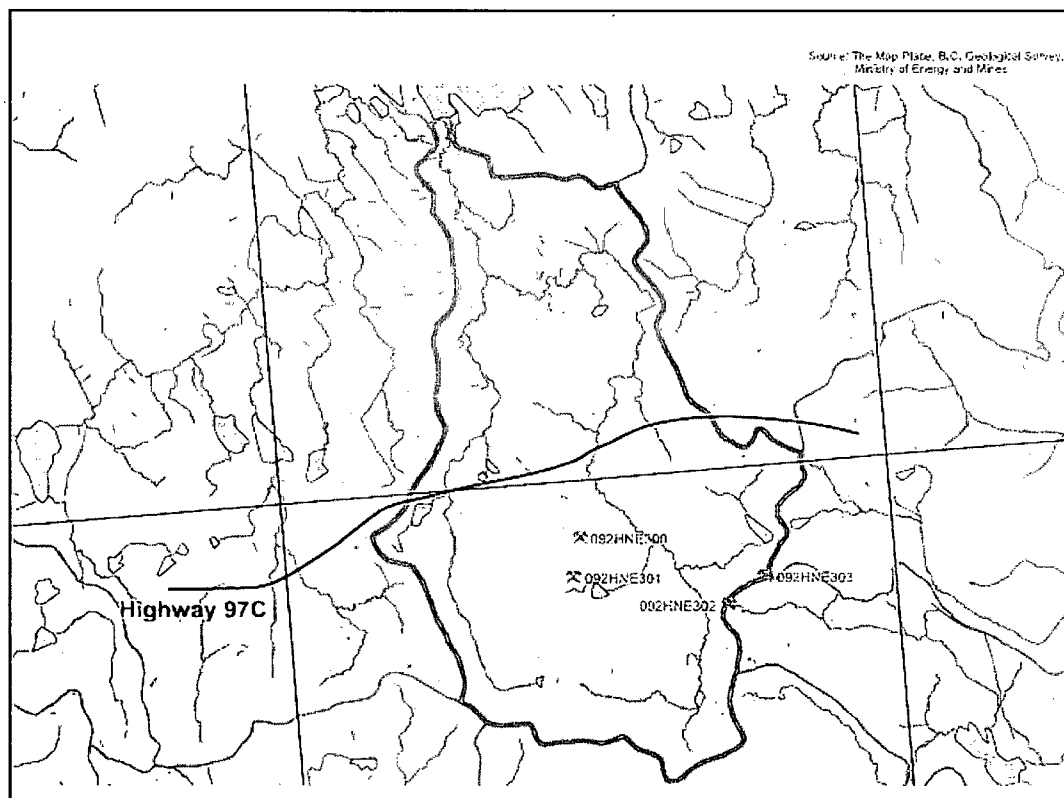
Figure 1.1 Map of the Pennask Project Site (Adopted from Zenah W, et al 2004)

The discharge water quality in ditches was tested by BWP Consulting in 2000. Fedrigo (2000) noted that pH values ranged from 3.4 to 3.7 along the south ditch and approximately 3.7 in the north. Kevin et al (2003) reported that water chemistry from the rock quarry included a laboratory pH of 3.5, sulphate of 351 mg/L (calculated from sulphur), total copper of 0.305 mg/L, and total zinc of 0.899 mg/L.

A pilot test of a remediation method using limestone to neutralize ARD was started in 2001. The method requires a replacement of crushed limestone four times annually; thus, the long-term evaluation and maintenance cost analysis are unsure at present time.

Based on the above discussion, the cover methods are not suitable for this project, due to the local geographic condition. The chemical treatment requires building treatment plants and removing whole rocks to a landfill site. This is not practical due to the extremely high cost. Thus, this research studied proposed coating methods as a possible solution to solve the problem, and preliminarily studied the feasibility and efficiency of the method.

1.2 OBJECTIVE AND SCOPE OF THIS STUDY

The research described in this thesis is a preliminary study of a new approach in preventing ARD generation. The coating method uses coating materials on the exterior of rock samples to exclude contact with air and moisture and thereby avoid sulphur oxidation, and eventually prevent ARD generation. This study tested coating materials under different conditions and examined different methods by which to simulate natural conditions, such as rain and freezing.

The main objectives of this preliminary research were to, 1) characterize rock samples, 2) explore candidate coating materials, 3) examine the performance of coating materials in preventing ARD generation at different conditions, and 4) evaluate and recommend suitable coating materials for a field pilot test. Those objectives were carried out as detailed below:

Site Observation and Rock Sample Analysis

In this phase, 1) the geotechnical and weathering conditions at the ARD generation area were observed, pH of discharged water in ditches on both sides of the highway was measured, and rock samples from primary ARD generation zones were collected; and, 2) physical and chemical properties of rock samples were characterized by both whole rock analysis, e.g.

major oxides and elements analysis, and by ARD generation characteristics, e.g. pH, conductivity and metal concentration changes.

Exploration and Examination of Possible Candidate Materials

The property of coating materials in preventing ARD generation was determined by, 1) the capacity of the coating material to prevent ARD generation under different conditions, such as water-submerged, and water-showered, 2) the coating materials' capacity to prevent ARD generation after thawing-freezing cycles, and heating-cooling cycles, 3) the bonding ability of the coating materials with rocks, and 4) observation of the changes of coating layers by thin section analysis technique. Finally, this study evaluated and recommended the suitable coating materials for the coating method.

1.3 RESEARCH PLAN

In order to achieve the above research objectives, the research plan was developed with four main phases of laboratory tests. This schematic workflow of the research plan is summarized in Figure 1.2.

The research carried out four categories of tests: 1) whole rock analysis was used to determine the rock sample's physical and chemical properties, e.g. major oxides and elements of rock samples; 2) ARD generation tests were designed to identify the ARD generating characteristics of the rock samples, and thin section analysis was used to observe the coating layers of coating materials; 3) a bonding capacity test was used to determine bonding capacity between coating materials and rocks; and 4) coating material capacity tests of freezing and thawing, and heating and cooling were used to examine the performance of

coating materials in preventing ARD generation under different conditions.

Based on results obtained from the above tests, this study evaluated coating material performance and recommended possible coating materials.

1.4 RESEARCH CONTRIBUTIONS

The use of this coating method, a new approach to prevent ARD generation, was proposed for the Pennask project. The results may also be used and expanded for use in the mining industry where most ARD projects are located.

The coating method is a radical treatment measure, has no maintenance costs, and can be used in new projects and to upgrade existing projects in mining and highway industry. Although this preliminary study only developed the basic concepts of the coating method, and evaluated and studied available coating materials, the information is helpful in developing further research and applications for field implementation.

Bonding capacity analysis between coating materials and rock samples would be useful in engineering design and material development.

This study simulated ARD generation under various circumstances, e.g. water-rock ratios and agitation. These data will enrich ARD research and further studies.

The thin section technique provided a close observation of the coating material performance under different conditions, and would be helpful in future studies.

1.5   ORGANIZATION OF THESIS

This thesis is composed of six chapters.

Chapter1 reviews the problem and the environmental impact of the problem, identifies the scope and objectives of the research, details the plan for this research, and contributes to the research.

Chapter 2 reviews background information of ARD generation, outlines the performance of current controlling methods, and discusses primary treatment methods.

Chapter 3 explains basic concepts of the coating method and analyzes coating materials.

Chapter 4 describes the test equipment and materials used in the research, and outlines the test methods, technique, and conditions.

Chapter 5 presents and discusses test results of ARD generation tests, coating material capacity tests, coating material duration tests, bonding capacity tests, and thin section analysis.

Chapter 6 concludes research findings, and outlines recommendations for future research.

Objective

Exploring coating materials, examining the performance of coating materials in preventing ARD generation.

To determine physical, and chemical properties of rock samples

To characterize ARD generation properties

To investigate and test the performance of coating materials in terms of preventing ARD generation under different conditions

To determine bonding ability between coating materials and rock

To evaluate appropriate coating materials

Pannesk rock samples

Physical & Chemical characterization
- ICP/MS

Rock samples + water

ARD generation test

Rock samples + coating materials

Bonding capacity test
Thin section analysis

Rock samples + coating materials + water

ARD preventing test
Freezing-thawing test
Heating-cooling test

Data

Major oxides, and elements of rock samples

pH, electronic conductivity and metal concentrations vs. time

Bonding tensile, and characteristics of bonding layer

pH, electronic conductivity and metal concentration vs. time

Discussion

Compare the performance of coating materials under different conditions, by different methods and techniques

Evaluate and recommend coating materials for coating method

Figure 1.2 Objective of the Research

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 INTRODUCTION

ARD is the result of a series of chemical and biochemical reactions, where sulfide minerals in rocks reacting with water and air is oxidized to sulfuric acid with metal release. Accordingly, ARD usually is associated with high acidity and enriched metal concentrations, with a yellow, dark brown or black color, and either with or without odour. The pH value of most ARD flows range from 2.5 to 4.5 with the lowest value recorded as 0.52 (Williams, 1998). The pH values are beyond the range of 5.5 to 9.0, which is the most appropriate pH for fish and most aquatic life. Another problem of ARD is the solubilization and metalization of heavy metals, e.g. lead, zinc, copper, nickel, manganese, cesium, cobalt, and etc., which are harmful to human health, e.g. lead will damage the human nervous system. Therefore, if ARD flows directly into the environment without treatment, it would: 1) deteriorate water quality, which in turn damages aquatic life, and 2) contaminate soil, ground water, and sediment in streams, which would impact insects and plants, and potentially impact human health through the food and water.

Since the mining industry is the most significant ARD generation source, ARD research has been largely related to the mining industry. Historically, mine activities can be traced to ancient times, e.g. coal had been used in China since 1100 BC, and silver mines were operated in southern Spain as early as 950 BC. Although the earliest observation of acid mine drainage was measured in Pennsylvania, USA in 1698 (Paine, 1978), the environmental impact of ADR was negligible due to low productivity. ARD become a problem as a result of the increasing demand for coal in the period of 1870's to 1890's,

which triggered the activity of mine development, and as the by-product, greatly speeded up ARD generation (Paine, 1978). Large amounts of ARD flowed into adjacent water bodies, deteriorating water quality, damaging the fishery, and finally impacting human health. Therefore, ARD's impact on the environment has become a serious mine-related environmental issue and has generated great concern worldwide.

The U.S. Bureau of Mines estimated that abandoned coal and metal mines, and the associated piles of mine waste adversely affect over 12,000 miles of river and streams, and over 180,000 acres of lakes and reservoirs in the United States (Evangelou, 1995, from Klieinmann, 1989). About 450 abandoned mine tailings that may produce ARD are located in Japan (MMAG, 2003). About 3.6 billion tons of mine-related wastewater is produced in China with different degrees of acidity, only 30% of which were treated before being discharged into rivers (CIGEM, 2003). Other ARD damage has been reported worldwide, e.g. Zimbabwe (Williams, 1998), Spain (Marques, 2001), Korea (Lee, 2003, Yu, 1996), etc.

In Canada, Atlantic coals are known as high pyretic sulphur coals with an average sulfide content ranging from 6% to 10%. The base metal industry, such as lead, copper, nickel, and zinc also obtains its metal from sulfide ores. According to the survey of Feasby et al (1994), 155 ARD generating mines have been identified across Canada. In B.C, 12 historical, 9 recently closed sites, and 5 operating mines are known as acid-generating mines.

In recent years, new ARD-generating sources from outside the traditional mine industry are of concern as well, such as ARD leachate from the slope of sulphur-containing rock along highway corridors (Buchanan, 2001, Zenah W, et.al 2004).

2.2 THE MECHANISM OF ARD GENERATION

2.2.1 ARD Generation

As discussed above, ARD is generated by complex chemical and biochemical reactions. The primary process is that sulfides are oxidized to sulfuric acid and metals are released. Although many metal sulfide minerals may produce ARD, iron sulfides are the most common source of ARD generation. Ferguson (1987) summarized primary ingredients for ARD generation as, 1) sulfide minerals, 2) water or a humid atmosphere, and 3) an oxidant, particularly oxygen from the atmosphere or from chemical sources. Processes of ARD generation are described by Kleinmann et al (1981), K.D. Ferguson at al. (1987) as occurring at three stages: 1) chemical oxidation, 2) biological oxidation, and 3) oxidation of other sulfates. The following equations provided the basic oxidation processes of a typical iron sulfide, i.e. pyrite (FeS_2).
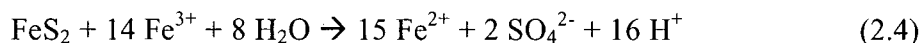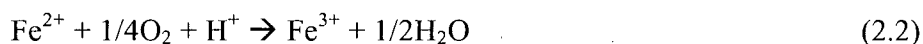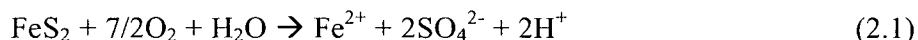
$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{2.1}$$

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \tag{2.2}$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{2.3}$$

$$FeS_2 + 14 Fe^{3+} + 8 H_2O \rightarrow 15 Fe^{2+} + 2 SO_4^{2-} + 16 H^+ \tag{2.4}$$

First, pyrite is oxidized by oxygen and water to ferrous (Fe^{2+}), and then, Fe^{2+} is oxidized to ferric (Fe^{3+}) by oxygen. When the concentration of Fe^{3+} increases, Fe^{3+} becomes oxidant and oxidizes more pyrite into Fe^{2+}.

The processes have also been discussed by Nordtrom (1982) and are presented in Figure 2.1. It indicates that, as pH is increasing, the equation 2.1 changes slightly, but the equation 2.2 increases dramatically. At lower pH range, pyrite is oxidized to Fe^{2+} faster than Fe^{2+} is oxidized by O_2 to Fe^{3+}. Since the ferric iron can be reduced by pyrite itself, the, pyrite would be continually oxidized as long as ferric iron is regenerated.
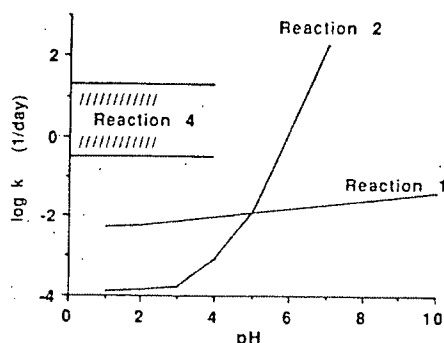
Figure 2.1 Comparison of Rate Constants as a Function of pH. Reactioin4 oxidation of pyrite by Fe^{3+}: Reaction2, oxidation of Fe^{2+} by O_2, and Reaction1, oxidation of pyrite by O2. Reactions 1,2, and 4 are given in the text as equation 2.1, 2.2 and 2.4. (From Evangelou 1995, which from Nordstrom, 1982)

2.2.2 Biochemical Oxidation

At pH ranging from 2.5 to 3.5, bacteria, typically T. ferrooxidans, catalyze or enhance sulfate oxidation and greatly speed up the oxidization of ferrous iron to ferric iron (Jaynes et al., 1984,). T. ferrooxidans is non-obligate chemoautotrophe and is acidophilic. It oxides Fe^{2+}, S^0, and metal sulfides, as well as other reduced inorganic sulphur compounds. In general, the mechanism of pyrite oxidization by bacteria can be categorized as, 1) direct metabolic reactions, which refers to bacteria in physical contact with samples, and 2) indirect metabolic reaction (un-contacted physically). The most common reaction is direct metabolic, which may be presented by following two reactions.

$$FeS_2 + O_2 \text{ (Bacteria)} \rightarrow Fe^{2+} + 2SO_4^{2-} + H^+ \qquad \text{(Torma, 1988)} \qquad (2.5)$$

$$4FeS_2 + 15O_2 + 2H_2O(\text{Bacteria}) \rightarrow 2Fe(SO_4)_3 + 2H_2SO_4 \text{ (Palencia et al. 1998)} \qquad (2.6)$$
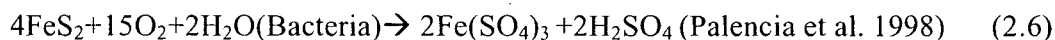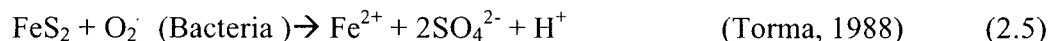
Evangelou (1995) indicated that the rate of bacteria oxidation is 100 times faster than oxygen alone (Figure 2.2), and the significant difference between the results with bacteria

and without is given in Figure 2.2. The oxidation with bacteria increases dramatically after 20 days, while the one without bacteria is changed only slightly during this time.
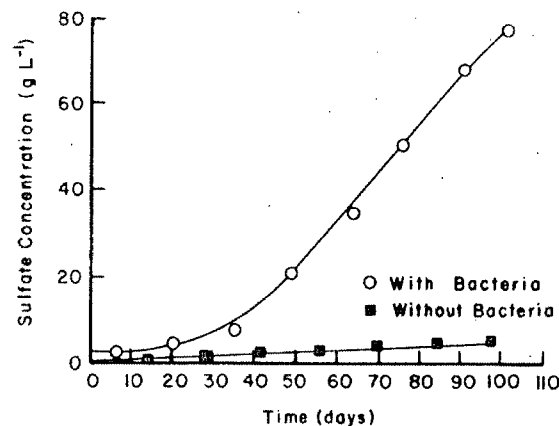
Figure2.2 Pyrite Oxidation Kinetics in Mine Water ($21°C$ and pH=3) in the Presence and Absence of Bacteria. (From Evangelou 1995, which from Scharer et al., 1991)

The bacteria activity strongly depends on pH and temperature. The half time of ferrooxdans during oxidation of ferrous with oxygen of 0.001mol L^{-2} Fe^{2+} in an abiotic system was found to be 2.86 days at pH 5.5, 286 days at pH 4.5, and 3740 days at pH 1.45. Figure 2.3 indicates the influence of pH on T. ferroxidans activity. T. ferroxidans has relative activity in pH ranging from 1.5 to 5, with the potential pH ranging approximately from 2.5 to 4.0. Figure 2.4 indicates the relative activity of T.ferroxidans influenced by temperature. The most activated temperature of T.ferroxidans is approximately at $25°$ to $40°C$.
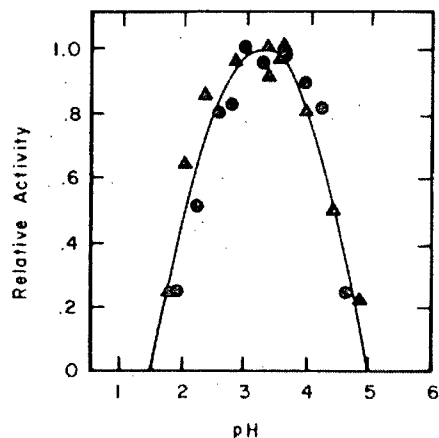
Figure2.3 Influence of pH on Relative Activity of T. Ferrooxidans. (From
Evangelou 1995, from Jaynes et al., 1984)
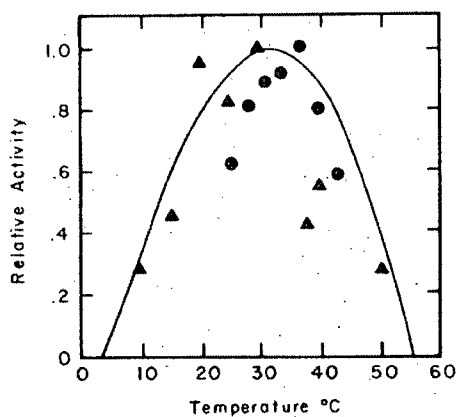
Figure 2.4 Influence of Temperature on Relative Activity of T.
Ferrooxidans. (From Evangelou 1995, from Jaynes et al., 1984)

2.2.3 The Mechanism of Pyrite Oxidation

As discussed in 2.2.2, reactions 2.1 to 2.6 represent an active equilibrium of compounds
during pyrite oxidation; however those equations do not present the rate and chemical
electronic details. Evangelou (1995) indicated that pyrite oxidation is a surface controlled

reaction, but specific mechanisms involved may vary, depending on the nature of the oxidant, e.g. O_2, Fe^{3+}, H_2O_2. Pyrites or pyritic crystals vary in size from 5µm to greater than 400µm with different shapes (Evangelou, 1995 taken from Caruccio and Geidel, 1978). The most reactive form of pyrite is framboidal, which is a grape-like agglomeration of approximately 0.25µm in diameter (Figure 2.5).
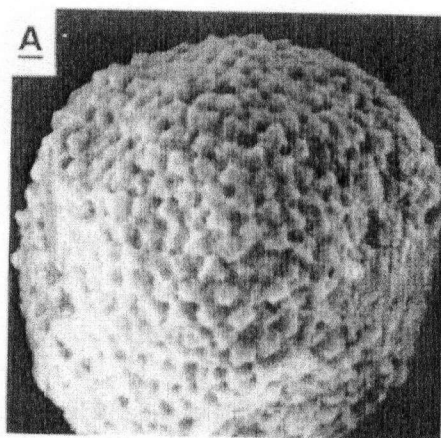
Figure 2.5. Picture of Framboidal With High Surface Area and High Porosity -- One Type of Pyrite (From Evangelou 1995, from Jzhang et al 1993)

Singer and Stumm (1970) suggested that Fe^{3+} is the major pyrite oxidant in acidic pH region, while O_2 is expected to be the direct pyrite oxidant at pH range from neutral to alkaline. Evangelou (1995) explained that Fe^{3+} can bind chemically to pyrite surface whereas O_2 cannot. According to the orbital theory, Fe^{3+} has a vacant orbital to bind to pyrite surface via sulfur to form a persulfido bridge $(Fe-S-S-Fe(H_2O)_5(OH))^{2+}$, which is an intermediate transition state. Through this bridge an electron can be transferred from the highest occupied molecular orbital of S_2^{2-} to the lowest unoccupied molecular orbital of Fe^{3+}. O_2 cannot form this intermediate with pyrite surface. This causes the difference of oxidation mechanism between Fe^{3+} and O_2.

2.3 ARD PREVENTING AND CONTROL METHODS

Many ARD prevention and control methods have been studied during the past half-century. Robertson and Barton-Bridge (1988) categorized those methods into three categories: 1) control of acid generation, 2) control of ARD migration, and 3) collection and treatment of ARD. These three categories also indicate control levels of ARD prevention and treatment in both effectiveness and reliability. The most preferable method is controlling ARD generation, while the most common available methods are collection and treatment methods. Table 2.1 summaries the primary current available methods.

Table 2.1. Available AMD Control Measures (adopted from Barton-Bridge et al., 1989)

	Control Measures
Control of acid generation	• Conditioning of tailing or waste rock to remove or exclude sulfide minerals • Covers and seals to exclude water • Covers and seals to exclude oxygen (including water cover) • Waste segregation and blending to control pH • Base additives to control pH • Bactericides to control bacterial oxidation of sulfide minerals
Control of ARD migration	• Covers and seals to exclude infiltration of precipitation • Controlled placement of waste to minimize infiltration • Diversion of surface water • Interception of ground water
Collection and treatment of ARD	Surface and ground water collection system together with treatment as follows: • Active system, e.g. chemical treatment plant • Passive system, e.g. treatment by wetlands

William (1998) summarized current available mitigation strategies to prevent impact of ML/ARD as 1) avoidance, 2) underwater storage, 3) blending of PAG and NPAG materials, 4) covers, and 5) collection and treatment (Table 2.2).

Table 2.2 Available Mitigation Strategies (From William, 1998)

Methods	Consideration of methods
Avoidance	From the perspective of environmental protection and minimizing liability and risk, the most effective mitigation strategy, and the first that should be considered, is avoidance through prediction and mine planning.
Underwater Storage	If problematic rock types are to be excavated or exposed, underwater storage is generally the most effective means of preventing ARD and reducing metal leaching.
Chemical Treatment	Where contaminated drainage can be collected, effective treatment can prevent further ARD migration, reduce downstream metal concentrations and prevent off-site impacts
Blending and Covers	While blending and surface covers hold great promise as methods to reduce metal leaching, outstanding concerns regarding reliability and effectiveness presently restrict their use.
Waste Segregation	The objectives in waste segregation, to reduce oxygen and/or drainage inputs and increase in-situ neutralization, are typically a hybrid of those for covers and segregated blending.

Posey (2001) summarized the latest technologies and methods that are currently being used for the mine waste treatment, and categorized methods as, 1) ARD prevention strategies, and 2) water treatment and control strategies.

William (1998) summarized also items for selecting the best mitigation strategy as, 1) achieve environmental objectives of the receiving water, 2) minimize environmental risk, 3) minimize alienation of land and watercourses, 4) minimize reclamation liability, and 5) consideration of minesite as a whole.

Underwater Storage

Underwater storage is the most efficient and secure long-term control measure with minimum maintenance. However, it is often only feasible for new mines due to the high cost of either re-handling existing waste or tailings deposit in order to place these under water, or of constructing structures to maintain flooded conditions in the long term (Barton-Bridge, 1988). It is usually unacceptable to use natural water bodies.

Guideline (1998) pointed out the design procedures required, including, 1) determining the geochemistry of acid rock drainage and trace metals, 2) data collection and database development, e.g., water balance, capital, site selection and dam design, deposition strategies, and risk analysis, and 3) operational monitoring.

William (1998) summarized design requirements of under water storage as: 1) material characterization, e.g., suitability of waste materials for underwater disposal, storage capacity, 2) delaying of flooding, e.g. the condition before water submergence, 3) incomplete flooding, e.g., to protect against possible damage during the period un-covered by water, 4) maintenance of flooding, i.e. sufficient to prevent significant oxidation and metal release even during extreme climatic conditions, 5) long-term performance of impoundment structures, and 6) management for and after closure.

Soil Cover

Barton-Bridge (1988) divided soil cover as simple soil cover (one layer) and complex soil cover (multi layer), and discussed details of soil cover design. For complex soil cover, there are several layers, and each of them performs a specific function to improve water and oxygen exclusion and long-term stability. Those layers include, 1) the erosion control layer, the layer to prevent erosion (it may be provided by vegetation or a layer of coarse gravel or rip-rap), 2) the moisture retention zone, the layer to limit desiccation of

underlying layer and provides a growth medium to support vegetation, 3) the upper Drainage / Suction break layer, the layer to prevent drainage water moving laterally, and to prevent moisture loss from the infiltration barrier, 4) the infiltration barrier, the layer to prevent the downward infiltration of moisture and the diffusion of oxygen into the waste. It is often built by fine-grained soil or synthetic materials, 5) the lower capillary barrier, the layer beneath the infiltration barrier to reduce infiltration, and 6) the basic layer, the layer using alkaline materials to reduce the pH of infiltrating water and therefore acid generation rates.

Posey (2001) indicated that strategies for preventing ARD flow are those seeking either to reduce metal and acid concentrations or to reduce metal loads. Reducing concentration needs water treatment, while the loading reduction requires segregating "clean stream" from "dirty stream". The prevention strategies include, 1) upland surface water diversions, which refers to the way of diverting ARD via ditches or other topographic modifications, 2) waste rock caps, which are composed of low permeability soils, or a combination of materials such as topsoil or growth media, and 3) waste rock covers, which minimize the function of caps, without preventing water infiltration. This method functions through controlling infiltration rates by, a) limiting cover permeability, b) limiting surface retention by controlling surface roughness, and c) promoting surface runoff through sloping and ditching.

Evapo-transpiration cover (E-T) is a new approach for more arid areas. It is functioned by, 1) storing water for a certain design period, 2) allowing some of the stored water to evaporate, and 3) allowing some of the water to be transferred through plants presented in the cover itself. The function of this method may be influenced by vegetation species, water uptake characteristics, transpiration rates and length of the growth season. The effectiveness is also influenced by climatic, physiographic, and anthropogenic features (Posey, 2001).

Chemical Treatment

Barton-Bridge (1988) indicates, at some existing facilities, the only practical available option to control ARD is to collect and treat contaminated drainage. The main disadvantage of chemical treatment is that it requires continuous operation and maintenance, and a high risk of equipment or power failure, which makes back-up or contingency measure necessary, as well as a need to dispose of large volumes of sludge.

Smith (2000) discussed a set of ARD leachate treatment plants for surface and ground leachate treatment in order to meet discharge standards of the USA. Those plants include: 1) active systems, e.g. chemical treatment plants, and 2) passive systems, e.g. treatment by wetlands. A treatment system of remediation of ARD or acid ground water requires two main steps: 1) addition of chemicals to precipitate dissolved metals, and 2) physically separating precipitate solids from the water so the water can be lawfully discharged from the site.

Posey (2001) discussed ARD water treatment and control strategies as perpetual water treatments, and "walk-away" solutions. The treatments are categorized as, 1) active water treatment, which mainly relies on standard alkali-addition procedures, e.g. lime, sodium hydroxide, and sodium carbonate. Most metals can be removed by carbonate addition including arsenic, cobalt, copper, cadmium, iron, and lead, but manganese and zinc are not readily removed. Therefore, those two are the driving forces of water treatment mechanics at ARD cleanups, and 2) passive or single-pass water treatment system, which are notably artificial or manufactured wetland treatment systems. The system is not really passive, but requires periodic maintenance and is limited in working effectively to simultaneously, a) remove multiple metals, b) achieve regulatory levels, c) work in waters of variable composition, d) work year round, e) work where temperatures range from far below to far above freezing, and f) work for solutions of pH less than about 4.0. However, some passive systems have shown success, such as, the Biopass® system in treating draindown

fluids from abandoned cyanide deposits, leaching cyanide and metal cyanide species in a neutral to alkaline media.

New Developing Water Treatment Technologies

The Permeable Reactive Barriers (PRB) are used for, 1) minimizing oxygen infiltration by sequestering oxygen, 2) providing an organic "food" source to sulfate, reducing bacteria to reduce sulfate to sulfide and, perhaps, precipitate metal sulfides, and 3) sequestering metals or sulfate in the barrier material by providing critical reactant along a ground water flow path. The Deep Aquifer Remediation Tools (DARTS) serve the same function, but are placed in more deeply-contaminated zones or plumes. It is a developing technology that offers on-site remediation via adding liquid organic nutrients to promote sulfate reduction, and metal sulfide precipitation in a saturated system (Possy, 2001). Another research innovation is mineral passivation by using coating materials to coat rock surfaces with potassium permanganate and silicate. This has been proposed and tested in the laboratory by Evangelou (1995).

Recently, the UK Environmental Agency (2003) published a guide for using Permeable Reactive Barriers (PRBs) to prevent ARD, and several sites using this method have been constructed.

The effect of ARD may be minimized by controlling ARD generation reaction, by preventing contaminants from entering the environment, or by collecting and treating the contaminated drainage. There is no universal treatment measure that may apply to all conditions. The treatment method relies on the unique condition of each individual site.

CHAPTER 3

COATING METHODS AND COATING MATERIALS

3.1 INTRODUCTION OF THE COATING METHOD

As discussed in Chapter 2, there are several methods currently being used for preventing and treating ARD in the mine industry with advantages and limitations. Underwater storage is reliable but difficult to apply for existing projects. Clay cover is simple but lacks long-term reliability. Chemical treatment plants only can be considered as a short-term measure due to the high maintenance cost. Biologic treatment lacks long-term results. Some new developing methods are still in the research stage. None of them are appropriate for the circumstances at the Pennask Creek project in view of engineering feasibility or cost efficiency. Thus, this study proposed the coating method - a new approach to meet the requirements of this project.

Since oxygen and water are the two primary elements that control ARD generation, the basic principle of preventing ARD generation is to avoid or reduce the contact of the rock with oxygen and water. Figure 3.1 illustrates the essential factors that control ARD generation. There are different ways to reach this goal, e.g. underwater storage to exclude air contact by a water barrier, and soil cover to exclude water penetration by a low permeability clay layer. The coating method is used as a very low permeability material to coat rock surfaces to exclude both air and water contact.

The conditions at each site are unique and differ from one to other in, 1) geological conditions e.g. slope angles, 2) mineralogical conditions, e.g. rock type, 3) geographic conditions, e.g. slope, altitude, sunshine, and 4) weathering, e.g. temperature, rainfall, and humidity. Therefore, it is difficult to develop a universal one-for-all coating method which

fits all conditions. According to the differences in coating materials and working conditions, different ways need to be developed to reach the designed goals, e.g. for a single rock or a large flat rock surface. This may be easily coated in one layer by brushes or rollers, while for complex surfaces or piled rock slopes, tools such as sprayers are required, and more than one layer may be required to provide sufficient coverage for all aspects.
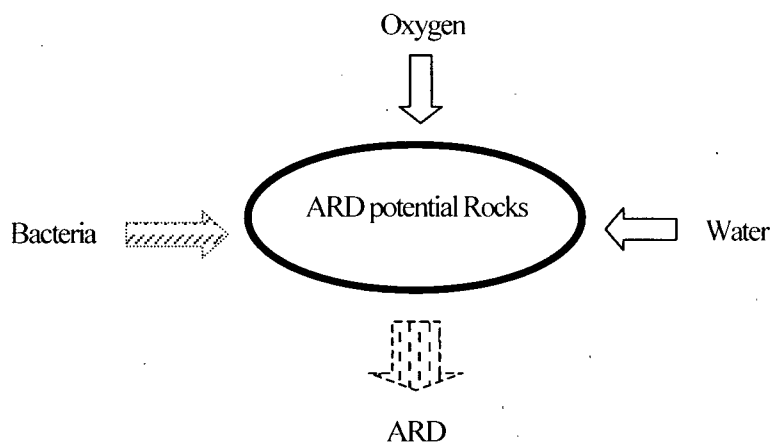
Figure 3.1 A Conceptual Model of ARD Generation Controlling Factors. Oxygen, water and rock are essential factors of ARD generation, and bacteria accelerate the oxidation rate.

In general, according to the performance of the coating layer, coating methods can be categorized into one layer method and multi-layer method (Table 3.1). The one-layer method uses a single coating layer to exclude the interaction of water and air, while the multi-layer method consists of two or more layers to perform the same function, i.e., to exclude the interaction of water and air. Since the single-layer method has only one layer to perform both excluding air and water, and adhering to the rock surface, it requires the coating materials with a higher property of adherence and imperviousness. Figure 3.2 indicates a conceptual model of different coating methods.

Table3.1 Summary of Requirements and Possible Candidate Materials for Coating Method

Category	Position and performance of coating material	Candidate Materials	Requirements
One-layer method	Surface barrier	Polymers	Low permeability Acid resistance
		Concrete	Adhesive to rock surface Weather resistance
Multi-layer method	Primer Layer	Concrete Cement	Adhesive to rock surface Support surface coating layer
	Coating layer	Sealers Paints HPCs	Low permeability Acid resistance Weather resistance

Figure 3.3 presents an illustration of natural factors that may interact with coating materials and influence their function. There are two categories, the atmospheric layer and the ground layer. The atmospheric layer refers to those factors from atmosphere, e.g. temperature, oxygen, UV, wind, rain, etc. The other category refers to the factor groups from ground, e.g. flood, erosion, physical, chemical and biological reaction with the surface of coating materials, etc.
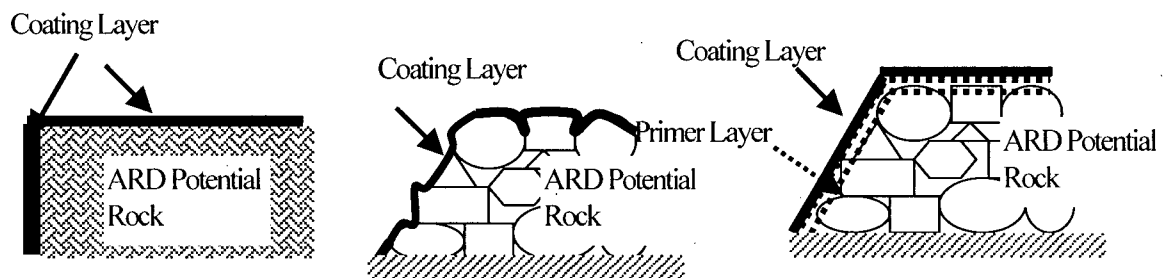
Figure 3.2 A Conceptual Model of the Coating Method. The left and middle models show the one-layer method. The left model is a flat surface and the middle one is a piled slope. The right model uses a multi-layer coating, which includes surface barrier layer and one or more primer layers.
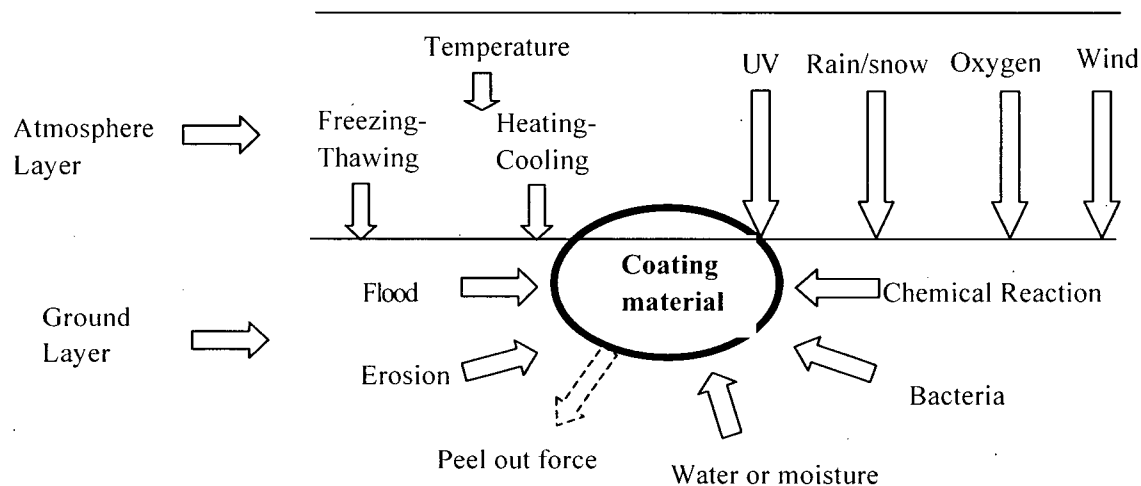
Figure 3.3. An Illustration of the Environmental Influence on Coating Material

In order to resist these factors and perform required functions by the coating method, coating materials are required to meet the following general requirements.

1) Low permeability is the basic requirement. This property can assure that the coating layer is able to exclude water contact, or to limit the moisture interface in order to avoid oxidation, or reduce the possibility of being oxidized.

2) Acid resistance is a necessary property because the coating layer must function in an acidic environment.

3) Bonding capacity with the rock surface is another important property of coating materials. Anti-peeling capacity is required for long-term stability and reliability.

4) Weathering-resistant ability is required because the coating layer is exposed to the natural environment, and influenced by rain, freezing, heat, wind, UV, etc. Coating materials have to be functional under all possible conditions.

5) Cost efficiency is an important factor, because it may influence the final decision.

3.2 COMPONENTS OF COATING MATERIALS AND THEIR CHARACTERISTICS

The materials used to protect a concrete surface that might qualify for the purpose of preventing and controlling ARD generation, include, 1) polymers seals and coating, e.g. basins, sealers, coating and paints, and 2) concretes and mortars, e.g. polymer concrete, fibre reinforced concrete and mortar, and ash added concrete.

Almusallam (2003) categorized concrete protection methods as, 1) protective concrete surface coatings, 2) metallic, epoxy, and polymeric coatings on steel, and 3) corrosion inhibitors. U.S. Highway (1998) conducted a comprehensive survey and research to clarify and characterize how to categorize and evaluate the performance of concrete sealers and coating materials used in the highway industry. The report classified concrete sealers into two classes: 1) penetrants, which are sealers that penetrate into concrete and react with the substance, e.g. silanse can go as deep as 2.5 -6.4 cm. The penetrants can be subcategorized as, a) water-repellents, which repel water, and usually form a coating layer on the surface with the thickness of 0.13mm, b) pore-blockers, which fill pores, and usually form a surface layer with a thickness of 0.13-0.26mm; 2) coating materials, which adhere to the surface and form a barrier. Those coating layers are thicker than penetrants. In general, primary components in common use, such as concrete sealers with their characteristics, can be categorized in the following groups.

Silicon-Based

There are three suggested common silicon-based materials according to their chemical structure. 1) **Silanes, Siloxanes and Silicontes,** called T structure group, consists of three silicon functional groups and one organo-functional group. They usually provide a thin water-repellent coating on the inside of the pore walls in concrete. 2) **Silicate and fluosillcate,** commonly called Q — structure, are another group of silicon-based sealers, which contain no organo-functional group. Depending on the manufacturing process, they can be pore blockers, or solutions in water, in which sodium silicate is

mixed with potassium silicate and fluosilicates. 3) **Silicones,** called D-structure, which include two silicon-functional and two organo-functional groups. Silicones are water repellent, and sell on the market as 5% solutions in organic solvents or water solvents.

Epoxies

Most common epoxies used as sealers contain two main compounds: bisphenol A (disphenylolpropane) and epichlorohyrin. The curing agents for epoxies are aliphatic polyamines and their derivations (e.g. diethylenetriamine). The reaction between bisphenol A and epichlorohydrin produces a linear polymer with a repeating unit structure.

Epoxies are highly viscous. When concentrated to greater than 50%, the sealer acts as a barrier coat. Advantages of epoxies include, a) no reaction with the concrete substrate, b) low-order shrinkage, c) no by-products, d) good adhesion to concrete, e) tough and durable, and f) excellent resistance to acid.

Acrylics

Acrylics are polymers or copolymers of acrylic acid, methacrylic acid esters of those acids or acrylonitrile. Methyl methacrylate is the most common base for acrylic concrete sealers. The main properties of acrylics include, a) low viscosity – can penetrate concrete without using any carrier or solvent, b) water based acrylic latexes, which can be water-repellents, c) non-carrier and solvent-based acrylic, which can be pore blockers, and d) have a good resistance to weather (UV) and acids.

Urethanes (polyurethanes)

Reactive resins are the result of reactions of isocyanates with either polyols (poly functional alcohols) or polyesters (or low molecular weight polyesters). Urethanes can be provided on the market as a conventional two-component (resin-hardener) system,

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or as a one-component system, such as undiluted urethanes – barrier coating, or pore-blocker if dissolved with organic solvents, e.g. mineral spirits, and xylene.

Polyesters

Polyesters are products of the reaction between difunctional alcohols (diols) and anhydrides of dibastic organic acids. The two most commonly used polyesters are based on a reaction either between maleic (a dibasic acid) anhydride and bisphenol A (diphenyl propane, a diol) or acrylic acid and epoxy (vinyl ester). The characteristics of polyester are, 1) undiluted polyesters – surface barrier coating, 2) pore-blocker if dissolved with organic solvents, e.g. mineral spirits, xylene, and 3) excellent resistance to chemicals.

Vinyls

Vinyls are products that are based on acrylic and methacrylic acids. Vinyls have excellent resistance to weathering.

3.3 AVAILABLE COATING MATERIALS

3.3.1 Polymer Materials

A wide diversity of market available sealers and coating materials are based on polymers, and have been successfully used in preventing erosion on rock and concrete.

Almusallam et al. (2003) studied the performance of five typical concrete sealers in an acidic environment, which include acrylic, polymer emulsion, epoxy, polyurethane and chlorinated rubber coating. The five sealers were tested in double samples. According to the authors, the recommended materials for preventing wetness are epoxy, chlorinated rubber, and acrylic, and for resisting acid attack are epoxy, polyurethane, and acrylic.

Fourteen kinds of market-available candidate materials that possibly qualify for the coating method were summarized in Table 3.2, in which the manufacturers, production names, components, advantages, and limitations were included.

3.3.2 New Generation of Concrete

Monteiro et al. (2003) reported on a study result of a set of long-term (over 40 years) laboratory tests carried out by the U.S. Bureau of Reclamation (USBR). In the study, the failure of the concrete sample is defined as the expansion of the sample being greater than 0.5%. The results show that the time of failure of the concrete samples decreases with increasing water and cement ratio and C_3A (Tricalcium aluminate, $3CaOAl_2O_3$) content in the concrete. For the concrete samples with a mixture of water and cement ratio below 0.45 and C_3A content less then 8%, the "safety" phase (non-failure) can last for nearly 40 years.

Vipulanandan, et al (2002), conducted a set of experiments to test polymer concrete as a coated layer in a sulfuric acid environment. The result showed that the polymer concrete functioned well in resisting acid attack. Therefore, the polymer concrete may be used as primer layers in the coating method. However, the high cost may keep it out of competition in the current engineering market. Therefore, it was withdrawn from this research.

3.3.3 Fly Ash Mixed Concrete

Li (2003) reported a set of test results using fly ash mixed concrete to increase the bonding strength of new-to-old concrete. Concrete with fly ash binder presented encouraging results in both samples of short-term (28 days) and long-term (1 year) tests.

Table3.2. Coating Materials and Their Characteristics

Usage	Products Name	Components	Advantage	Notes
One-layer Coating System	20 Hydrocoat	Water-based Epoxy	Rock and concrete Dry and moist	
	Carlisle CCW-703	Two component Polyurethane	Over surface Water proof	Not for exposed surface Temperature> 40F
	Chemorlast	Acrylic	Excellent adhesion Resist UV	Does not apply for the surface risk of rain and freezing
	54SG Sauereisen	Potassium silicate bounded	Acid resist (pH 0 — 7)	
	RadonSeal (Stone armor L5, NS)	Silicon	Apply nature stone Acid-resist	
	Universal Stone Sealer	Unknown Water based	Apply on nature stone	
	StoneTech Professional™ Exterior Stone & Masonry Sealer	Water-based silicone water repellent	Quick dry Apply on stone surface	Acid –resisting capacity is unknown
	Renew-Crete Sealer	Solvent based Acrylic Water-repellent	Hard surface Quick dry	
Multi-layer Coating System	Mermas 200 CW	Epoxy Paint	Over rock and concrete, wide range of application	
	Tripoxy	Polyamide + epoxy enamel	Very dense film Resist alkalis and acid	
	Anglo Polyshield	polyurethane	Over stone and concrete	
Multi-layer Primer	Tasman	Epoxy resin	Over rock and concrete	

CHAPTER 4

EXPERIMENTAL DESIGN AND MATERIAL PREPARATION

4.1 TEST MATERIALS

Two kinds of test materials were used in this research: 1) acid potential rock samples collected from the Pennask site, and 2) market available coatings and sealers.

4.1.1 Rock Samples

The Pennask Site is located in the Pennask Creek Area along Highway 97C, where ARD was generated and has impacted the adjacent area. The physical, chemical and mineralogical characteristics of the area were reported by Kevin A. Morin (2003), Buchanan (2001), and Grunenberg (2001), and the information was summarized in Table 4.1. Rock samples were collected in the typical ARD generation zones in order to represent the site condition. The rock samples were collected in two categories: 1) larger than 12 cm, and 2) smaller than 12 cm in size. Smaller samples were used for ARD generation tests, and thin section analysis. Large samples were used for coating capacity tests, freezing and thawing tests, heating and cooling tests, and bonding capacity tests. 400 kilograms of samples were collected from six different sampling locations. The methodology of sampling is summarized in Table 4.2.

4.1.2 Coating Materials

Coating materials were obtained by getting testing samples from companies, and by

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purchasing them from manufacturers.

Table 4.1 Summary of the Characteristics of the Pennask Site (from Kevin, 2003, Buchanan, 2001, and Grunenberg, 2001)

	Properties	Characteristics
Rock in Slope	Physical	90% of exposed bedrock is made up of fine-grained sedimentary rock containing varying quantities of pyrite. Bed rock in cut surface is weathered to 10 –20 m
	Chemical	Pyrite is present as primary micro-bedding and very fine grained disseminate, and disseminate, and secondary fracture fillings. Pyrite content ranges from less than 1% to greater than 10% in the rock
	Mineralogical	Ferrocrete is very rusty red in color and is present as iron cementing of surficial sediments overlying bedrock
Water in Ditch	Physical	pH value of water ranging from 3.1 to 3.5
	Chemical	High concentrations of Al, Cd, Ca, Co, Cu, Fe, Mg, Mn, Ni, K, Si, Na, Y, Zn (2-300 times that of the background)

Table 4.2 Sampling Strategy

	Description
Principle of sampling	• Collected samples from surface layers of all sizes • Sampled from typical ARD generating locations based on previous studies and appearance • Collected samples at different spatial areas at each sampling location • Recorded sampling locations by photographs and notes • Recorded new findings and interesting facts during sampling
Type of samples	Large size samples (larger than 12 cm in dimension) were prepared for bonding capacity tests, coating capacity tests, and freezing and heating tests
	Small size samples (smaller than 5 cm in dimension) were used for ARD generating tests and thin section analysis
Storage of samples	Samples were packaged into four buckets and stored in a temperature-controlled room at 25 °C

Four kinds of liquid coating materials were tested in this study: 1) Tripoxy 41, an epoxy based coating material from Triangle Coatings Inc, of San Leandro, CA, designed as epoxy-41; 2) Tripoxy 43, an epoxy based coating materials from Triangle Coatings Inc, of San Leandro, CA, designed as epoxy-43; 3) Wet Look Lacquer, an aromatic acetone based coating materials from Triangle Coatings Inc, of San Leandro, CA, designed as acetone-W; and 4) Stone-Armor, a silicone-based coating material from Radon Mitigation & Waterproofing Concrete Sealer Company, of Shelton, CT, designed as silicone-S. Epoxy-41 and epoxy-43 are two-component materials, and the other two are one-component. Epoxy-41 requires the mixture of Tripoxy I White and Tripoxy I curing Agent one to one by volume. Epoxy-43 requires mixing Tripoxy HB White and Tripoxy HB curing Agent in proportion of one to four by volume. The detailed information of coating materials is shown in Table 4.3 (Please also see the Table 3.2 for the characteristics of production). The information about the manufacturers and chemical components of products is listed in Appendix A.

4.1.3 Sample Coating Procedure

Twenty pieces of rock samples were coated for capacity tests, freezing-thawing tests, heating and cooling tests, and thin section analysis. The procedure of coating rock samples was as follows:

1) Selected the rock samples that had larger flat surface and similar shape and weight.
2) Washed the rock samples with tap water to remove dust and other surface-attached compounds.
3) Air dried the samples at a room temperature of 25°C for over 24 hours.
4) Coated air-dried rock samples by coating materials with brushes two to three times.
5) Air-dried the coated rock samples in a room temperature of 25 °C for over one week.

Table 4.3 Summary of Components of Coating Materials

Sample ID	Product Name	Components	Chemical Contents	Remarks
Epoxy-41	Tripoxy 41	Tripoxy I White	Xylene 1-Methoxy-2- propanol Buyl	Mix A1 and A2 one to one in volume
		Tripoxy I Curing Agent	Isopropyl Alcohol Butyl Alcohol 2-Butoxyethanol Xylene	
Epoxy-43	Tripoxy 43	Tripoxy HB White	Xylene 1-Methoxy-2- propanol Buyl Alcohhol	Mix B1 and B2 one to four in volume
		Tripoxy HB Curing Agent	Xylene Butyl Alcohol	
Acetone-W	Wet Look Lacquer	Wet Look Lacquer 11-02	Acetone 4-chlorobenzotreifluoide Aromatic Hydrocarbon Mixture	Apply directly
Silicone-S	Stone Armor	Stone Armor	Silicates, Bonding catalysts	Apply after stirring

A rock sample before and after coating by Epoxy-41 is shown in Figure 4.1. Most rock samples have weathering on their surface. The coating material covered the rock surface completely.
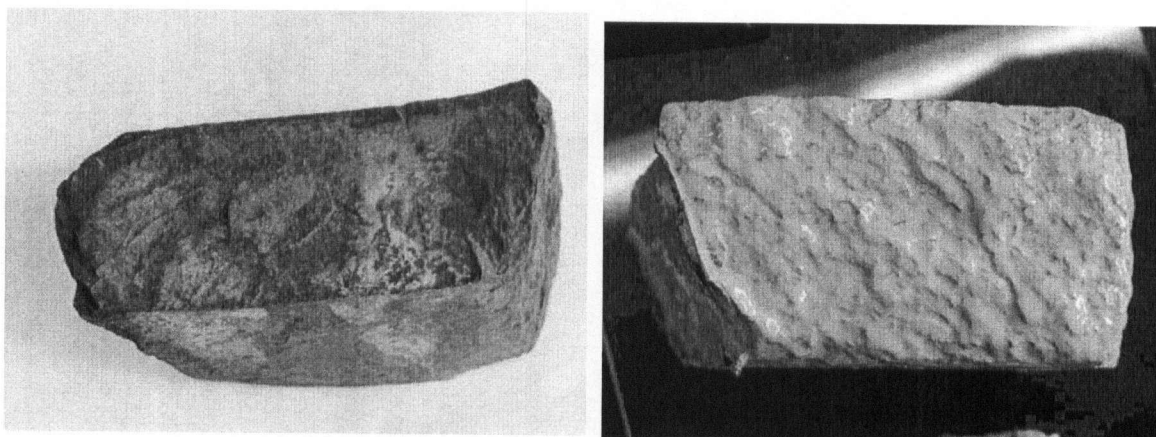
Figure 4.1 Pictures of Coated Rock Sample: Left is a washed sample after air-drying without coating. Right is after coating with Eposxy-41.

4.2 LABORATORY TEST

Laboratory tests were conducted to study the physical and chemical properties, and ARD generation characteristics of the rock samples, and the coating capacity of coating materials in preventing ARD generation of rock samples at different circumstances. Six sets of tests or analyses were carried out to study the ARD generation characteristics of the rock samples. Five different test methods or techniques were employed to study different aspects of the performance of coating materials. The laboratory test program is summarized in Table 4.4.

Table 4.4 Summary of Laboratory Tests

Test Name	Purpose	Period	Results
Whole rock analysis ***	Determined elements of rock samples	28 days	Element concentration
ARD generation test	Studied ARD generating characteristics	92 days	conductivity, pH and metal concentration
Coating capacity test	Studied the capacity of coating materials submerged in water	88 days	conductivity, pH and metal concentrations
Freezing and thawing test	Studied performance of coating layer under the condition of freezing and thawing cycle, plus coating capacity test	96 days	conductivity, pH and metal concentrations
Heating and cooling test	Studied performance of coating layer under the condition of heating and cooling cycle, plus coating capacity test	115 days	conductivity, pH and metal concentrations
Bonding capacity test	Examined the bonding strength of coating materials	120 days	Tensile strength
Thin section	Observed coating layer in details	46 days	Pictures of coating layer

*** Conducted by ACME analytical Laboratories Ltd.

4.2.1 Water Sample Collection and Parameter Measurement

Water Sample Collection and Storage

Water samples from each cell were collected at designed periods, which in general were once every 3 days for the first week, and once every week thereafter. Conductivity and pH were measured immediately after sampling, and metal concentrations were determined every month for comparison. Before measurement, the samples were stored in polyethylene tubes below 10 degree Celsius in a refrigerator.

The pH Measurement

The pH was measured by using the OPION Banchtop pH/ISE meter (Model 470A). The meter was calibrated before every new measurement or whenever necessary by the calibration standard liquids with pH of 2.0, 4.0 and 7.0. In order to maintain high accuracy, the standards were measured after every 5 measurements. If the error exceeded 0.05, the meter was recalibrated, and the results of samples were re-measured.

The pH was measured immediately after sampling in the coating capacity test, freezing and thawing test, and heating and cooling test, but was measured every month with the metal concentration in the ARD generation test and part of the coating capacity test.

Conductivity Measurement

Conductivity was measured by OAKTON CON10 Conductivity/TDS Meter. The calibration standard used was 0.01M KCl solutions. The conductivity of this solution at $25^{\circ}C$ is 1413 $\mu s/cm$. The meter was calibrated monthly.

The conductivity was measured immediately after sampling in the coating capacity test, freezing and thawing test, and heating and cooling test, but every month in the ARD generation test and part of the coating capacity test.

Metal Concentration Determination

Metal concentrations were determined by atomic absorption spectrophotometry (AAS), with the model of Varian SpectrAA220 Fast Sequential Atomic Absorption Spectrophotometer. Standard solutions were prepared by taking samples from Fisher 1000 mg/l certified reference standards, and diluting to the desired concentration with 0.5% nitric acid (HNO_3).

Water samples were collected from each testing cell with 30 ml syringes, and stored in 50 ml centrifuge tubes. After measuring pH and conductivity, the samples were stored in a refrigerator for determining the metal concentration. No dilution was applied to the water samples.

Each time, 25 ml water was taken from the water samples for metal concentrations analysis, including Cu, Zn, Ni, Ca, Mg, and Fe. To avoid the interaction among the different metals, only one element was determined each time. In the ARD generation test and some of the coating capacity tests, three elements were measured at the same time. During the measurement, distilled a water or standard metal solution was inserted in every ten water samples as the quality control method, to maintain the accuracy of the measurement. When any unreasonable result was found, the measurement was repeated.

4.2.2   Total Chemical Analysis

The analysis was employed to understand the chemical composition of the rock samples. Six samples from each sampling location were sent to ACME ANALYTICAL LABORATORIES LTD for whole rock analysis. Each test sample was a mixture of 5 pieces of small rock from each sampling location with approximately 30 grams in total. The samples were analyzed by ICP/MS (Model Perkin Elmer Elan 6000 and/or Perkin Elmer Elan DRC 9000) for major oxides and elements. The detailed procedures and methods used in the analysis are listed in Appendix B.

4.2.3   ARD Generation Test

The ARD generation test is designed to study ARD generating characteristics of rock samples. In general, the factors that influenced the ARD generation test include, 1) particle size, 2) leachant type, 3) water-and-rock ratio, 4) agitation, and 5) temperature. Since the temperature was constant, the remaining four factors were involved in this study.

The Test Equipment

The coating capacity test system consists of, 1) test cells used to place the rock samples, 2) agitation system (including pumps and headers) used to circulate the water, 3) shower makers used to mix water and air, 4) covers used to prevent the water evaporation, and 5) tubes and connections.

Figure 4.2 A View of the Test System

The test system is illustrated as Figures 4.2 and 4.3. This test system was used in ARD generation, coating material capacity, the second step of the freezing and thawing, and the

heating and cooling tests.

The cells are cylinders made from polyethylene (Figure 4.2). The dimension of cells is 30 cm high with 30 cm in diameter. This size is considered to be large enough to limit the influence of walls on rock samples in contact with air and water. The transparency of the cells allows visibility to observe the rock sample changes.

Four cells were grouped together to carry out the test of four coating materials of epoxy-41, epoxy-43, silicone-S, and acetone-W at the same time and under the same conditions. In total, eight cells were prepared, which allowed testing of all four samples under two different conditions at the same time. The tests were, therefore, accomplished in the approximately 90 days.
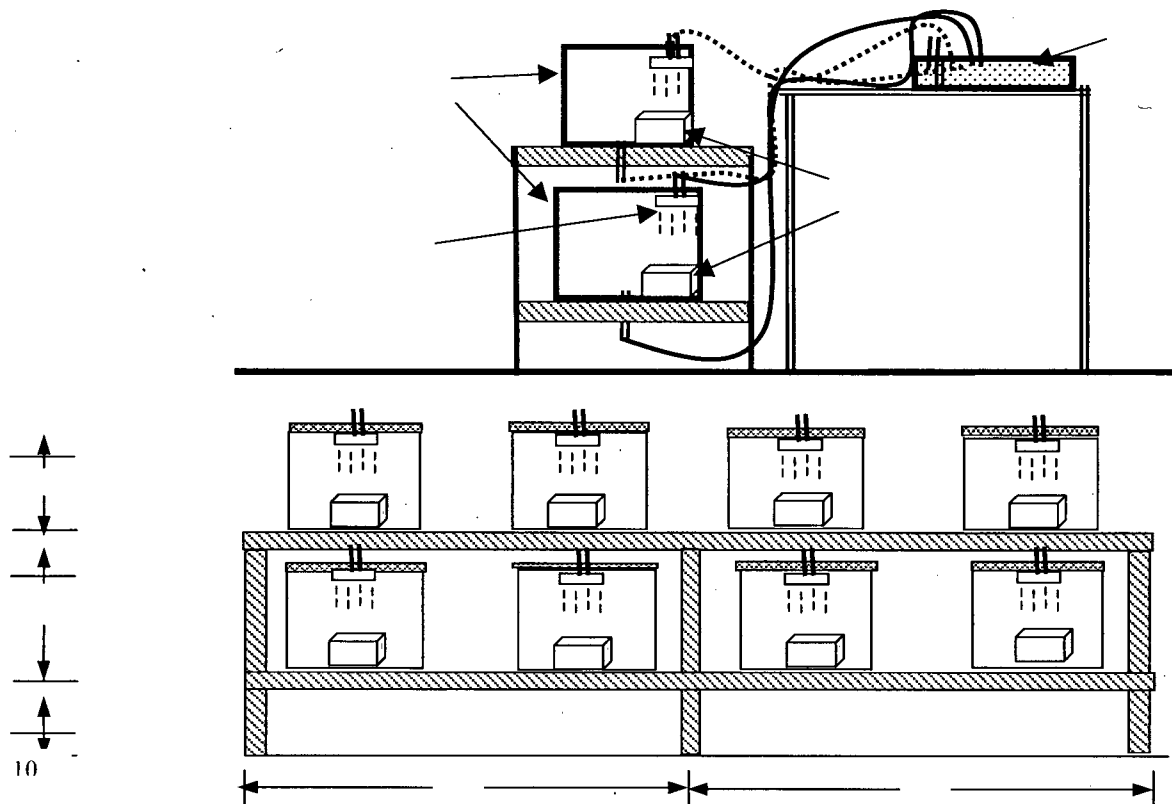
Shower makers are small cylinders made from polyethylene, with an open top end to receive water from the pump and a closed end at the bottom end with regularly arranged holes of 0.2 mm to allow the water to pass and shower down to the rock sample surface. The shower is used to accelerate the mixture of air and water to increase the oxygen content in the water.

The agitation system consists of Masterflex ®parts, L/S controllers, motors, tubes, and connections. Each cell has an independent water cycle system to avoid interface from others. The water was taken from the center of the cell's bottom through a tube, then pumped to the shower maker that is fixed on top of the cells, and then showered down to the rock samples inside the cells. The rate of the driver motor ranged from 6 to 600 ppm, with the flow rate ranging from 16.8 to 1680 ml/min. The constant rate of 840 ml/min was used during the test period. The pump headers were series #17.

The tubes are made of vinyl, and connectors are made of nylon. There is no metal surface in contact with water during the test processing. Water samples were collected by 30 ml polyethylene syringes, and stored in 50 ml polypropylene centrifuge tubes. There is no possibility for any part of the equipment to influence the metal concentration of the water during the whole testing procedure.

The Test Procedure

After the equipment was set up, rock samples were packed into the cells. The rock samples were a mixture of the rocks varying in size up to 10 cm. Special attention was taken to select rock samples for each cell similar in shape and size. Most rocks were from 2 cm to 6 cm.

Water was filled according to the designed water to rock ratio. Except for ARD-TW using tap water, all other tests employed distilled water. Initial water level was measured and marked

on the wall of the cells. Water level was maintained at constant volume by refilling the water after each sampling. Agitation was started after preparation, and continued for one hour every day.

Water samples were taken after the agitation and before refilling the water at designed periods by syringes. Conductivity and pH were measured after sampling. Metal concentrations were analyzed every month in order to maintain the same test conditions and comparison of test results. The measurements were followed as outlined in the explanation in section 4.2.1.

Experimental Conditions of The Test

Six sets of ARD generating tests were conducted to determine the influence of different control factors on ARD generating. Test conditions of the ARD generation tests are summarized in Table 4.5.

ARD-TW was designed to study the influence of water-and-rock ratio on ARD generation. Nine kilograms of rock samples were placed into three cells by hand without pressure; each with three kilograms with the size ranging from 0.5 cm to 10 cm. Tap water was put into the cells, with water to rock ratio of 3:1, 3:2, and 3:3 by weight. The test was conducted at a room temperature of 25°C for 31 days without agitation. 50 ml water samples were collected once every day during the first week, and every three days thereafter.

ARD-TW was stopped after one month due to the irregular results of pH, conductivity, and metal concentrations. It was clear that the results were influenced by the irregular daily changes of pH, conductivity and metal concentration of the tap water. It was not reasonable to distinguish the portions from the ARD generation and tap water changes.

Table 4.5 Summary of Test Conditions of ARD Generation Tests

	Sample submerge condition	Duration	Agitation	Measurement
ARD-TW	3 kg rocks in tap-water with water ratios of 3:1, 3:2, 3:3	31 days	N/A	pH, metals, conductivity
ARD-DW	6 kg rocks in distilled water with water rock ratios of 2:3, 3:3, 5:3	92 days	Water circulation	pH, metals, conductivity
ARD-N	10 kg rocks in 10 L distilled water	360 days	N/A	pH, metals, conductivity
ARD-S1	300 g rocks in distilled water with water rock ratio of 4:1	2 hours	Stirring	pH
ARD-S2	600 g rocks in 600 ml distilled water	30 minutes	Stirring	pH
ARD-DW	Distilled water	92 days	N/A	pH, conductivity

The ARD generation test was prepared for the same purpose as ARD-TW, but the tap water was replaced with distilled water. Six kilograms of rock samples with sizes ranging from 1 cm to 10 cm were placed into each cell with water to rock ratio of 2:3, 3:3 and 5:3. No agitation was applied for the first month, and water was circulated for one hour every day thereafter.

The ARD generation test lasted for 85 days at a room temperature of 25°C. Water samples were collected every hour for the first ten hours, every day for the first week, and every three days thereafter.

ARD-N was a test designed to test ARD generating characteristics under water-covered conditions. Ten kilograms of rock samples with particles in all size ranges were packed without washing into a cell, and then submerged with ten liters of distilled water. Water covered the rock samples completely with approximately a six cm water barrier on the top of

the rock samples.

The test was carried out at a room temperature of 25°C and lasted for 12 months without agitation. Water samples were collected after mixing different layers of water in the first month, and then collected from surface and bottom layers respectively thereafter. The sampling interval was once a day for the first two weeks, once every three days for the following two months, and once every two weeks thereafter.

ARD-S1 was a small-scale test prepared to observe pH changes in the first two hours at one-minute intervals. Water and rock ratio was set at 4:1 (weight ratio), and the rock samples were up to 3 cm in size without washing. The test was carried out at a room temperature of 25°C with the agitation from the stirring machine.

ARD-S2 was carried out to compare the results with ARD-S1 by using rock samples following washing. Six hundreds grams of rock samples in sizes from 1 to 5 cm were washed with tap water and air dried for 2 hours, and submerged with 600 ml distilled water. A stirring machine was used for agitation.

ARD-DW used pure distilled water to study pH and conductivity changes with time as a comparison with previous tests. Four liters of distilled water were added to a five-liter cup without covering, and water level was maintained constant during the whole test period. The test was carried out at a room temperature of 25°C, and lasted for 92 days without agitation. The samples were collected every 3 days.

4.2.4 Coating Material Capacity Test

This test was designed to study the coating capacity of coating materials under a

water-submerged condition by studying the changes of pH, conductivity, and metal concentrations. The parameters were examined to evaluate the performance of coating materials in excluding water from rock contact, and further avoiding oxidation of the rock samples. The test equipment was the same as used in the ARD generation test. Water was circulated by agitation to accelerate the mixture of oxygen in water.

Rock samples, coated with materials of epoxy-41, epoxy-43 and acetone-W, were air-dried for 7 days, and then hand packed separately into three cells. The silicone-S did not arrive before the test; therefore it was not included in this test. Since edges of samples had the weakest part of the coating layer, special attention was given to avoid damage to coating layers during the whole preparation. Each sample was submerged in 1.5 liters distilled water with about one third of its height exposed to the air. The water level was kept at approximately the same height as marked initial level during the test period.

The test lasted for 88 days at the room temperature of 25°C. Water was circulated by agitation during the whole test period. Fifty ml water samples were collected every three days for pH and conductivity measurements and metal concentration analysis.

4.2.5 Freezing and Thawing Test

Since the Pennask site is located in a mountainous area where the temperature drops below –20°C in the winter season, coating materials are required to be able to function under the condition of freezing-and-thawing cycles during the spring and fall seasons. This test was designed to study the performance of the coating materials under such conditions by, 1) observing the surface changes of coating layer during the freezing and thawing cycle, and 2) examining the durability and permeability of the coating layer though coating capacity test. Therefore, this test was carried out in two steps: 1) freezing and thawing recycle, and 2)

coating capacity test.

Processing of Freezing and Thawing Cycle

Four pieces of large rock samples (12 to 15 cm) and four smaller ones (2 to 5 cm) were selected and coated by coating materials epoxy-41, epoxy-43, acetone-W and silicone-S separately following the instruction of manufacturers. Coated rock samples, after one week of air-drying, were placed into the refrigerator for 8 to 24 hours at temperature of $-12^{\circ}C$. Samples were removed from the refrigerator and warmed to a room temperature of $25^{\circ}C$ for 8 to 24 hours. The cycle was repeated ten times. Surface changes and interaction of coating layers were observed visually. In order to simulate natural condition, the time of freezing and warming during this time was inconstant. This step of the test lasted for 13 days. Large samples in this test were prepared for the coating capacity test, and small samples were used to make thin section samples.

Coating Capacity Test for Freezing And Thawing Tested Samples

After freezing and thawing cycles, samples were submerged into 1.5 liters of distilled water for the coating capacity test. The test equipment and procedure were the same as in the previous material capacity test. The water level was maintained at two-thirds of the sample height during the test period.

This step of the test lasted for 83 days under room temperature of $25^{\circ}C$ with water circulation for one hour every day. Fifty ml of water samples were collected every 3 days after the water circulation for the whole test period, for pH and conductivity measurements and metal concentration analysis.

4.2.6   Heating and Cooling Test

The temperature of the Pennask Site may rise to 40 $^{\circ}$C in daytime and cool down below to 25°C at night during the summer season, so this heating and cooling test was designed to simulate the natural conditions of the site. During the test, the surface changes of the coating layer were visually observed, and the durability of the coating layer under water-submerged conditions was studied by the coating capacity test. The test was conducted in two steps: 1) heating and cooling cycles, and 2) coating capacity test.

Heating and Cooling Cycle

Four pieces of large rock samples (12 to 15 cm) and four smaller ones (2 to 5 cm) were selected and coated by coating materials of epoxy-41, epoxy-43, acetone-W and silicone-S separately. Coated samples were air dried for one week, and then were placed into an oven at the temperature of 45 $^{\circ}$C for 8 to 24 hours. Then samples were then removed from the oven and cooled down to a room temperature at 25°C for 8 to 24 hours. The process was repeated twelve times. Surface changes of the coating layers were observed visually during the test period. In order to simulate natural condition, the heating and cooling time was inconstant. This step lasted for 30 days.

Coating Capacity Test of The Heating And Thawing Samples

After the heating and cooling cycles, the rock samples were submerged in 1.5 liters of distilled water for coating capacity test. The test equipment and procedure were the same as the previous coating material capacity test.

The water level was kept at two thirds of the rock height during the test. Fifty ml water

samples were collected every three days after water circulation during the whole test period for pH and conductivity measurements, and the metal concentration analysis. The test lasted for 85 days under a room temperature of 25°C.

4.2.7 Thin Section

Thin section analysis is a technique used to determine spatial arrangements of a material's constituents. In this study, it was employed to observe and compare coating layers on rock samples, and the changes of coating layers after different test processing and circumstances.

In total, ten thin section samples were prepared. One was from natural rock sample (tap water washed and air-dried), three from the coating material capacity test (of epoxy-41, epoxy-43, and acetone-W), four from the freezing and thawing test plus the coating capacity test, and the last three from the heating and cooling test (of epoxy-41, epoxy-43, and acetone-W).

The equipment used in this test included a Micropet and a camera. The Micropet was a LaborLux 11 POL @ Leitz Wetzlar made in Germany. The camera was a MINOCTA X-700 with lenses of magnified rate of 8 times, which is made in Japan by EOS Lab.

The thin section samples were prepared by the technician from Geographic Lab in the Geographic Department of University of British Columbia. The thin section samples were standard samples with the thickness of approximately 60 μm. No heating was used during the sample preparation in order to avoid damage to the heating process of he coating layers. The thin section samples were then observed under the Micropet to study the difference of the coating layers amongst the different coating materials, testing procedures, and under different testing conditions. The micrographs were recorded by camera. The test lasted for 28 days.

4.2.8   The Bonding Capacity Test

This test is designed to study the tensile strength between coating materials and rock samples, 1) to determine the ability of coating materials adhering to rock surfaces to resist peeling damage, and 2) to determine the ability of sticking adjacent rock pieces together on the slope.

The bonding capacity test used AMST Standard C952 (Bond Strength of Mortar to Masonry Units), which was developed for testing bond strength between mortar and masonry units.

Configuration of the Test System and Equipment

The test system consisted of the test machine and loading jigs. The test machine was used to measure the tensile strength, and loading jigs were designed and prepared to hold samples during the test. The two-part model of loading jigs was made from aluminum in the Civil Engineering Department of University of British Columbia (Figure 4.3). The upper part is
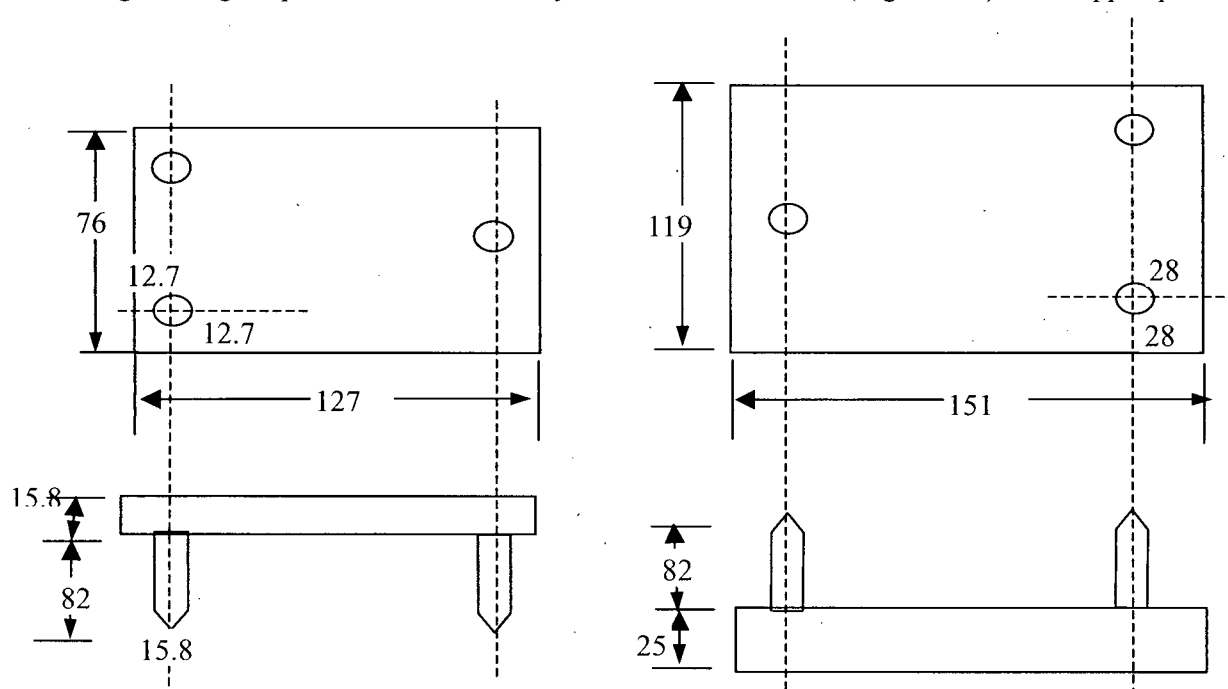

Figure 4.3 Design Details of Loading Jigs. Left is the upper and right is the lower part.

used to add the load to the test couplet, and lower part is used to hold the test couplet.
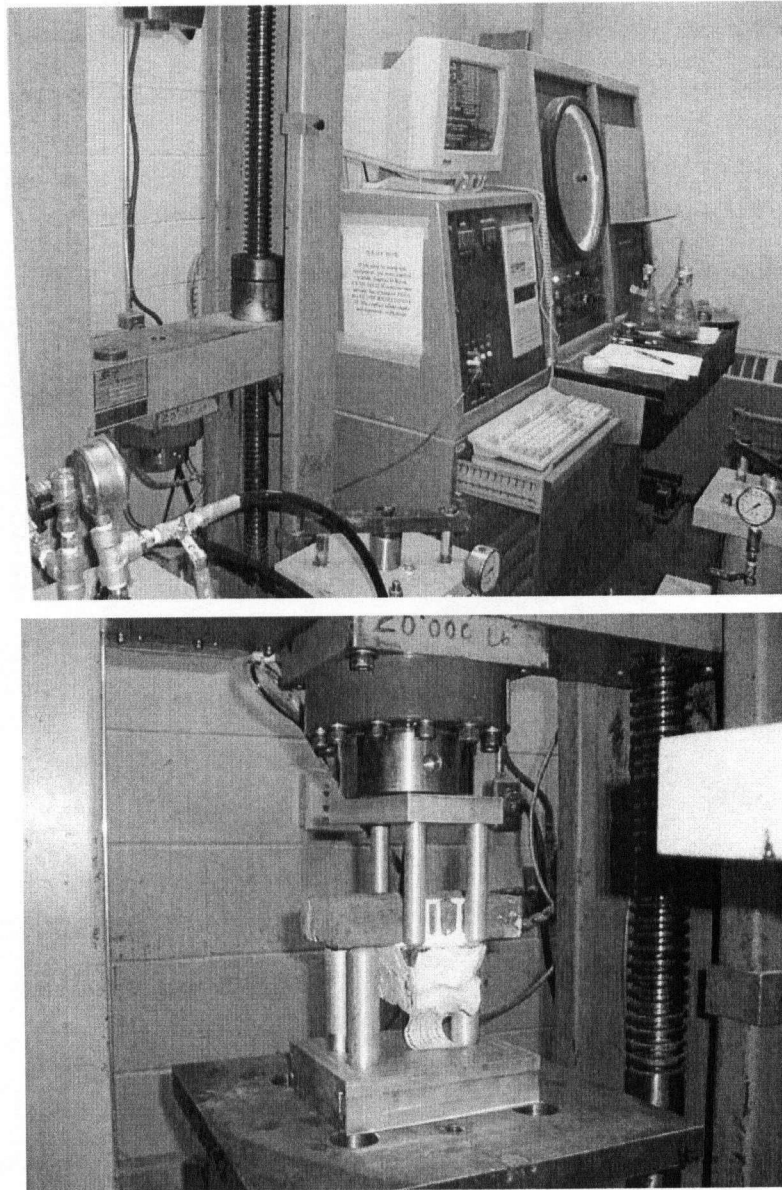
Figure 4.4 Pictures of Bounding Capacity Testing Equipment. Up: recoding machine. Lower: jig for holding samples.

Sample Preparation and Test Procedure

The test couplet consists of one piece of rock sample and one piece of concrete brick. The concrete brick was used to keep the bonding area approximately the same.

Three wood models in the size 65 x 7 x 5 cm (length x width x height) were prepared for casting in concrete. A high performance concrete mixture was prepared with 120 g silica fume added. The mixture is cement / stone / sand / water =1.5 / 3.0 / 3.0 / 0.3. The concrete was mixed by a mixing machine, cast in models by hand, and then stirred by a stir machine. The surface of the concrete was polished by trowel two hours after casing in.

The concrete was cured in air for twenty-four hours, and in water for one week. After that, the concrete was cut by a cutter into testing sizes of 12 x 7 x 5 cm (length x width x height), and air-dried at a constant temperature of 25°C for four weeks.

Six half-cut rock samples were bonded to six concrete bricks by epoxy-41, epoxy-43, and acetone-W. Two couplets for each coating material sample were prepared. The bonded test couplets were air-dried at 25°C temperature for 5 weeks. There were two testing samples prepared for each coating material. Each testing sample consisted of one piece of standard concrete brick and one piece of rock sample stuck together by one coating material.

After being air-dried for two months, the test couplets were set into jigs, placed on the test plate of the Universal Testing Machine, and then a load applied to push the samples away until the coating layer failed. The final readings of the loads were recorded. Special attention was given to adding the loads to the jig evenly and gradually with a constant speed. Each test lasted approximate 20 seconds. After each test, the bonding area of each test couplet was observed and measured.

CHAPTER 5

RESULTS AND DISCUSSION

5.1 SAMPLING AND SITE OBSERVATION

The Pennask Site is located on highway 97C in the Thompson-Okanogan region. The highway runs in an east-west direction at the site area, with a slope down to the west. The highway construction excavated a small mountain, so that the slopes on both sides of the highway are either rock-cut surface or piled collapsed rocks. The degree and the height of the slopes varied along the highway. Each side has a drainage ditch located at the foot of the slopes with growing grass. In the south ditch, there was a small visible creek flowing downstream, while the northern one was completely dry. Two fieldtrips were carried out in September 04th and 20th, 2003, the first fieldtrip led by Dr. Loretta Li and Mr. Buchanan for site observation, and the second trip for field measurements and samples collection.

The South Side

The southern side of the highway is the primary ARD generating source with two major ARD generating zones, one located near the east end, and the other approximately 20m west of downstream. The slopes of both locations were covered with rocks of different size (Appendix E-1).

The drainage began at the first major ARD generation location, and became greater as it flowed down stream (Appendix E-2). There were two smaller creeks with totally different colors side by side in the second ARD generation location. On one side, the water coming from the bottom made a tiny creek that looked clear with pH of 5.52, while the one beside it

was brown with red dusty flow on the top, with a pH of 3.33 (Figure 5.1). The brown-color drainage came from the bottom of the slope. The source of the drainage can be inferred as groundwater, or the water, which has penetrated though the rock cracks from the slope background.

Figure 5.1. Clean and Brown Small Creeks Flow Side By Side on The Southern Ditch

Half the length of the ditch downstream was covered by crushed limestone as a remediation measure for the ARD drainage (Appendix E-3). The limestone need to replaced one to four times per year. At the west end of the ditch, there was a small pond to catch the drainage. The drainage color was brown with an average pH value of 3.22 (Appendix E-4).

Further down stream, there was a settlement reservoir near Highway Creek. The whole way from the pond to the reservoir was covered by crushed limestone to treat the ARD before it entered the Highway Creek (Appendix E-5).

The North Side

On the north side, limestone had just been replaced for one month, so the stone surface appeared a fresh-stone color during the first fieldtrip (Appendix E-6); however, the color had changed to dark brown on the second trip two months later (Appendix E-7). Below the limestone, there was a geomembrane layer to prevent the drainage penetrating into the soil layer beneath it. The red-and-black-colored drainage from the end pond, after flowing approximately 40m over fresh limestone, became clear as it entered the settlement reservoir

on the downstream end of the ditch (Appendix E-8 and E-9). The reservoir was designed to store approximately 6 months drainage during the summer season, which is half of the total volume.

The pH along the way from the highway to the reservoir changed from 4.0 to 5.5.

Sampling

Rock samples were collected from four sampling locations at two primary ARD generating zones, P101, P102, P103 and P104 during the first fieldtrip, and from P201 and P202 during the second fieldtrip (Figure 5.2). P201, P101, and Pl02 were located in the first ARD generating zone, while P202, P103, and P104 were in the second zone. Most samples of tests were from P201 and P202. The distance between the two sampling locations was approximately 30m (Appendix E-1). In total, 400 kilograms of samples were collected.
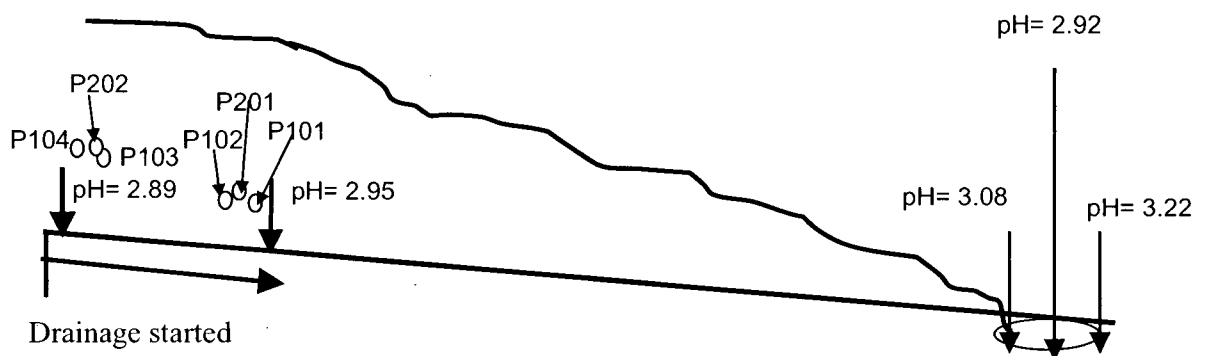

Figure 5.2 Illustration of The Profile of Sampling Location and pH Distribution of Southern Side of ARD Generation Area Along Highway 97C Near Pennask Creek. Drainage started from the left-end, and received seepage at the point of second pH measurement. P101-P104 and P201-P202 were sampling locations.

5.2 LABORATORY TEST RESULTS

5.2.1 Analysis of the Physical and Chemical Characteristics of the Rock

Four pieces of rock samples from each sampling location were analyzed for major oxides (Table 5.1) and elements (Table 5.2). Details are listed in the Appendix C.

Table 5.1 The Major Oxidations of Rock Samples

Oxidations		P101	P102	P103	P104	P201	P202	STANDARD SO-17/CSB
SiO_2	%	71.25	65.32	76.03	60.11	73.75	72.31	61.42
Al_2O_3	%	12.89	14.64	10.03	17.30	11.26	11.42	13.78
FeO_3	%	3.82	6.15	4.26	6.08	4.33	4.64	5.82
MgO	%	1.69	2.26	1.25	3.11	1.80	1.89	2.34
CaO	%	0.94	1.29	0.80	2.20	0.91	0.64	4.66
Na_2O	%	2.62	3.40	1.98	3.35	2.29	1.64	4.14
TOT/S	%	0.08	0.57	0.18	0.06	0.06	0.30	5.31

There is no significant difference amongst the six sampling locations. SiO_2 was the most common oxide of rock samples, which ranged from 60.11 % (P104) to 76.03 % (P103) with an average of 69.79 %. Following it, Al_2O_3 reached concentrations from 10.03 % (P103) to 17.3 % (P104) with an average of 12.92 %. Those two made up more than 70% of the total. The total S ranged from 0.06% to 0.57%, which was not considered to be a high concentration, but there were significant differences among the samples.

Table 5.2 The Main Elements of Rock Samples

ELEMENT	SAMPLES	P101	P102	P103	P104	P201	P202	STANDARD SO-17
Cs	ppm	7.5	5	3.4	2.8	3	8.5	3.9
Rb	ppm	51.9	53.7	41.4	51.3	44.4	60.3	23.2
Sr	ppm	156.6	211	130.6	210.6	160.6	99.5	307.5
V	ppm	67	98	66	117	82	97	127
W	ppm	1.6	1.2	2	8.4	3	1.1	10.3
Zr	ppm	103.6	137.8	99.8	205.3	115	106.1	355
Y	ppm	34	36.1	20.4	38.4	33.8	21.9	27.3
Cu	ppm	24.7	18.9	28.8	46.3	31.3	39.7	146.6
Pb	ppm	6.2	5.4	6.2	4.3	3.2	5.6	25.3
Zn	ppm	43	55	51	65	50	62	141
Ni	ppm	8	21.1	8.4	25.7	11.8	13.9	25.6
As	ppm	4.2	8.7	48.8	47.6	18.8	11.1	18.2
Cd	ppm	0.1	0.1	0.1	0.1	0.1	0.2	5.8
Hg	ppm	< .01	0.01	< .01	< .01	< .01	< .01	0.18

Forty-three elements were analyzed. High concentration elements are summarized in Table 5.2. Sr and Zr were over 100 ppm; Sr ranged from 99.5 to 211 with an average of 161.5 ppm and Zr ranged from 99.8 to 205.3 ppm with an average of 127.9 ppm. Rb and V were over 50 ppm, in which Rb ranged 41.4 to 60.3, with the average of 50.5 ppm, while the V ranged from 66 to 117 with the average of 87.8 ppm. The element with the lowest concentration was Hg, which was less than 0.01 ppm. Zn and Cu concentrations were relatively high, Zn ranged from 43 to 65 with an average of 54.3 ppm, while Cu ranged from 18.9 to 46.3 with an average of 31.6 ppm. In previous study (Buchanan, 2001), the values of Cu, Ni and Zn

ranged from 43 to 45 ppm, 20 to 23 ppm, and 76 to 90 ppm respectively in adjacent areas. In comparison, this results show that Cu was at the same level, while Zn and Ni were slightly lower.

5.2.2   ARD Generation Test

ARD generation tests were conducted to study ARD generating characteristics of the rock samples. The primary controlling factors influencing ARD generation are water-rock ratio, agitation, leachant, and temperature. Five sets of tests were carried out at a room temperature of 25°C to study the influence of these primary factors.

ARD-TW (ARD generation test with tap-water) was designed to investigate the factor of water-rock ratio. Tap water was used as a leachant to simulate natural conditions. However, since the pH and metal concentrations of tap water changed irregularly over time, the test was unable to determine the influence of water to rock ratio. Therefore, the results are withdrawn from the discussion.

The ARD generation test was carried out for the same purpose, but used distilled water to replace the tap water. The test results are given in Figure 5.3 to Figure 5.26.

pH Change

The change in pH with time is given in Figure 5.3. During the test period, the three samples showed a similar changing pattern but slightly different values. The pH decreased sharply on the first day, and changed slowly thereafter. Water to rock ratio of 2:3 gave the lowest value, while the ratio of 5:3 gave the highest value. The lowest pH value was 3.5, which was near the pH value measured in the south ditch drainage at the Pennask Site. The water to rock ratio

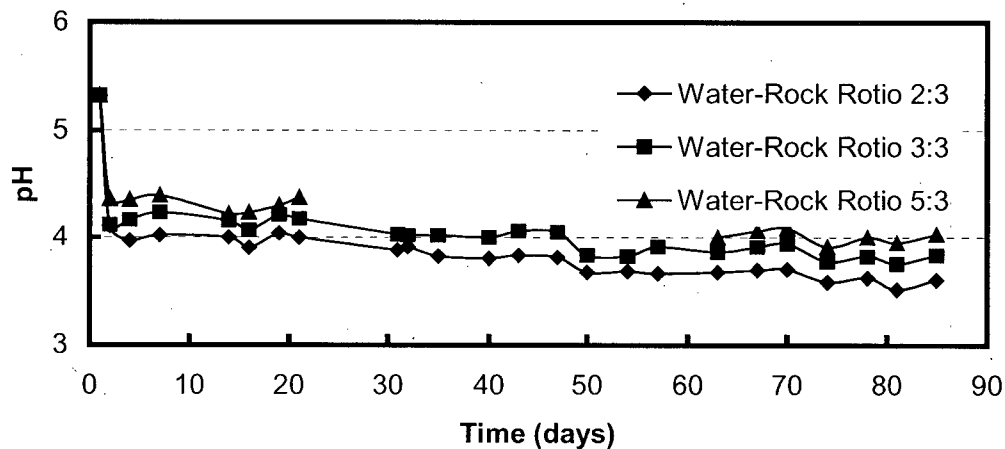influenced pH; the lower the water to rock ratio, the higher the pH.

Figure 5.3 pH Changes vs. Time of ARD Generation Test

Since the pH represents the acidity of the liquid, and the acidity of this test was caused by the oxidation of rock samples, the pH change presented the degree of oxidation of the rock samples.

In order to understand the details of the sharp decrease in the first day, one-hour interval pH change was measured (Figure 5.4). The initial pH value was the value of the distilled water. The primary pH decrease occurred during the first two hours, and the difference amongst samples became obvious after two hours. Water to rock ratio of 5:3 gave the highest pH value, while the ratio of 2:3 gave the lowest. The influence of water to rock ratio upon pH became clear after two hours.

ARD-S1, a smaller scale test, was carried out to observe the pH change in the first two hours. 300 grams of unwashed rock samples were packed in a cell and then submerged with 600 ml distilled water. The test result is shown in Figure 5.5. The initial pH was the value of the distilled water. A rapid decrease occurred immediately after the test started. The pH value, already 0.6 lower than the initial value of 5.23, decreased 0.2 within the first 15 minutes,

another 0.2 in the following 20 minutes, and became almost stable at the value of 4.16 after 50 minutes. It is postulated that the dramatic decrease of the pH value was caused by the immediate reaction between water and very fine particles in the rock samples. The smaller the particle, the larger the surface area, and the faster the chemical reaction.
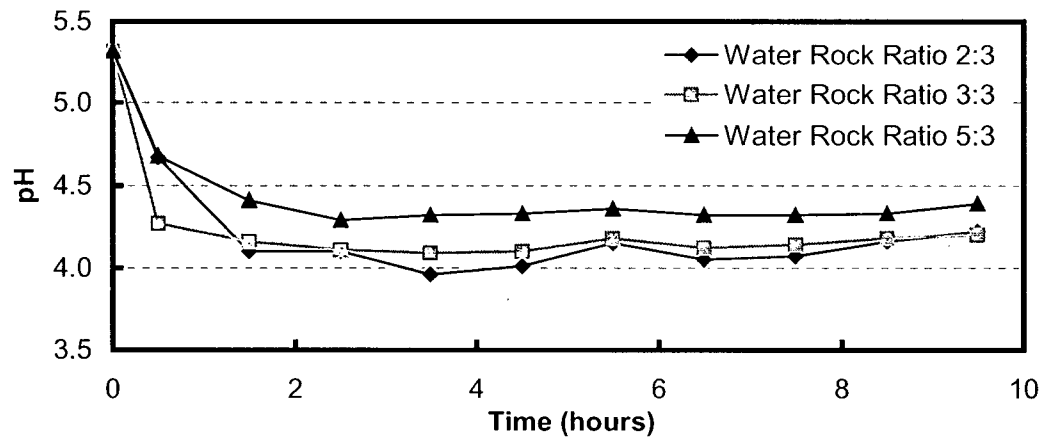
Figure 5.4 pH Changes vs. Time of First Nine Hours in ARD Generation Test
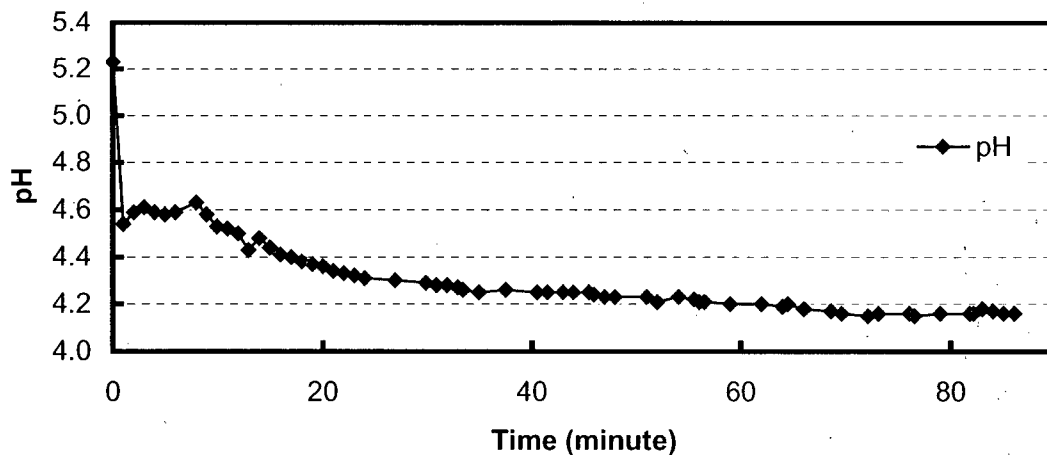

Figure 5.5 pH Changes vs. Time of the Small Scale ARD Generation Test with Unwashed Rock Samples(ARD-S1)

ARD-S2, a parallel test that used washed rock samples to replace the unwashed rock samples, was conducted to confirm the above assumption. Six hundred grams of rock samples ranging from 1 cm to 5 cm in dimension was washed with tap water, and air-dried for one hour, and

then packed into a cell submerged with 600 ml distilled water. The pH change with time was measured (Figure 5.6). There was no sharp decrease in the first minute as that of ARD-S1. In the second minute, the rocks on the top were moved to lower the probe of the pH meter, after that, the pH decreased immediately below 4.8, increased and decreased for following 15 minutes and then gradually decreased to 4.55, which was higher than that of the result from un-washed rock samples.
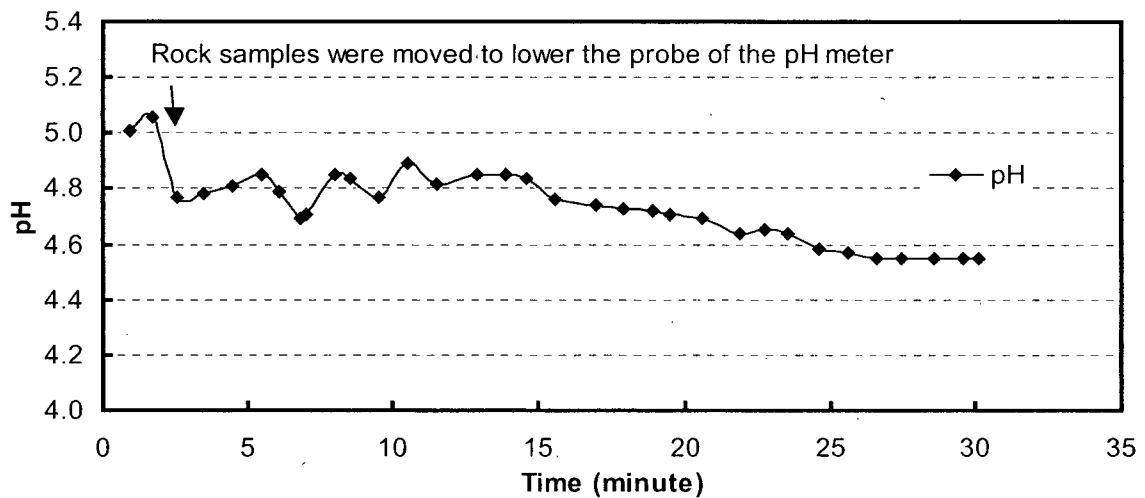

Figure 5.6 pH Changing with Time in Smaller Scale ARD Generation Test with Washed Rocks (ARD-S2)
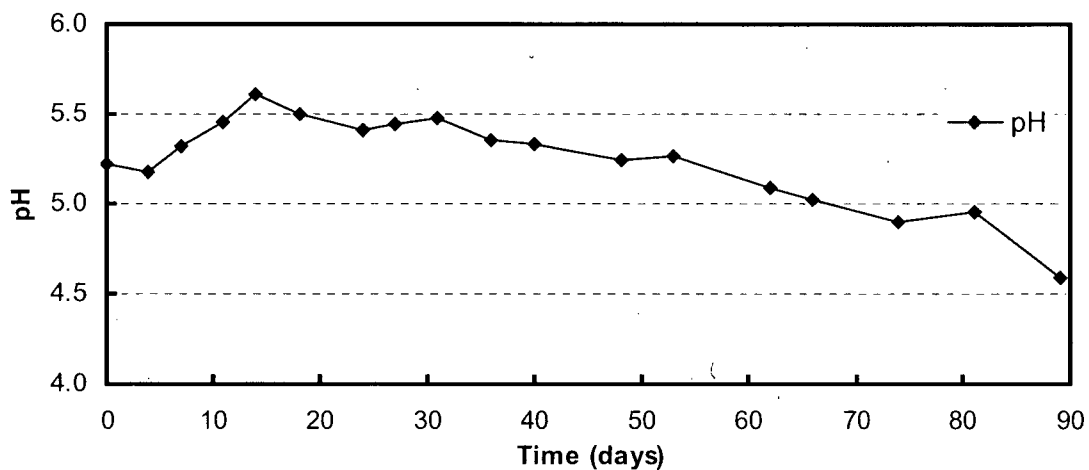

Figure 5.7 pH Changes vs. Time of Distilled Water in Room Temperature Without Cover

The pH change with time of distilled water is given in Figure 5.7. There was no sharp decrease in the first day as founded from the ARD generation test. On the other hand, the pH even increased slightly during the first 15 days. Since the distilled water was refilled after every measurement to keep the water level constant, it was postulated that the pH of the initial water was lower than that of the added water.

The water to rock ratio influenced the pH of the leachate water. The higher the water to rock ratio, the lower the pH. The rapid decrease of the pH change occurring at the beginning was considered to be caused by an immediate reaction between water and fine particles. There was no similar decrease in the tests with distilled water and washed rock samples.

Conductivity of Leachate in ARD Generation Test

Conductivity is a property of a liquid representing its ability to conduct an electric current. It changes when the chemical components within the solution are changed. Pure distilled water has values below 50 μS/cm, while the value in ARD leachate may be over 500 μS/cm. Hence, conductivity is a useful parameter to represent the increase of ions due to the sulfide oxidation.

The conductivity change with time of the ARD generation test is shown in Figure 5.8. The conductivity of three samples increased for the test period, rapidly increasing in the first two days, slowing thereafter, and finally tending to be constant after approximately 60 days. There was no significant difference to the change pattern amongst the three samples. However, the sample with water to rock ratio of 2:3 had the highest final value of 317 μS/cm, while the sample with ratio of 5:3 had the lowest value of 195 μS/cm. This indicates that the lower the water to rock ratio, the higher the conductivity value. The peak at approximately 14 days is considered to be due to the water level during sampling being lower than normal.
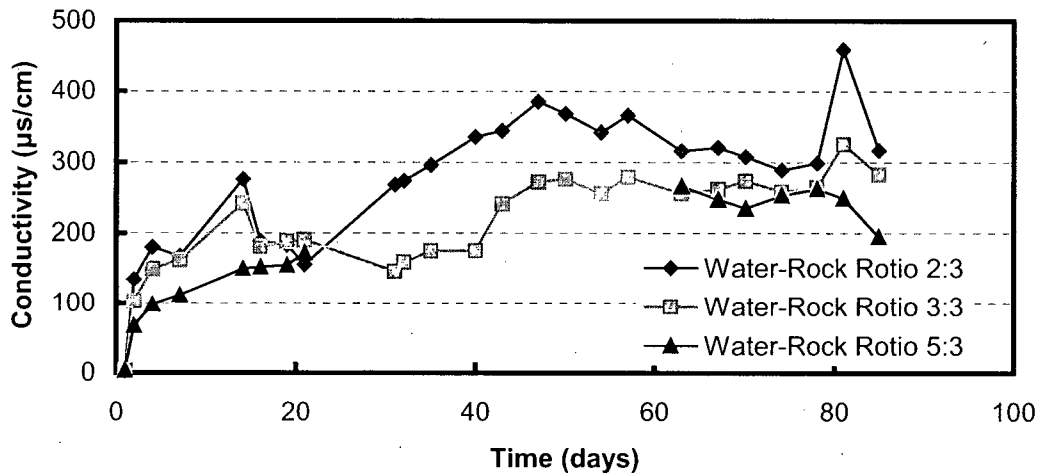
Figure 5.8 Conductivity vs. Time in ARD Generation Test

The conductivity change in the first nine hours is shown in Figure 5.9. The primary increase occurred in the first 3 hours, and then the rate of increase lessened. This result shows a tendency similar to that of pH changes, but in reverse.
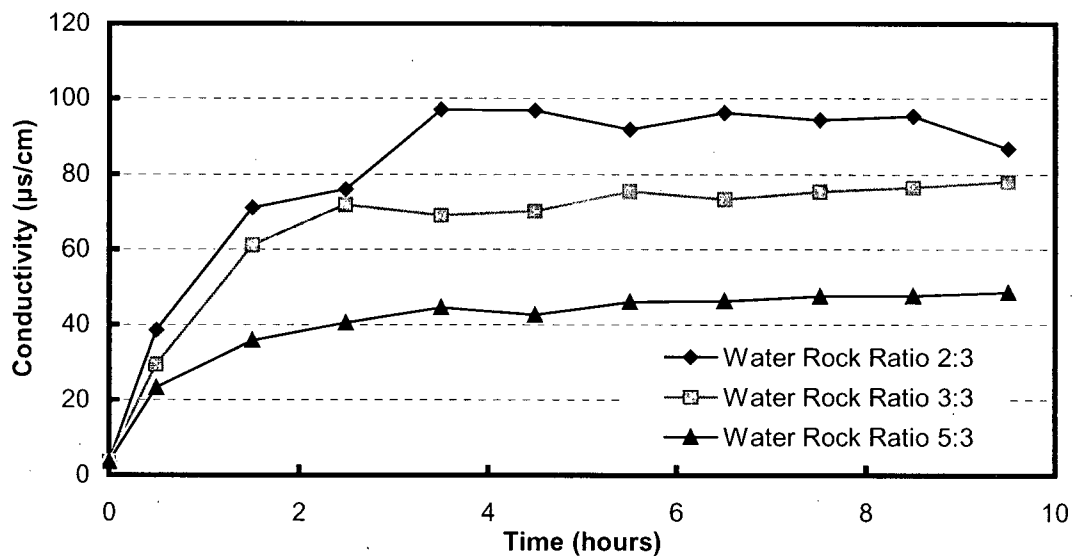
Figure 5.9 Conductivity Changes vs. Time in First Nine Hours of ARD Generation Test

The conductivity change with time of ARD-N (ARD generation test with ten kilograms rock samples and ten liters of distilled water) is given in Figure 5.10. The conductivity continually increased during the test period. There was no significant difference between the surface layer and bottom layer. The peak in 20 days was caused by the water level being lower then normal.
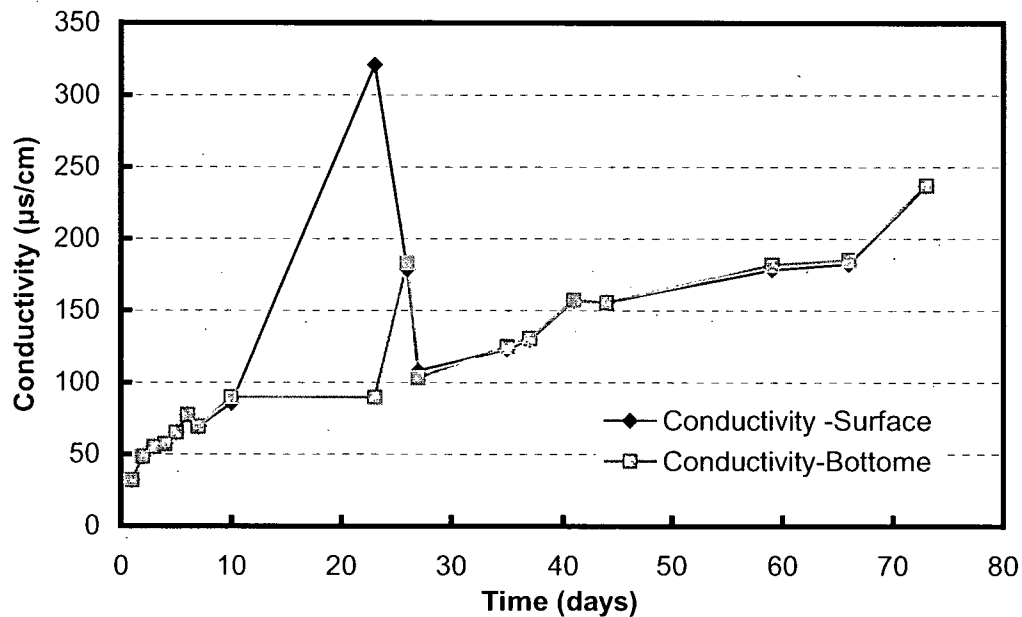
Figure 5.10 Conductivity vs. Time in ARD-N Test

The conductivity of the distilled water showed a different changing pattern. In the first 20 days, the increase was very slow, and then became much faster (Figure 5.11). It is assumed that soluble cations/anions were released gradually from about 20-90 days exposed to the air.

The conductivity from all cells with rock samples was higher than that of the distilled water, which indicates that rock samples reacted with water and air, and changed the chemical content of the water. In other words, the rock samples were partially oxidized.
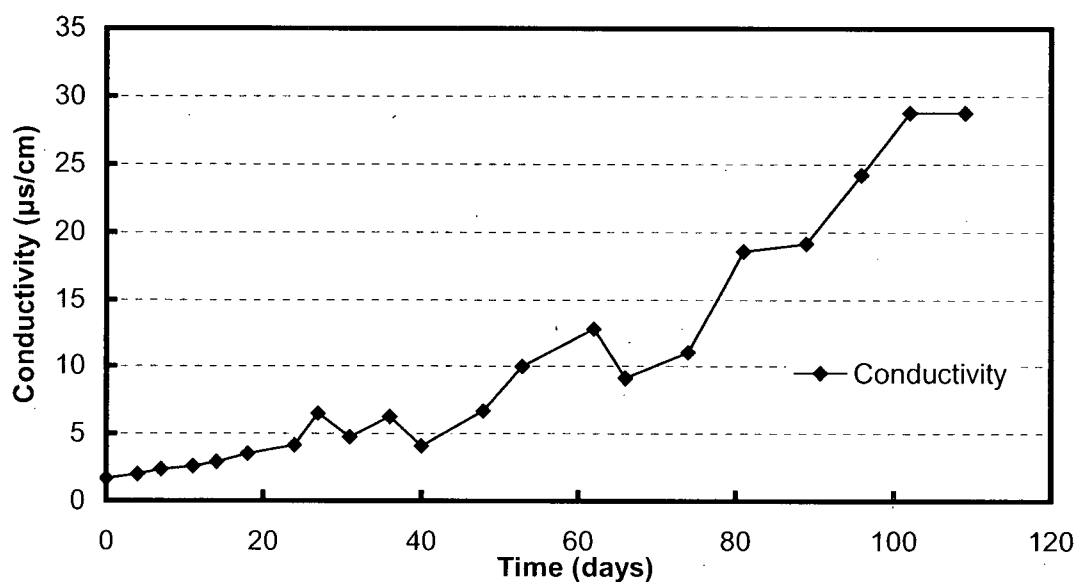
Figure 5.11 Conductivity vs. Time of Distilled Water in Room
Temperature Without Cover

The Correlation of pH And Conductivity

The correlation between pH and conductivity is given in Figures 5.12 to 5.14. There was a
strong correlation between the pH and conductivity for all samples.

$$y = 5E+08x^{-10.881}$$
$$R^2 = 0.886$$
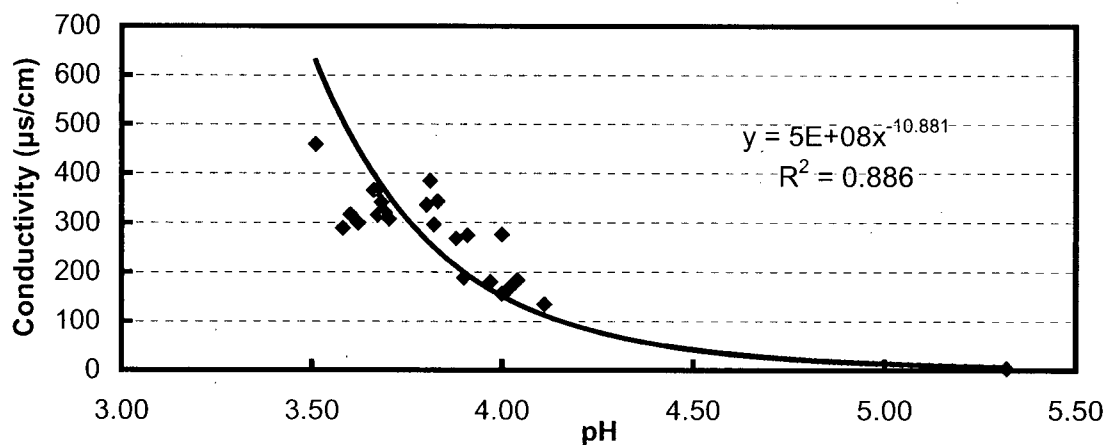
Figure 5.12 pH and Conductivity Correlation in ARD Generatioin Test
of Water and Rock Ratio 3:5
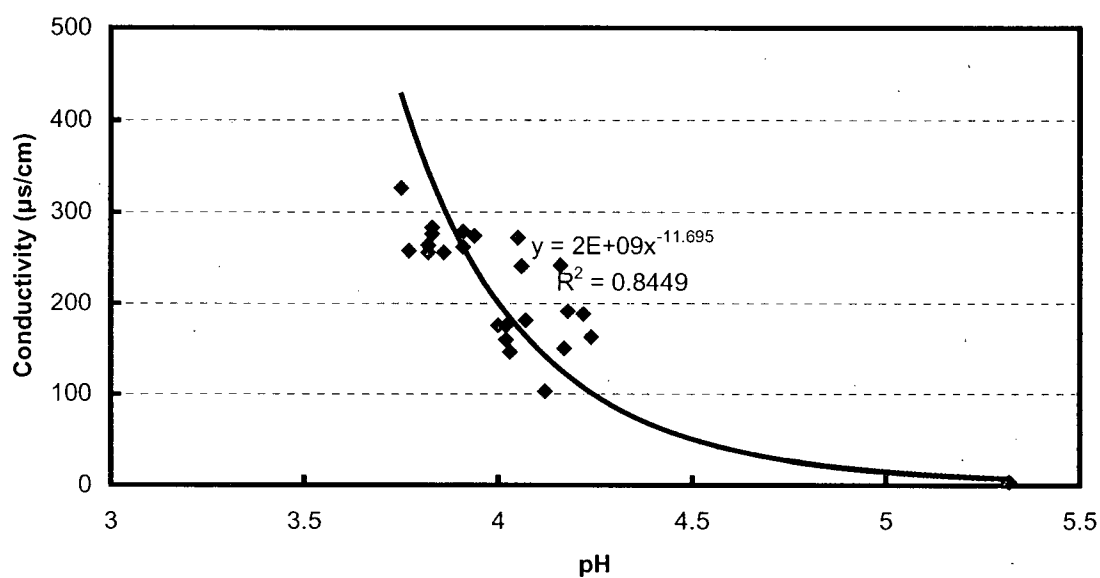
Figure 5.13 pH and Conductivity Correlation in ARD Generation Test of Water-Rock
Ratio of 3:3

The equation on the first figure reads:

$$y = 2E+09x^{-11.695}$$
$$R^2 = 0.8449$$

Figure 5.14 pH and Conductivity Correlation of ARD Generation Test of
Water Rock Ratio 5:3

The equation on the second figure reads:

$$y = 5E+10x^{-13.626}$$
$$R^2 = 0.9043$$

Metal Concentration of ARD Generation Test

The metal concentrations of Cu, Zn, Na, Ni, Ca, and Fe from each water samples were determined by atomic absorption spectrophotometry. Cu, Zn and Ni were the main concern due to their environmental impacts. The higher concentration of Ca and Na made them relatively easy to determine, and thus they are a good reference for comparison between the different tests.

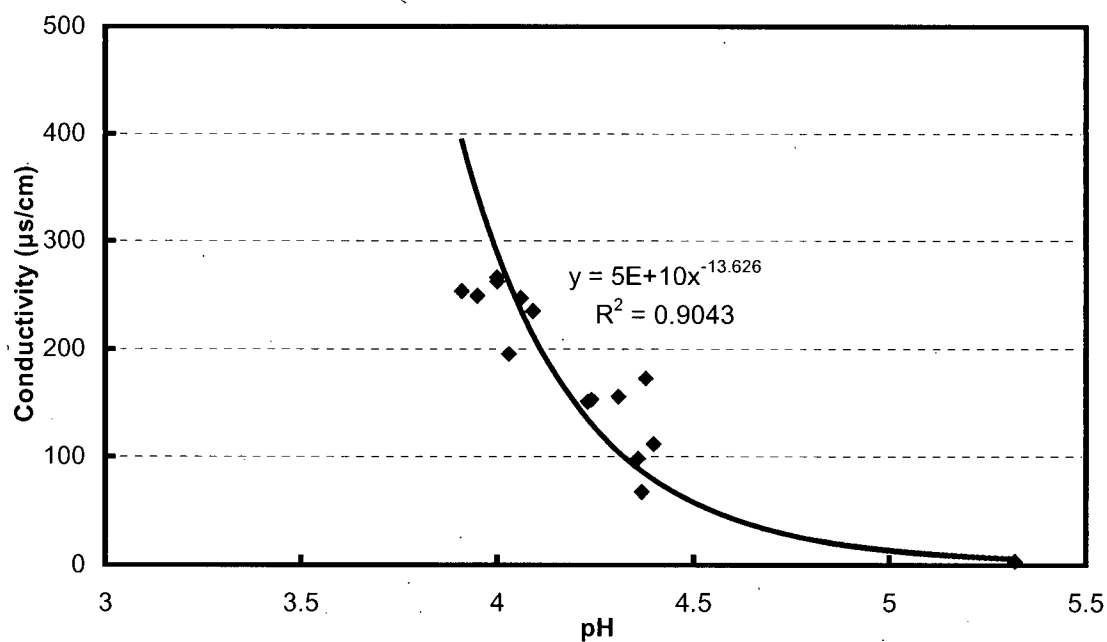Metal concentration changes with time are shown in Figure 5.14 to Figure 5.20. All metal concentrations increased during the test period but with different values. A sharp increase took place on the first 3 days. This corresponded to the sudden decrease of pH value and significant increase of the conductivity. Ca concentration was the highest, and approached 25 mg/l, while the Fe concentration was the lowest, only approximately 0.07mg/l. The remaining elements had concentrations in between. The peak at approximately 14 days was considered to be the result of lower water level.

The Cu concentration (Figure 5.14), Zn concentration (Figure 5.15), and Ni concentration (Figure 5.16) are subject to environmental regulations. All three metal concentrations show a tendency of constant increase during the test period, with obvious difference amongst three different water to rock ratios. The sample with the ratio of 2:3 maintained the highest value during the entire test period, while the sample with the ratio of 5:3 was the lowest. The water to rock ratio influenced Cu, Ni, and Zn concentrations.

Including Ca and Na, Zn had the highest concentration, which ranged from 0.3 mg/l to 0.6 mg/l at the end of the experiment. This value exceeded the Aquatic Life Standards of less than 0.3 mg/l. Ni concentration ranged from 0.15 to 0.25 mg/l, which was close to the standard of 0.25 to 1.5 mg/l. Cu concentration ranged from 0.05 to 0.25 mg/l, which was

greatly in excess of the standard of 0.02 – 0.09 mg/l.

Figure 5.15 Cu Concentration Changes vs. Time in ARD Generation
Test

Figure 5.16 Zn Concentration Changes vs. time in ARD Generation
Test
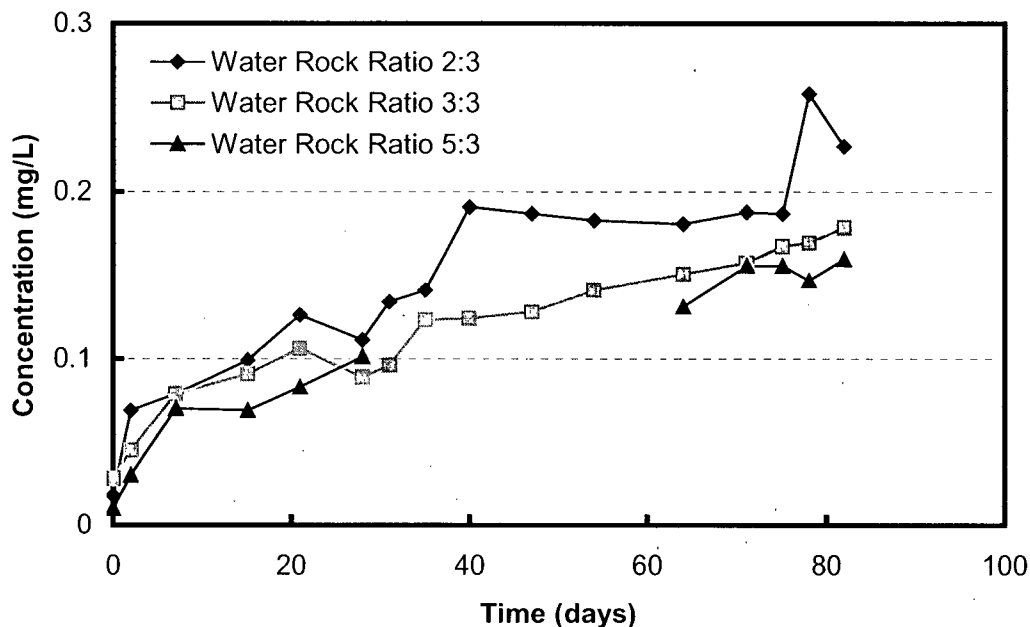
Figure 5.17 Ni Concentration Changes vs Time in ARD Generation Test

The Na concentration (Figure 5.18), Ca concentration (Figure 5.19) and Fe concentration (Figure 5.20) are not governed by environmental regulations. However, amongst these, Na and Ca had relatively high values while Fe had much lower values. Both Ca and Na sharply increased during the first one or two days, then slowed, and then increased again at approximately 45 days. For Na, the sample with water to rock ratio of 3:3 had the lowest concentration (below 2.0 mg/l) while the other two were higher. There was no significant difference between samples with a water rock ratio of 2:3 and 3:3. For Ca concentration, there was no significant difference among the three samples. For Fe concentration, although the values were low, the difference amongst the three samples became obvious in the last half period of the test. The sample with water to rock ratio of 2:3 had the highest value of 4.2 mg/l, while the water to rock ratio of 5:3 had the lowest value of 0.01 g/L. However, since Fe concentration was very low, the noise of the measurement might obscure any other tendencies. The water to rock ratio influenced Na and Fe, but did not show a strong influence
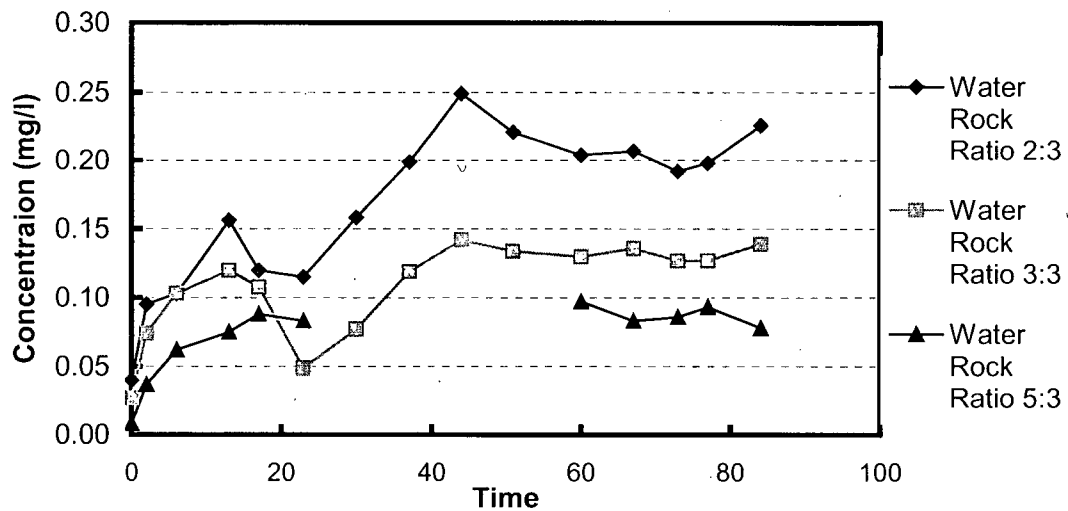
on Ca.
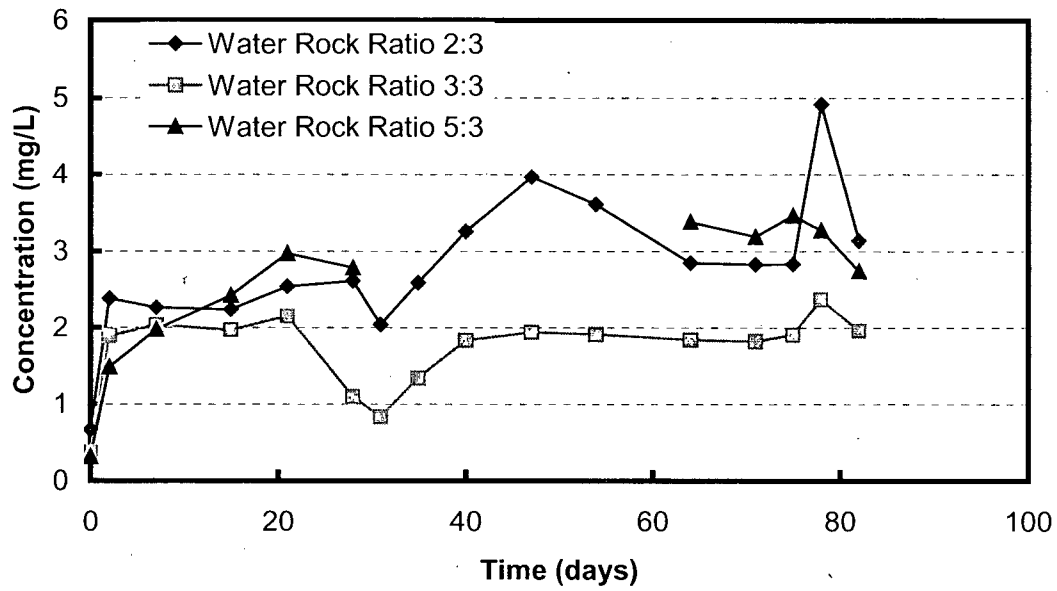
Figure 5.18 Na Concentration Changes vs. Time in ARD Generation Test
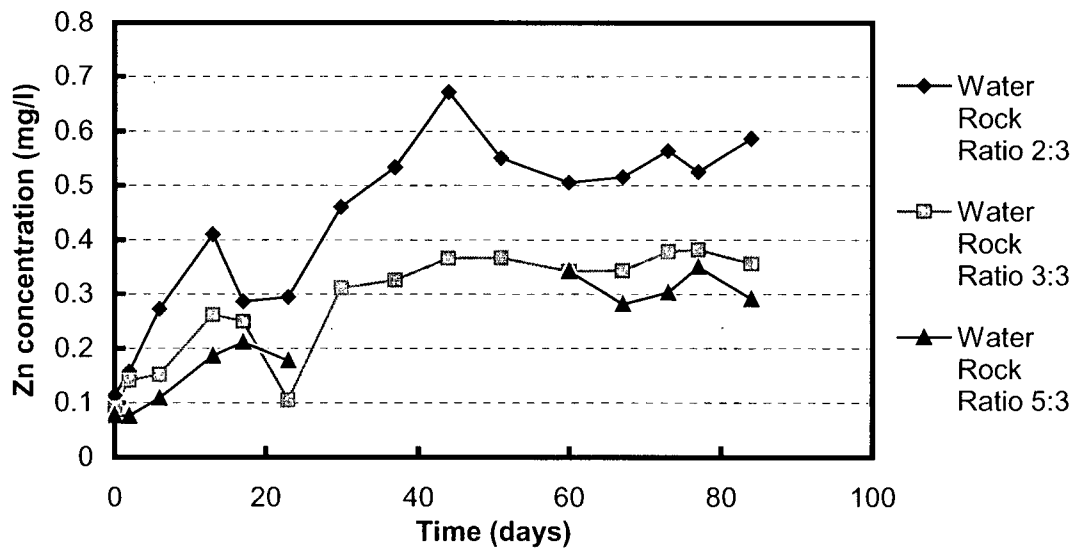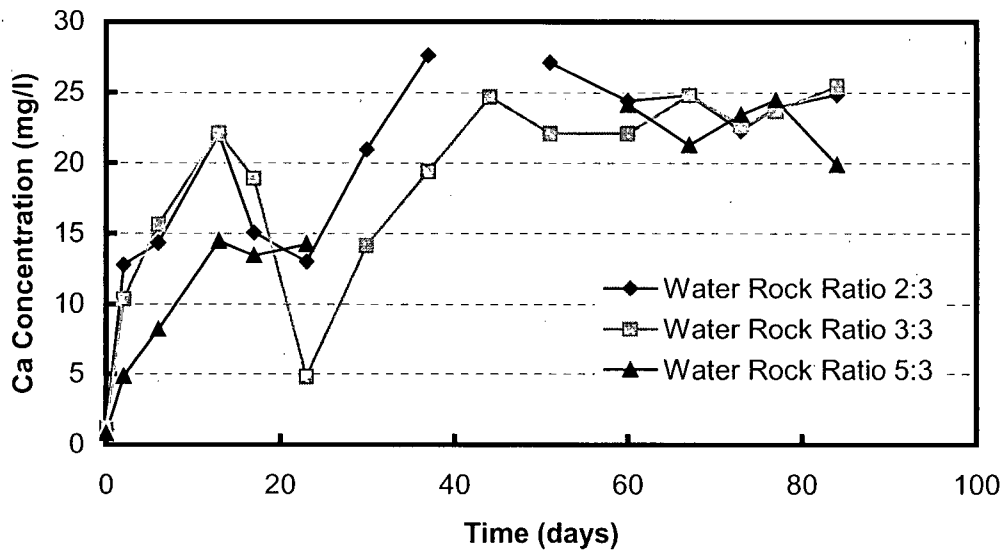

Figure 5.19 Ca Concentration Changes vs. Time in ARD Generation Test
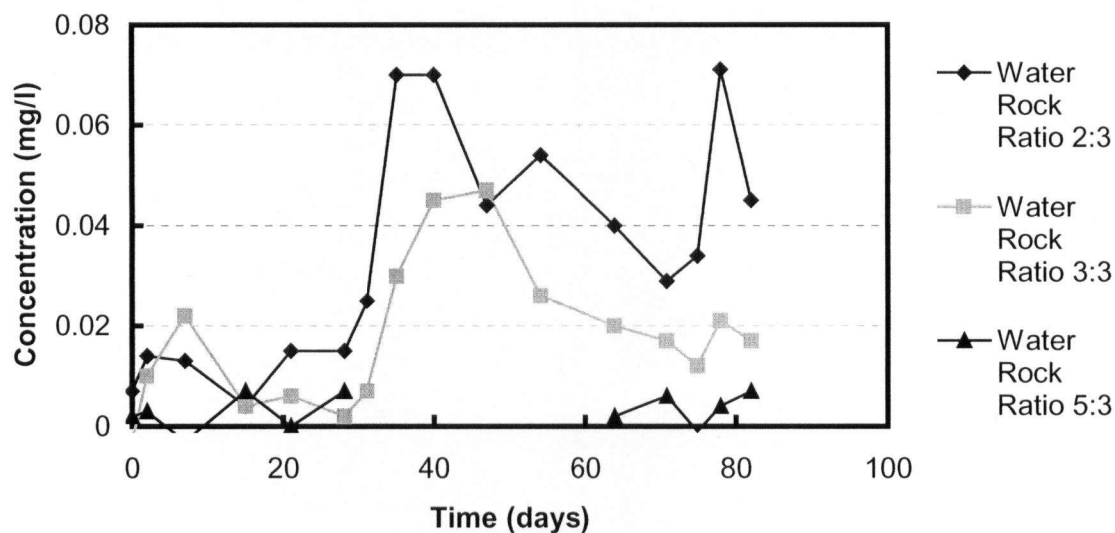
Figure 5.20 Fe Concentration Changes vs. Time in ARD Generation Test

The metal concentrations changing with time in ARD-N (ten kilograms rock samples and ten liters of distilled water) is given in Figure 5.22. ARD-N was tested without agitation for the entire test period. The data for the first 50 days are missing due to the failure of the metal concentration analysis. Metal concentrations of the surface layer and bottom layer were almost the same, and showed a similarly increasing parttern. Amongst the metals, Ca concentration was the highest (about 25.0 mg/l), and Mg concentration was intermediate (about 8.0 mg/l), while Zn and Cu were much lower (about 0.01 mg/l).

Figure 5.21. The green mater forming and growing inside the cell of ARD-N Test

After approximately 100 days, there was some green matter formed at the top-surface of the rock samples, which grew continually and finally covered the whole cell (Figure 5.21). However, no significant influence on metal concentrations was found.
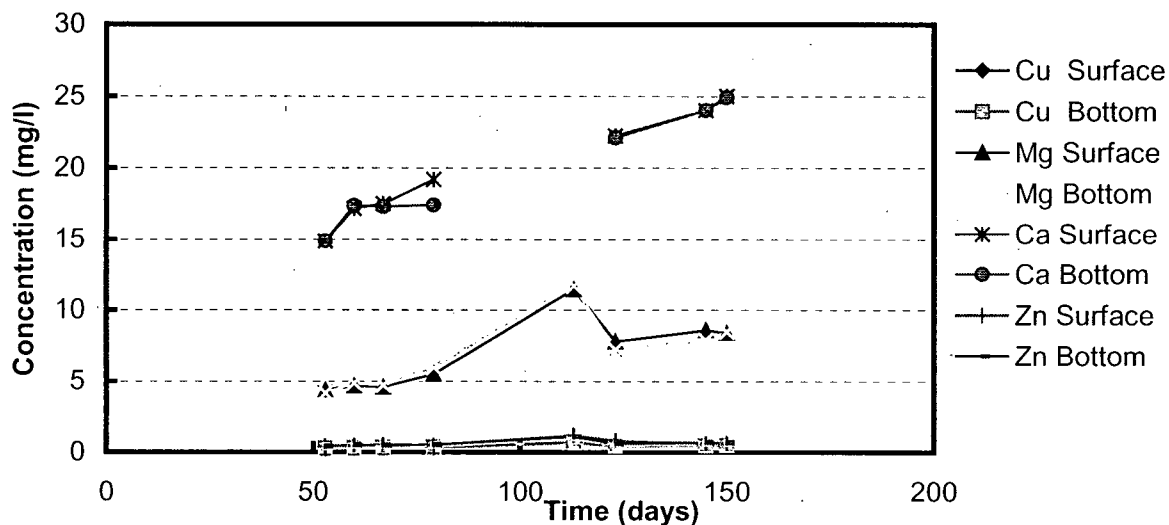
Figure 5.22 Metal Concentration Changes vs. Time in ARD-N Test with
Rock Water Ratio of 1:1

From the above discussion, it is clear that metal concentrations were increasing during the test period. However, the increasing rate and pattern were different among the metals. For all water to rock ratio, Ca had highest value, and Fe the lowest. The lower the water to rock ratio, the higher the metal concentration. Water to rock ratio influenced metal concentrations.

One month after the ARD generation test was started, water was circulated by agitation to accelerate oxygen mixing. After that, regardless of the water to rock ratio, all metal concentrations increased. The conductivity also showed a tendency to increase. It is suggested that the agitation influenced the ARD generating rate.

The correlation of pH and Cu and Zn concentrations with different water to rock ratios are given in Figures 5.22 to 5.28. There was a strong correlation between pH and Cu concentrations, and a good relationship between pH and Zn concentrations. This implies that it may be possible to estimate metal concentrations from pH by using these correlation

equations. However, in order to get precise results, further extensive tests are required.
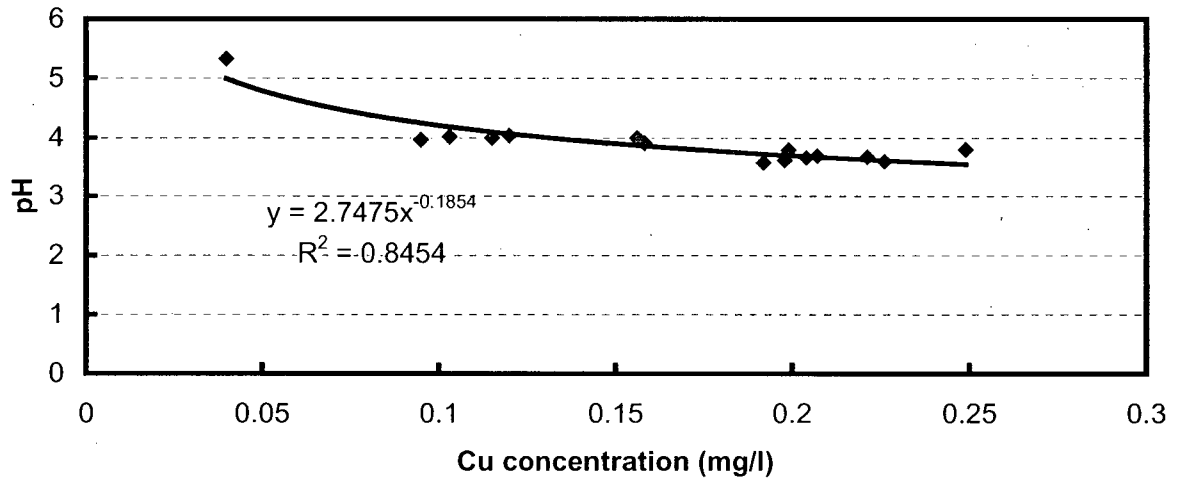
Figure 5.23 pH and Cu Concentration Correlation in ARD Generation Test
of Water Rock Ratio 2:3

In the first chart: $y = 2.7475x^{-0.1854}$, $R^2 = 0.8454$
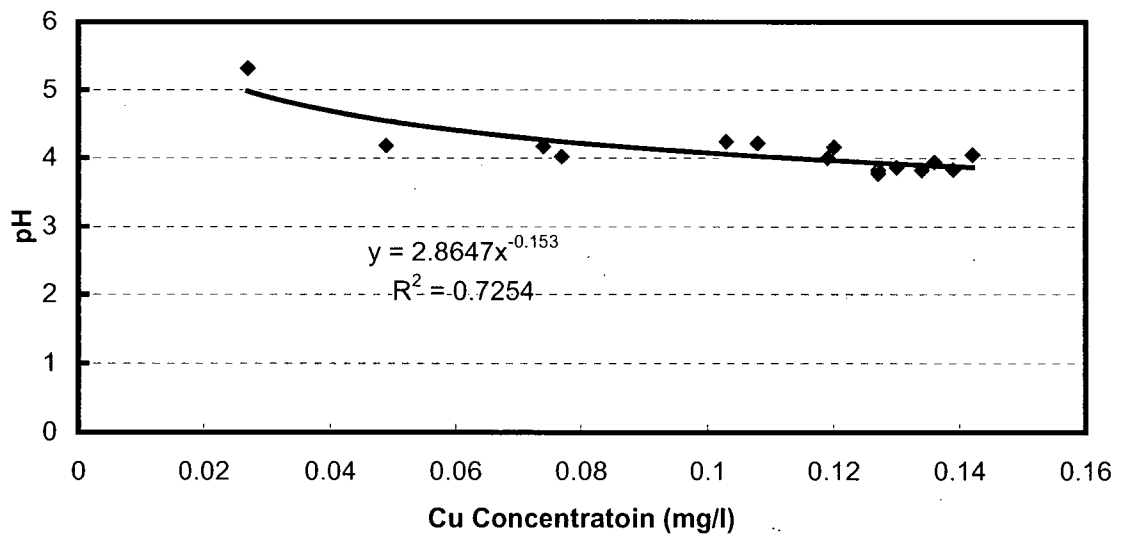
Figure 5.24 pH and Cu Concentration Correlaiton of ARD Generation Test
of Water Rock Ratio of 3:3

In the second chart: $y = 2.8647x^{-0.153}$, $R^2 = 0.7254$
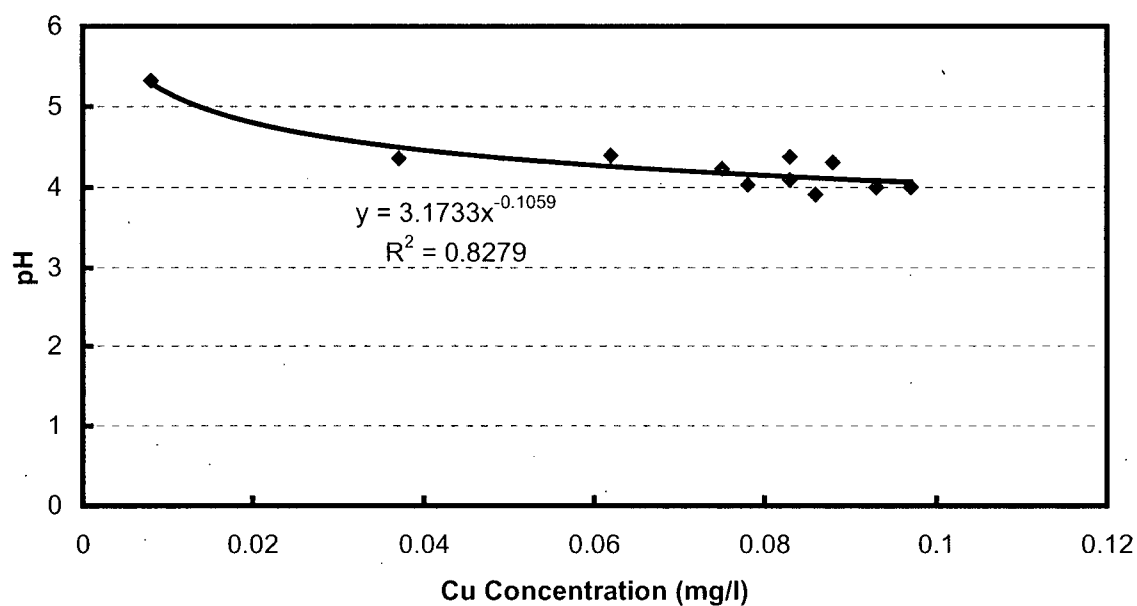
Figure 5.25 pH and Cu Concentration Correlation in ARD Generation
Test of Water Rock Ratio of 5:3
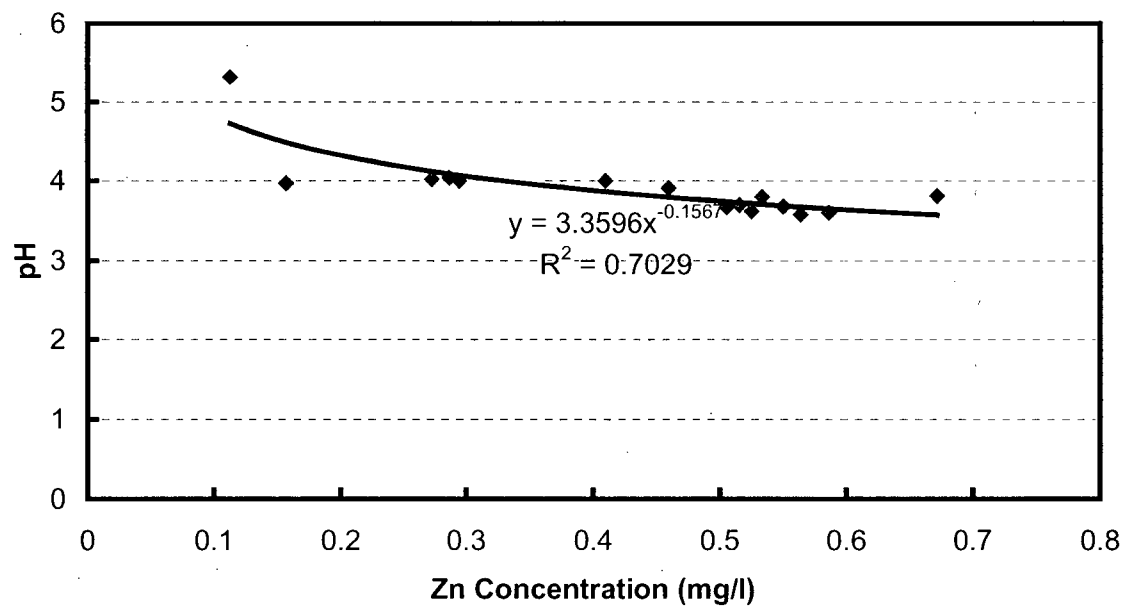
Figure 5.26 pH and Zn Concentration Correlation in ARD Generation
Test of Water Rock Ratio 2:3
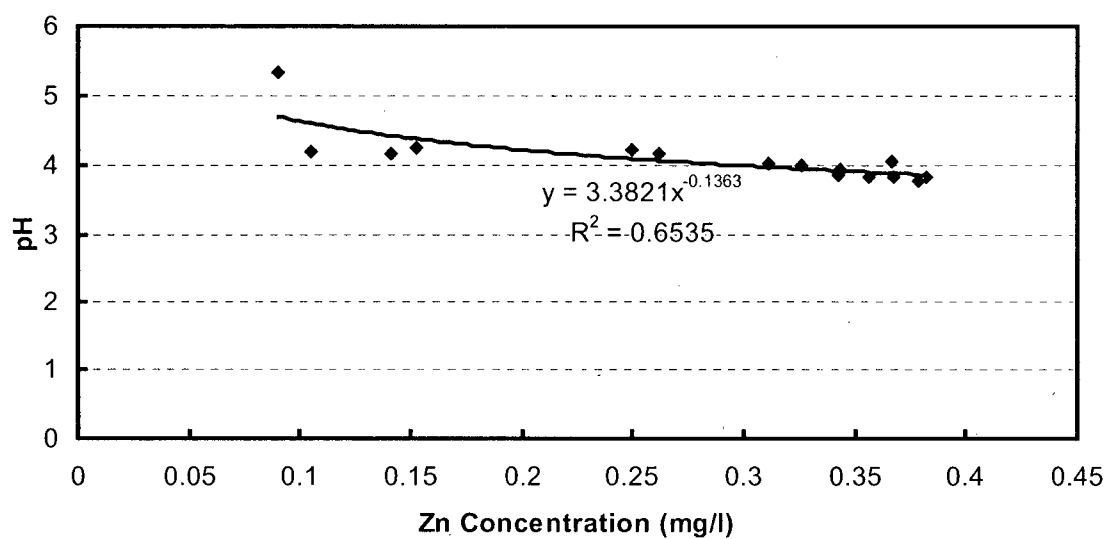
Figure 5.27 pH and Zn Concentration Correlation in ARD Generation Test
of Water Rock Ratio of 3:3
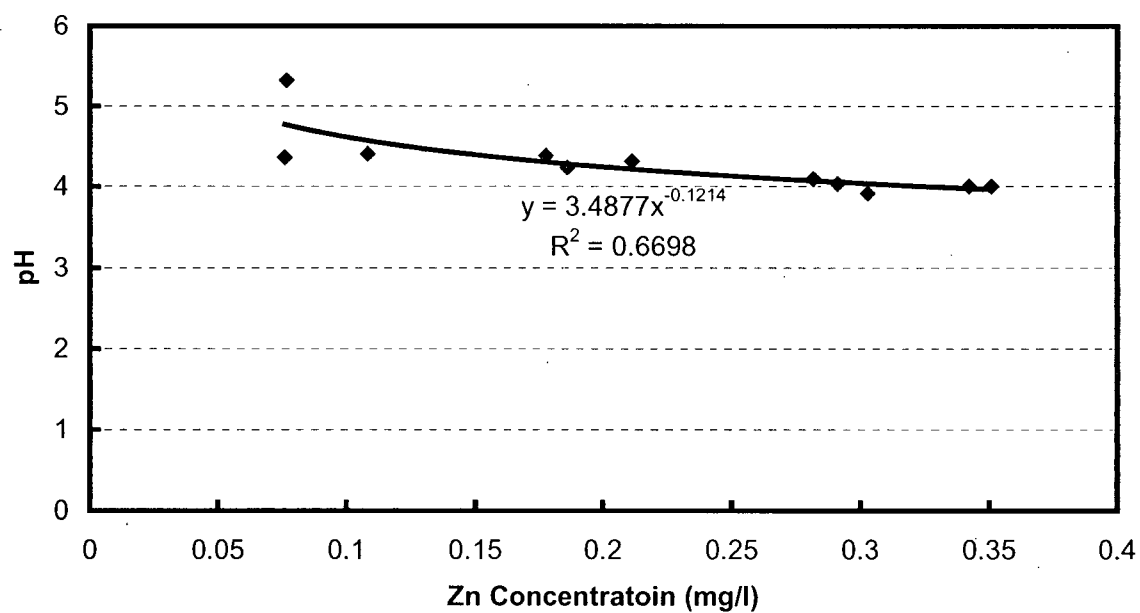
Figure 5.28 pH and Zn Concentration Correlation in ARD Generation Test
of Water Rock Ratio of 5:3

In the ARD generation test, the influence of water to rock ratios on ARD generation was tested. Different ratios led to different test results; hence, the ratio influenced the pH, conductivity, and metal concentration. The higher the ratio, the lower the pH, the higher the conductivity, and the higher the metal concentrations. In other words, the ratio influenced ARD generation processing.

pH and conductivity presented a strong correlation, and the pH and metal concentrations also showed a strong correlation.

Agitation caused an obvious increase of conductivity and metal concentration, and a decrease of pH. This result suggested that agitation accelerated the ARD generation processing.

The pH of this test ranged from 3.5 to 4.0, which was near the pH value measured in the southern ditch of the Pennask Site. The conductivity in this test ranged from 100 to 500 μS/cm, which is smaller than that of the field measurements, which ranged from 670 to 1260 μS/cm (Morin, 2003).

The metal concentrations of Cu ranged from 0.15 to 0.25 mg/l, which is near the measured value in the south ditch of 0.299 mg/l and lower than 1.85 mg/l of the north ditch. However, those values exceeded the Aquatic Life Standards of 0.02-0.09 mg/l. Zn concentration was 0.38 to 0.66 mg/l, which was much smaller than that of 5.86 mg/l in the south ditch and 39 mg/l in the north ditch. Ni concentration was 0.15 to 0.25 mg/l, which was lower than that of the south ditch of 0.89 mg/l and 1.85 mg/l, but exceeded the Aquatic Life Standards of 0.25-1.5 mg/l.

5.2.3 Coating Material Capacity Test

The coating material capacity test was designed to study the material's capacity to exclude the rock samples from the interaction of air and water. In order to approach the goal, the changes of pH, conductivity, and metal concentrations were studied during the test. Three coated rock samples of epoxy-41 (Tripoxy 41, a mixture of Tripoxy I White 150 and Tripoxy I Curing Agent, hereafter simplified as Epoxy-41), epoxy-43 (Tripoxy 43, a mixture of Tripoxy HB White Base and Tripoxy HB Curing Agent, hereafter simplified as Epoxy-43), and acetone-W (Wet Look Lacquer 11-02, hereafter simplified as Acetone-W) were submerged in 1.5 liters distilled water in three cells separately for 88 days. The results are given in Figures 5.29 to 5.44.

The pH change with time is shown in Figure 5.29. There was a rapid decrease in the first seven days, increasing in twenty to thirty days, and then decreasing again gradually. For the decreasing, there are three suggested reasons, 1) a failure or partial failure of the coating layer, 2) a poor performance of the coating layers, and 3) a weight difference of the rock samples.

The difference amongst the three samples became clear after 30 days. The pH of epoxy-41 was the highest with the end value of 4.4, while acetone-W was the lowest of 3.68, which was close to that of the ARD generating test and the value measured at the field. The peak in epoxy-41 occurring at 18 days was considered to be caused by the water lost in an accidental failure of a connector, the distilled water used for refilling having a different pH.

The conductivity change with time is given in Figure 5.30. There was an obvious difference amongst the three samples at the end. Acetone-W was the highest with the final value of 124 µS/cm, which was almost three times higher than that of epoxy-43 of 24.0 µS/cm and epoxy-41 of 32.6 µS/cm. However, it was only one third that of the ARD generating test. The

change patterns of this test corresponded to those of the pH changes.

The conductivity and pH showed a similarly changing pattern, but with reverse values. For example, acetone-W was highest in conductivity, but lowest in pH.
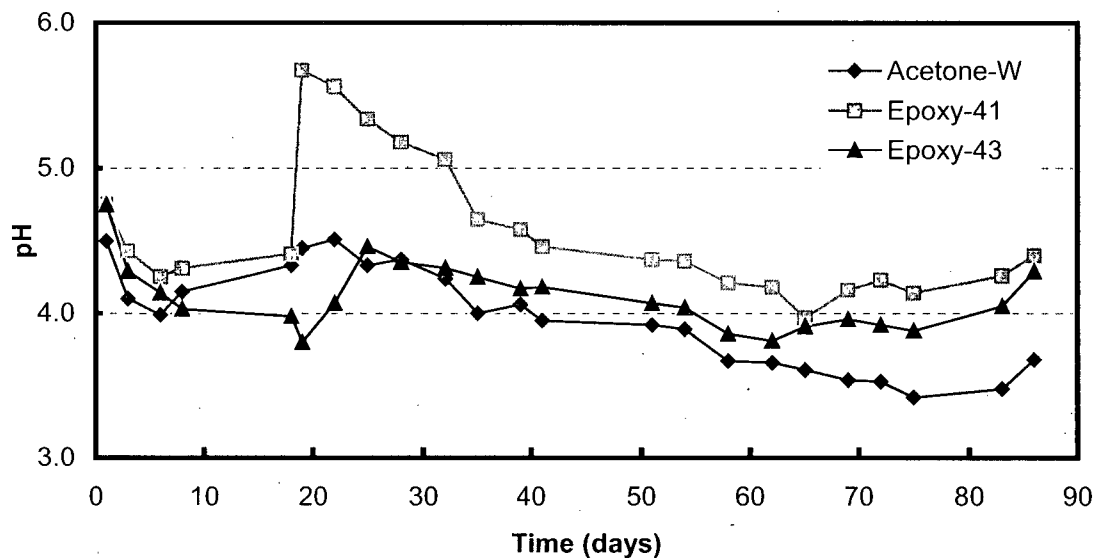
Figure 5.29 pH Chnages vs. Time in Coating Capacity Test
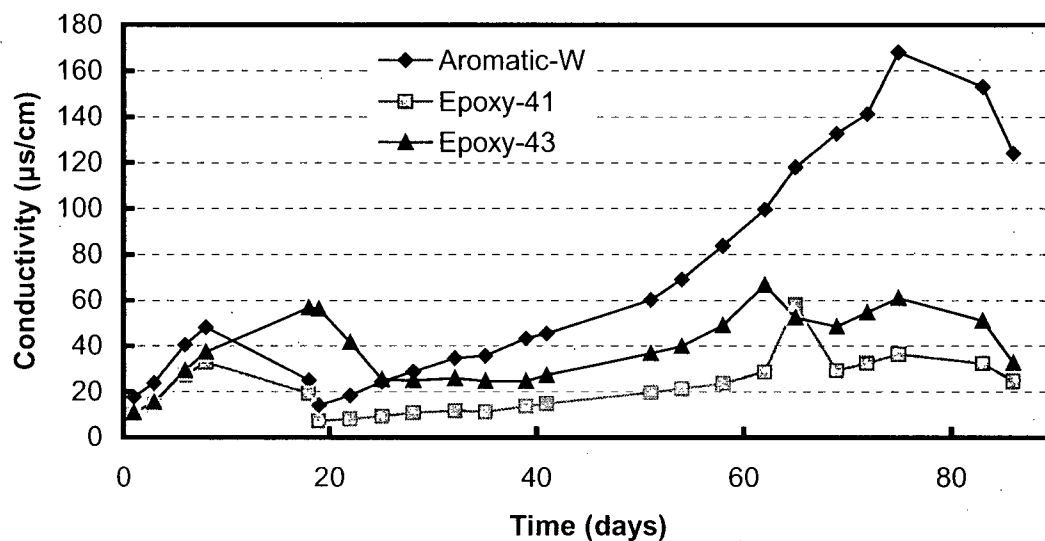
Figure 5.30 Conductivity Changes vs. Time in Coating Capacity Test

The correlation between the pH and conductivity are shown in Figures 5.31 to 5.33. There were strong correlations between pH and conductivity in all three samples. The results were similar to those of the ARD generation test.
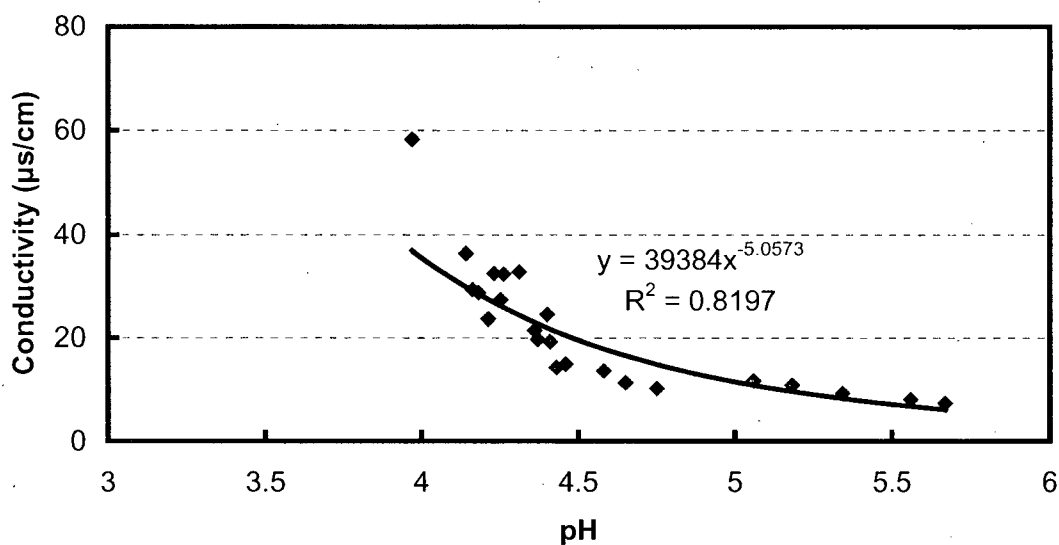
Figue 5.31 pH and Conductivity Correlation of Epoxy 41 in the Coating Capacity Test

The equation shown on the chart is $y = 39384x^{-5.0573}$ with $R^2 = 0.8197$.
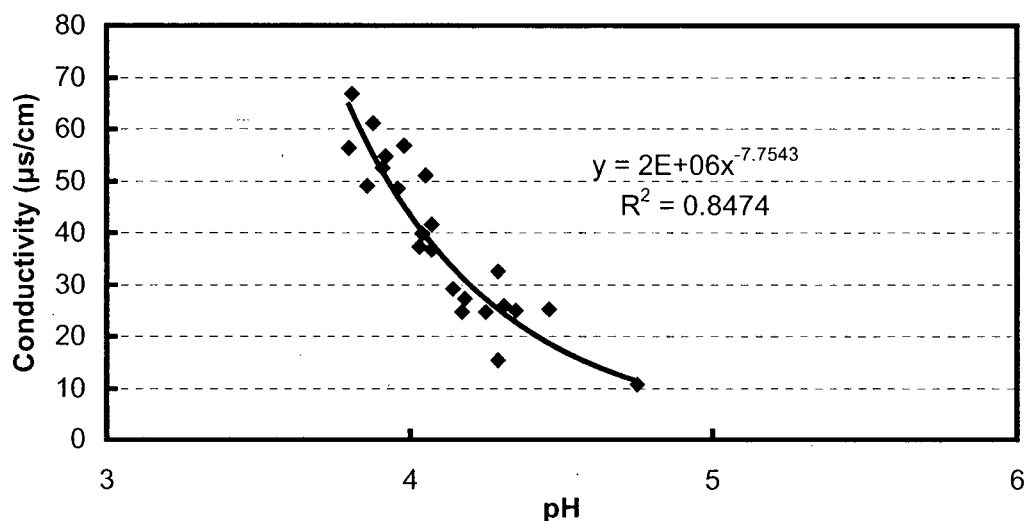
Figure 5.32 pH and Conductivity Correlation of Epoxy-43 in the Coating Capacity Test

The equation shown on the chart is $y = 2E+06x^{-7.7543}$ with $R^2 = 0.8474$.
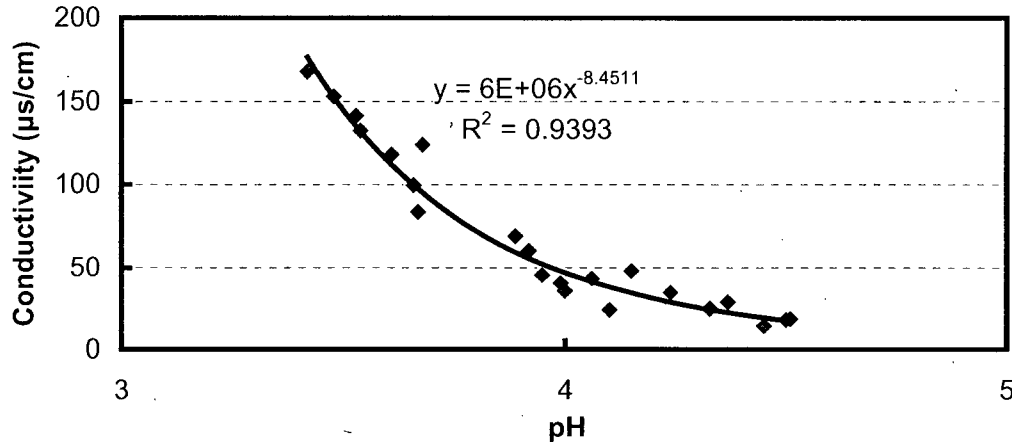
Figure 5.33 pH and Conductivity Correlation of Acetone-W
in the Coating Capacity Test

The metal concentrations changing with time are shown in Figures 5.34 to 5.39. All metal concentrations are increasing with time, except Ni. The remarkable difference between the ARD generation test and the coating capacity test was that the metal concentrations of the ARD generation test increased significantly immediately after filling with water, while those of the coating capacity test remained unchanged for approximately the first 20 to 40 days, then increased slowly, and then increased rapidly after 60 days. This suggests that the coating materials functioned well for the first 60 days, and failed or partially failed thereafter.

The metal concentrations showed different values. Mg was the highest, followed by Na, Zn, Cu, and Fe. For Cu concentration (Figure 5.34), acetone-W gave the highest value, which was almost two times higher than that of epoxy-41 and epoxy-43, and reached 0.23 mg/l, while epoxy-41 and epoxy-43 were 0.11 and 0.13 mg/l, respectively. These values were almost in the same range as those of the ARD generation test.

For Zn concentration (Figure 5.35), epoxy-41 gave the largest value and reached 0.76 mg/l, which was as high as that of the ARD generation test. The values of epoxy-43 were lower

with a maximum value of 0.44 mg/l, and acetone-W had the lowest value of 0.22 mg/l.
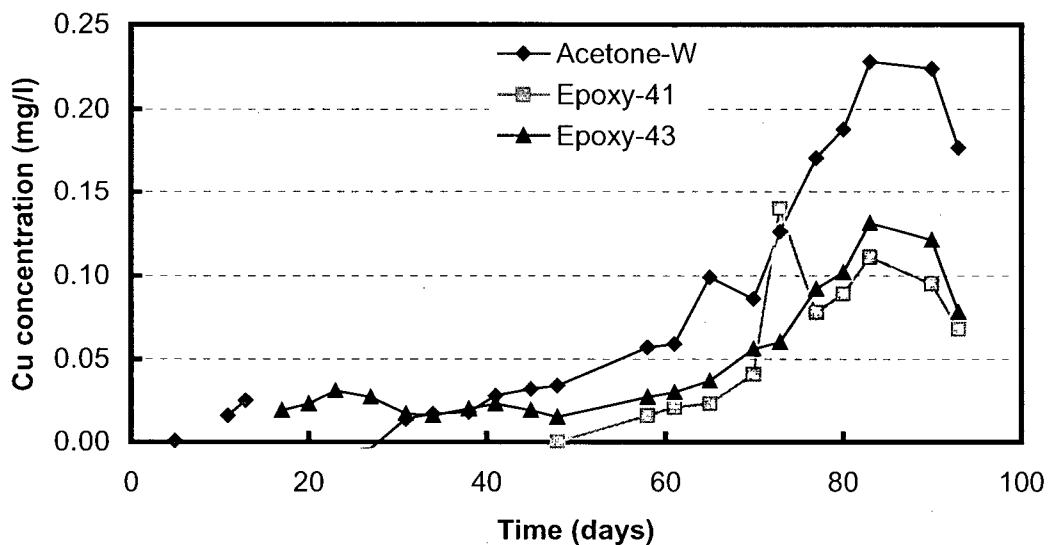
Figure 5.34 Cu Concentration vs. Time in Coating Capacity Test
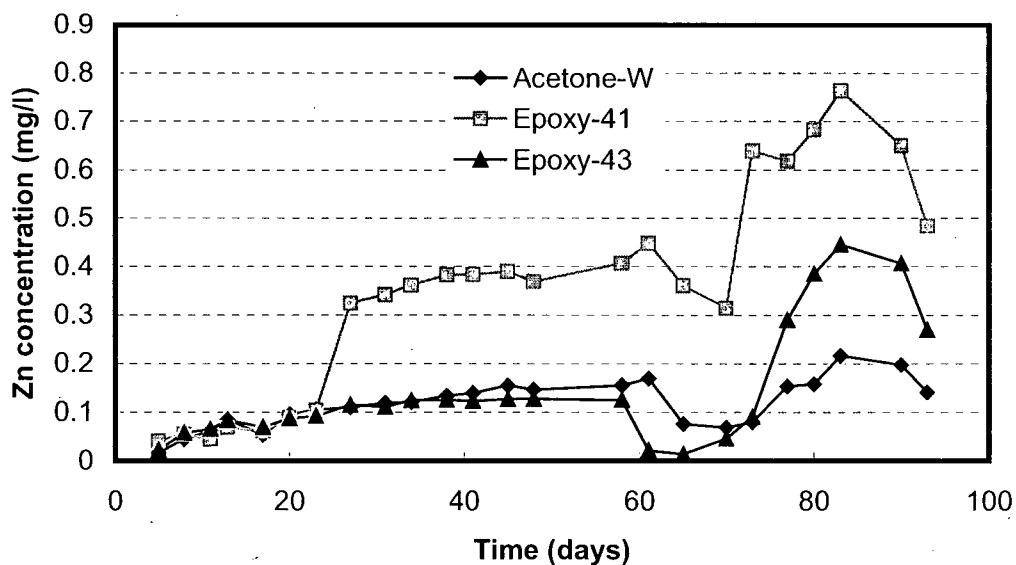
Figure 5.35 Zn Concentration vs Time in Coating Capacity Test

The concentrations of Zn and Cu did not show significant differences from those of the ARD generation test. There are two reasons that can be considered: 1) coating materials were unable to prevent the ARD generation, and 2) the sample might have continually changed during the storage in the refrigerator. The reason for a sudden increase at 23 days is unknown.

For Mg concentration (Figure 5.36), acetone-W showed an obviously greater value during the test period and reached 19 mg/l, while epoxy-41 and epoxy-43 maintained a similar change pattern with much smaller values at 0.2 mg/l. The final value of acetone-W was approximately 8 times higher than those of epoxy-41 and epoxy-43.
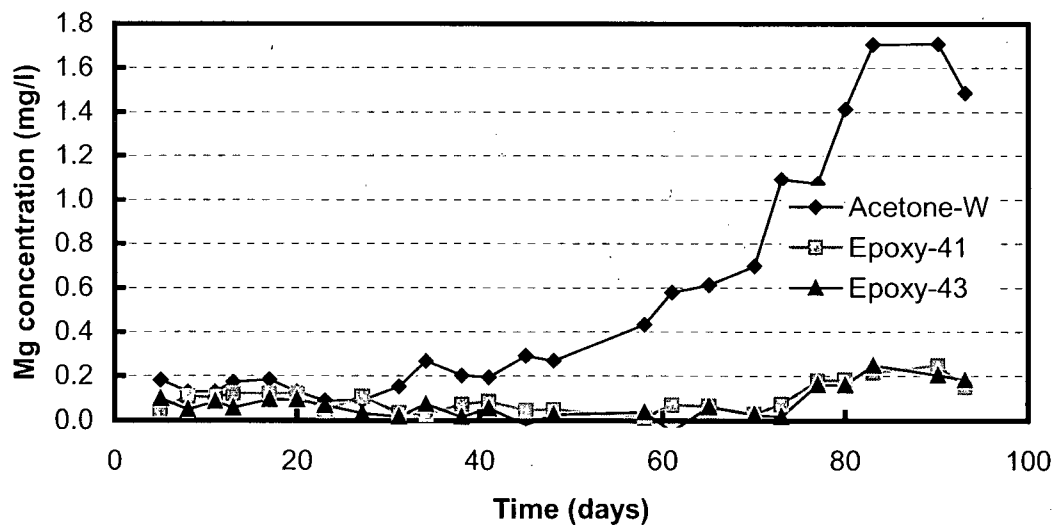
Figure 5.36 Mg Concentration vs. Time in Coating Capacity Test

The Ni concentration (Figure 5.37) changed irregularly for all three samples. This may be explained by that the measured values of concentration were too low, making the experimental noise as the deciding factor.

For Fe concentration (Figure 5.38), acetone-W showed the much higher values, and reached

2.5 mg/l, which was almost 30 times higher than that of epoxy-41 and epoxy-43. Epoxy-41 and epoxy-43 had similar values near 0.10 mg/l, which were similar to that of the ARD generation test. After 30 days, there was a rapid increase of acetone-W, suggesting a failure or partial failure of the coating layer. The reason for the sudden decrease of acetone-W at 78 days was unknown, probably caused by the water sample inside the test tube was too low so that the probe could not absorb the sample.
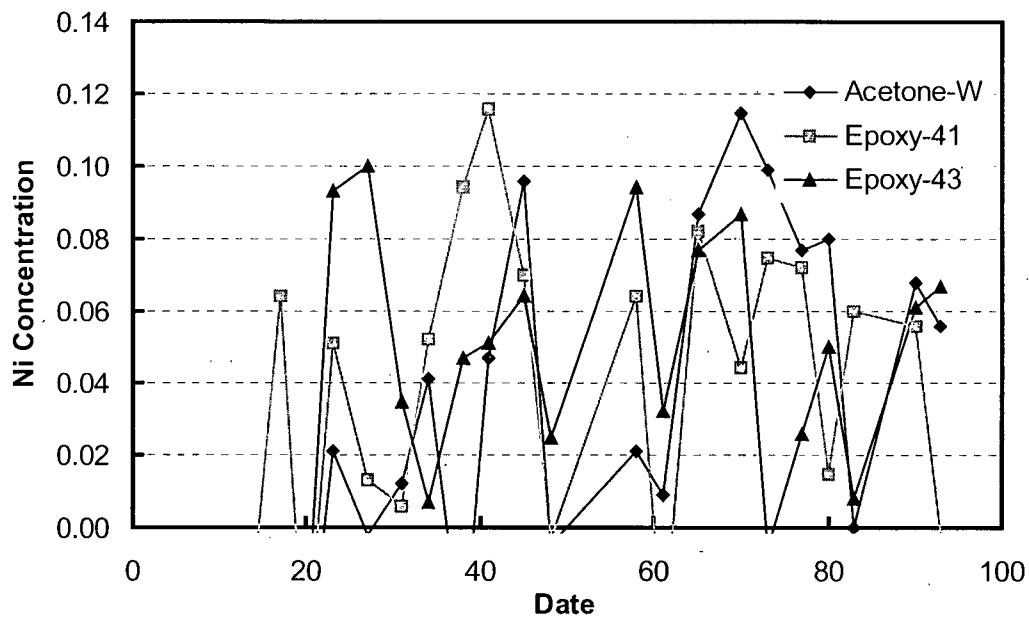
Figure 5.37 Ni Concentration vs. Time in Coating Capacity Test

For Na concentration (Figure 5.39), acetone-W was almost constant during the test period, and reached 1.5 mg/l, which was one third of that of the ARD generation test, while epoxy-41 presented a significant increase after 30 days, and epoxy-43 increased dramatically after 65 days to 1.3 mg/l.
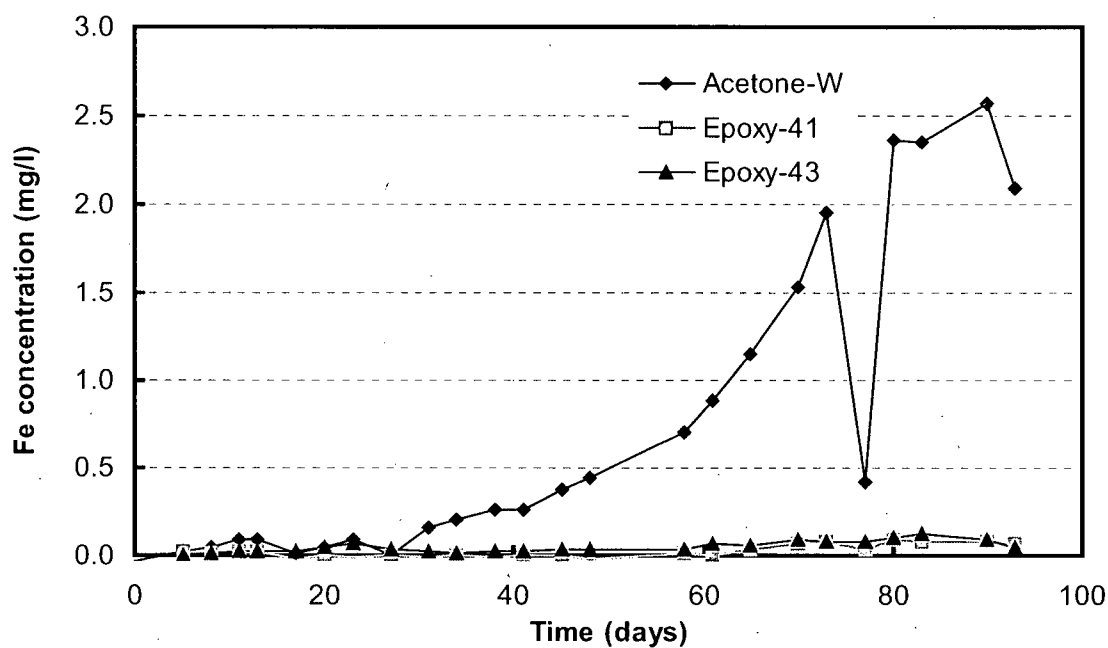
Figure 5.38 Fe Concentration vs. Time in Coating Capacity Test
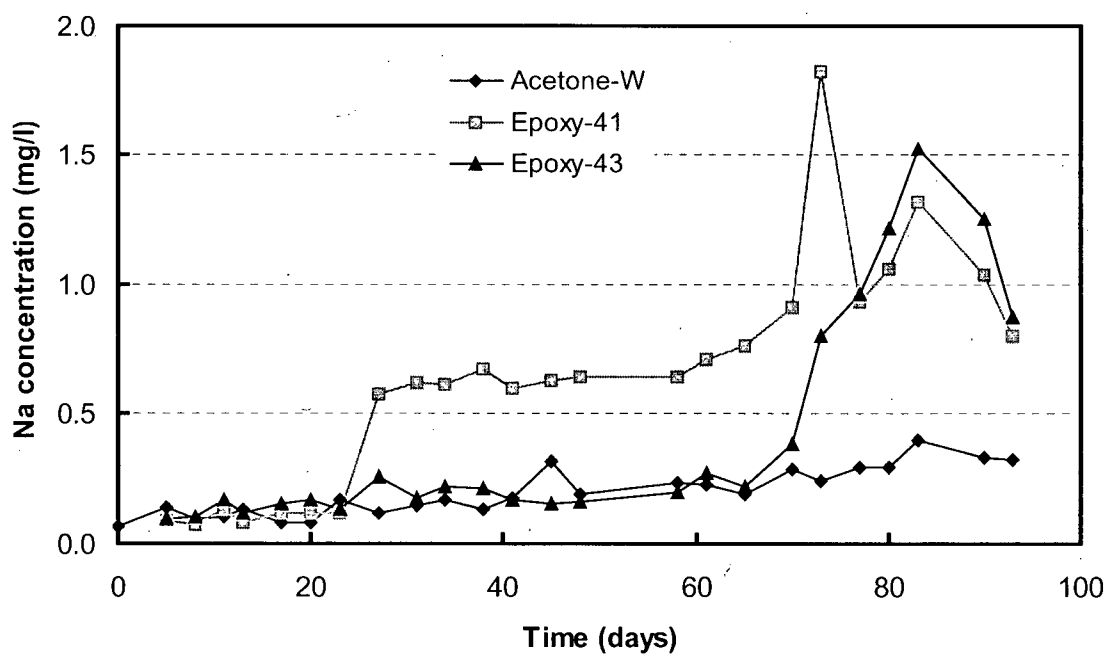
Figure 5.39 Na Concentration vs. Time in Coating Capacity Test

The correlation between pH and Cu concentrations from all samples is given in Figures 5.40 to 5.42. There was no strong correlation as found for the ARD generation test.
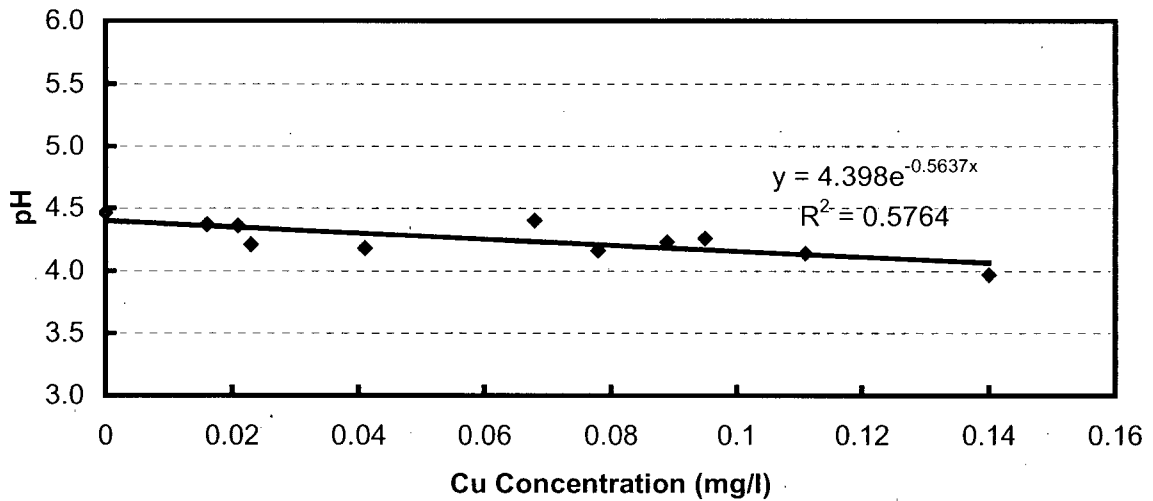
Figure 5.40 pH and Cu Concentration Correlation of epoxy-41 in Coating Capacity Test
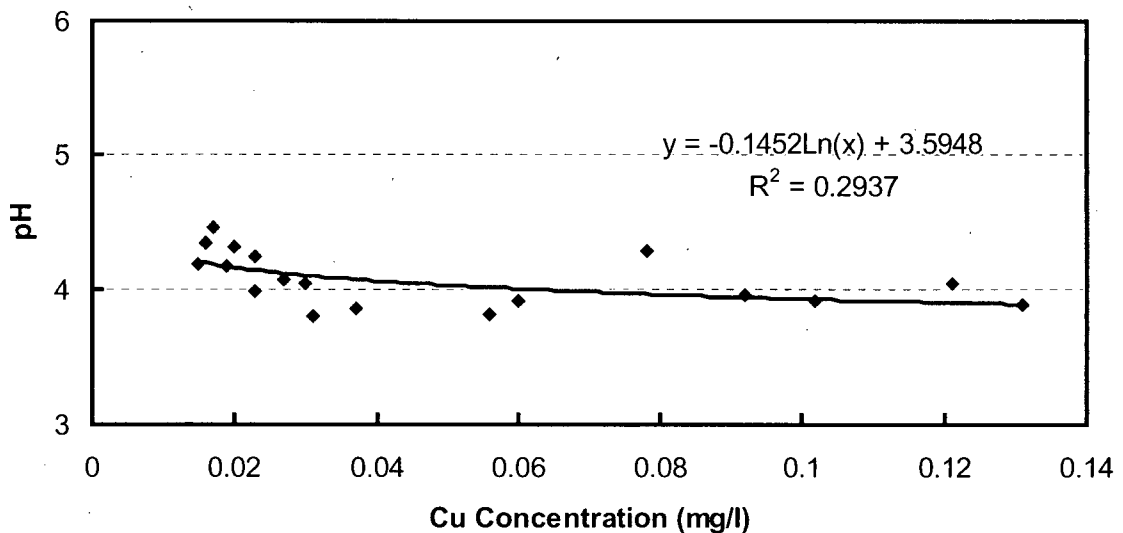
Figure 5.41 pH and Cu Concentration Correlaiton of epoxy-43 in Coating Capacity Test
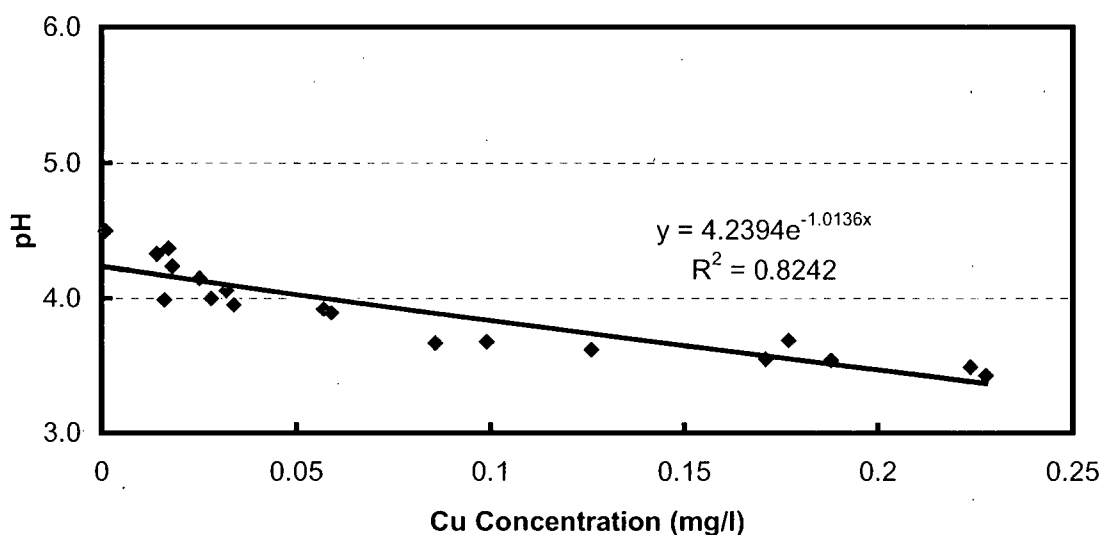
Figure 5. 42 pH and Cu Concentration Correlation of Acetone-W in Coating Capacity Test

In the coating capacity test, the changes in pH and conductivity with time showed a gradually increasing and decreasing trend without sudden changes, which were different from those of the ARD generation test. This indicated that the coating layer functioned as a barrier to prevent ARD generation. In another aspect, the pH of the test ranged from 3.5 to 4.5, which was almost the same as that of the ARD generation test, and also near field measurement. This implied that the ARD generation can be simple represented by pH decrease, and to clarify the correlation between them requires further study. The conductivity of the test was around 160 μS/cm, which was much lower than that of the field measurement of 670 to 1260 μS/cm (Morin, 2003).

The increasing patterns of metal concentrations were different from those of the ARD generation test. The fast increase began only after approximately 20 to 40 days in the coating capacity test, which is what happened in the ARD generation test immediately after it began. There was no significant difference in values of Cu and Zn concentrations between these two

sets of tests after approximately 90 days, and both exceeded the Aquatic Life Standards.

The metal concentration of Cu was 0.15 to 0.25 mg/l, which is near the measured value in the north ditch of 1.85 mg/l and lower than 0.299 mg/l of the south ditch. This exceeded the Aquatic Life Standards of 0.02-0.09 mg/l. Zn concentration was 0.38 to 0.66 mg/l, which was much lower than that of 5.86 mg/l in the south ditch and 39 mg/l of the north ditch. Ni concentration was 0.15 to 0.25 mg/l, which was lower than that of the south ditch of 0.89 mg/l and 1.85 mg/l, but exceeded the Aquatic Life Standards of 0.25-1.5 mg/l.

5.2.4   Freezing and Thawing Test

Four coated rock samples with four coating materials were frozen and thawed for twelve cycles. There was no obvious observable change on the coating layer surfaces of epoxy-41 epoxy-43, and acetone-W during and after the freezing and thawing cycles. There were some small white bubbles up to 0.2 mm in diameter, which appeared on an edge of the coating surface of acetone-W after the second cycle, and the bubbles remained until the end of the cycle, finally disappearing after one month of exposure to the air at room temperature. The mechanism of this phenomenon is unknown.

After freezing and thawing cycles, four large and four small coated rock samples were placed in four cells separately and submerged in distilled water for the material capacity test. In each cell, there were two samples coated with same material, in which one big and one small. The test lasted for ninety days and results are shown in Figures 5.43 to 5.62.

The pH values (Figure 5.43) presented a different changing pattern from these of the ARD generation test and the coating capacity test. The pH of epoxy-41 and silicone-S were decreased for the first 20 days and became roughly constant thereafter at 4.0 and 3.8 respectively. The pH of acetone-W increased on the first day, with no changes thereafter with

values of about 5.5. The pH of epoxy 43 increased in first day, and decreased to 4.8 after. Silicone-S had the lowest value of about 3.82, which was near to that of the ARD generating test, while epoxy-43 had values (above 5.5) even higher than that of distilled water of 5.16. It can be inferred that there are chemical reactions happening between the coating materials and the water.
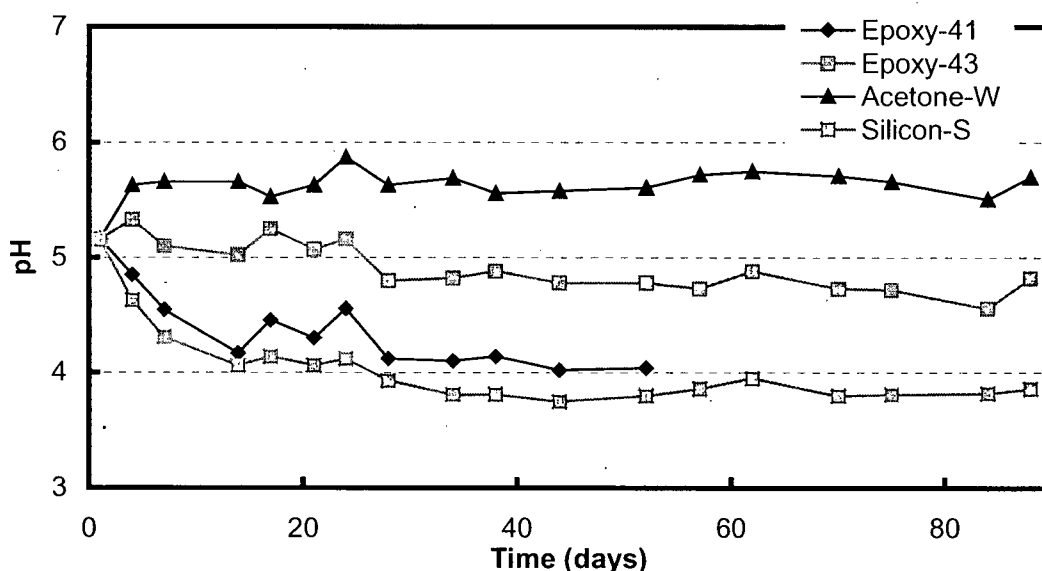
Figure 5. 43 pH Changes vs. Time in Freezing and Thawing Test

The conductivity change with time is shown in Figure 5.44. The conductivity of Silicone-S increased rapidly from the beginning and presented a significantly greater value than that of the others, reached 197 µS/cm. The value was not as high as that of the ARD generation test, but slightly higher than that of the coating capacity test. The others had almost the same value to that of the distilled water of 10- 27 µS/cm.
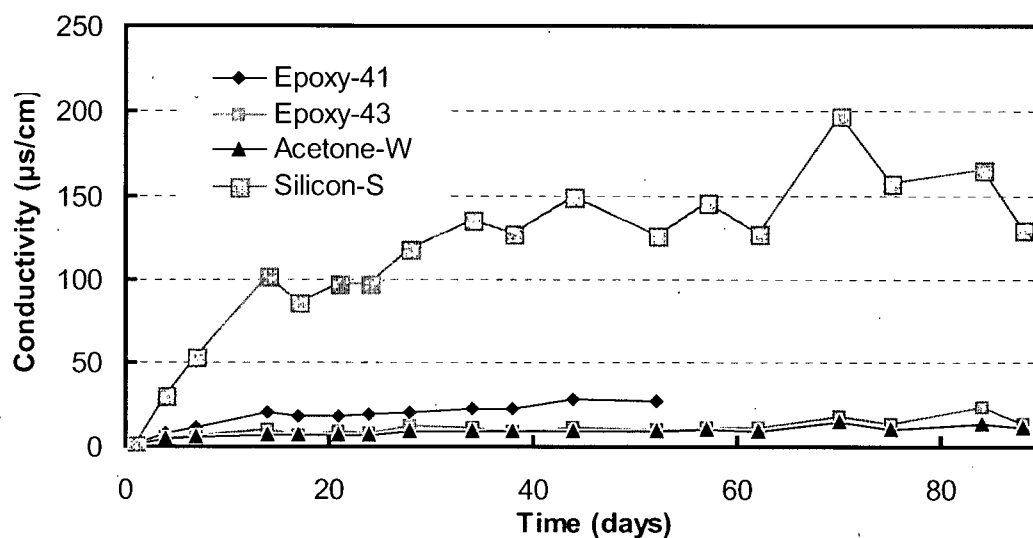
Figure 5.44 Conductivity vs. Time in Freezing and Thawing Test

Figure 5.45 to Figure 5.48 showed a strong correlation between conductivity and pH of all three samples, as that of the ARD generation test and the coating capacity test.

$$y = 1E+07x^{-9.1051}$$
$$R^2 = 0.8144$$
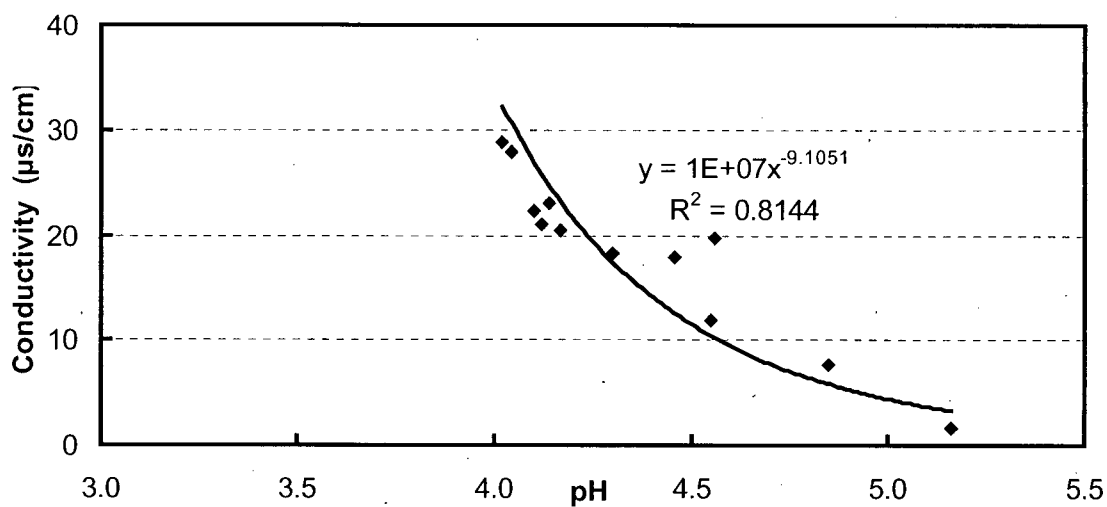
Figure 5.45 pH and Conductivity Correlation of Epoxy-41 in the Freezing and Thawing Test

$$y = -96.347\,\mathrm{Ln}(x) + 164.36$$
$$R^2 = 0.7134$$
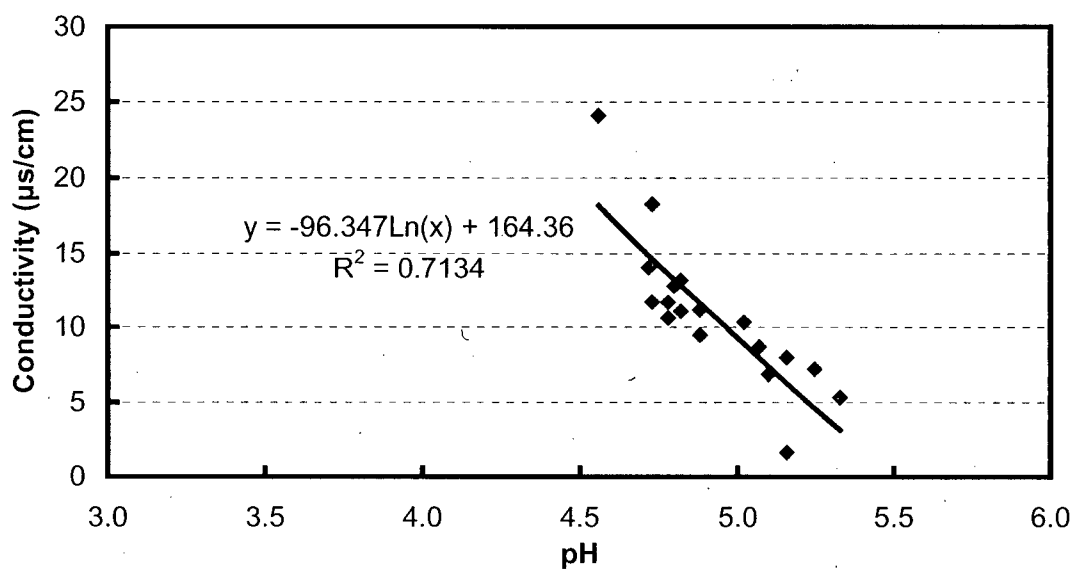
Fiigure 5.46 pH and Conductivity Correlation of Tropoxy-43 in the
Freezing and Thawing Test

$$y = 7\mathrm{E}\text{-}09x^{12.032}$$
$$R^2 = 0.4247$$
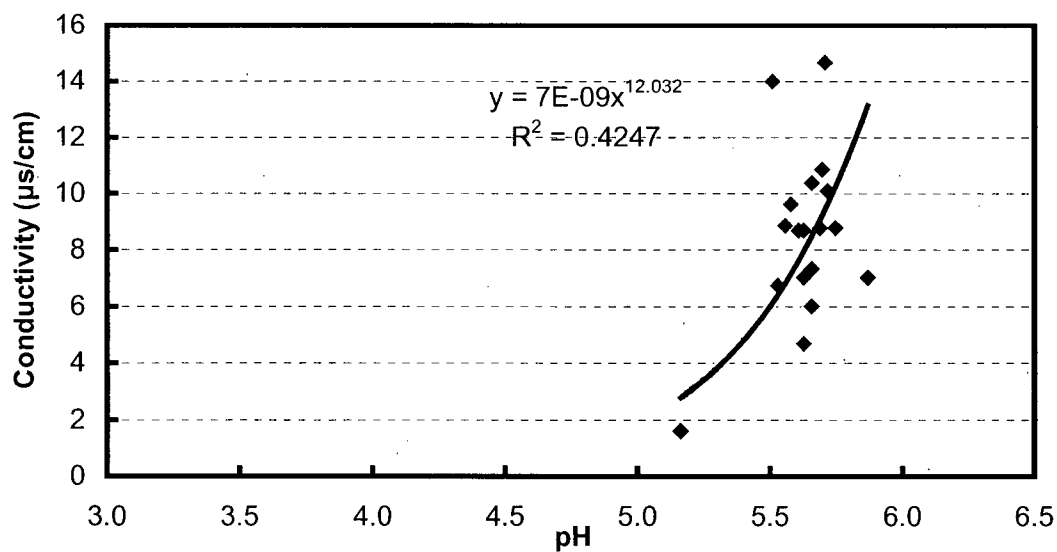
Figure 5.47 pH and Conductivity Correlation of Acetone-W in the
Freezing and Thawing Test
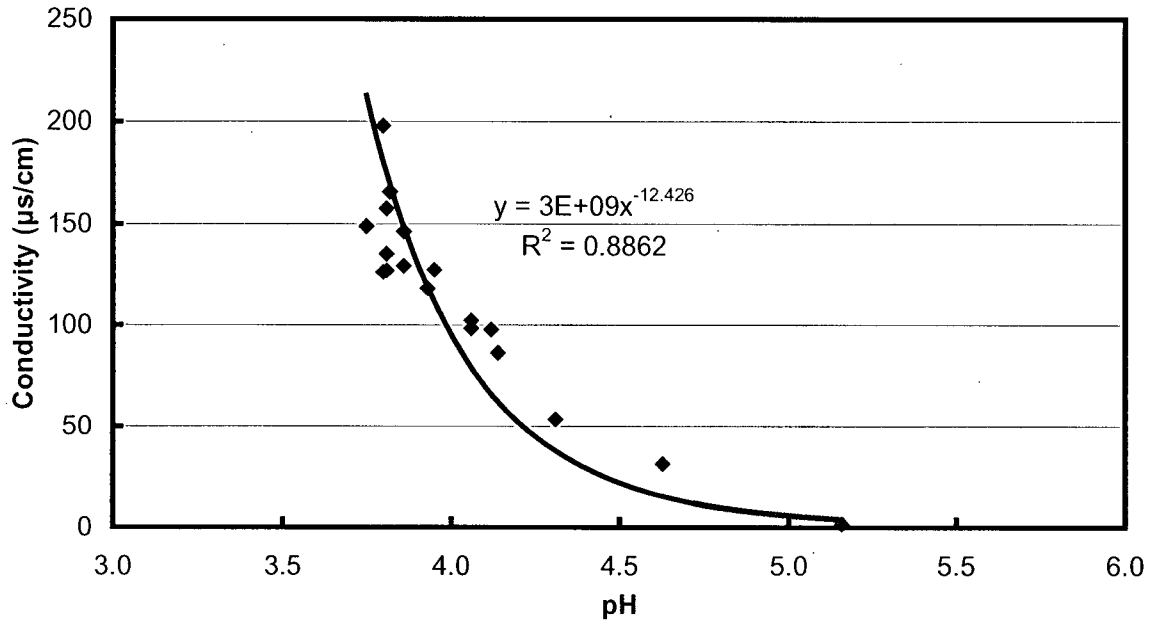
Figure 5.48 pH and Conductivity Correlation of Silicone-S in the Freezing
and Thawing Test

Metal concentration changes with time are given in Figures 5.49 to 5.53. The most remarkable difference between the freezing and thawing test and previous tests was that all metal concentrations of Silicone-S were approximately 5 to 20 times higher than that of the other three. Compared to this, the difference among epoxy-41, epoxy-43 and acetone-W was almost negligible.

The other difference was that metal concentrations ranked as Mg, Cu, Fe, Zn and Ni. The Cu concentration (Figure 5.49) was much higher than that of previous tests, and the value approached 1.0 mg/l in Silicone-S, even higher than that of the field measurement. It is suggested that the water samples might be contaminated. The Zn concentration (Figure 5.50) was much lower than that of previous tests with the value only one third of that of the ARD generation test and the capacity test, and ranged from 0.02 to 0.23 mg/l. the Ni concentration (Figure 5.51) showed the highest value in Silicone-S, but was smaller than that of previous tests lower than 0.05 mg/l. the Fe concentration (Figure 5.53) in Silicone-S ended with a

sudden decreasing trend, which was probably the influence of outside factors, such as water level, sampling time, etc.
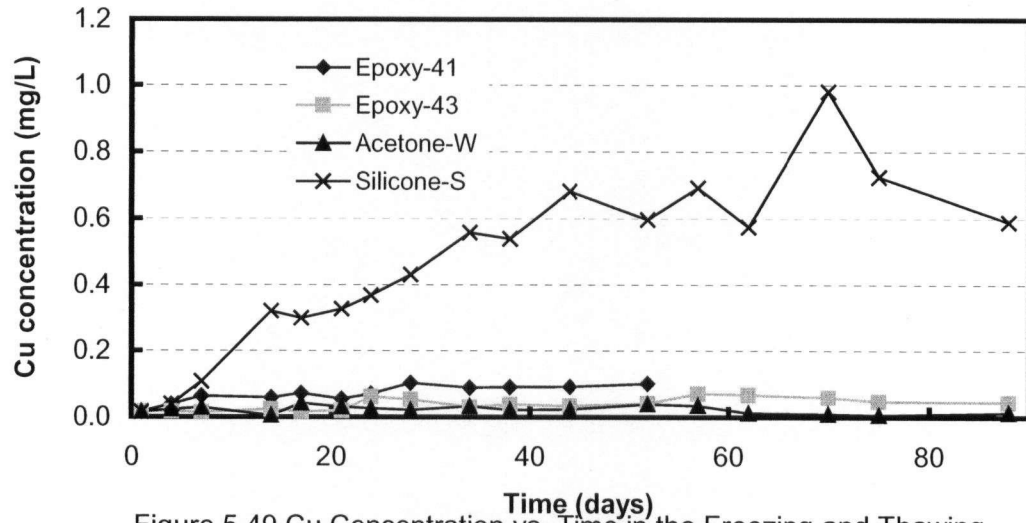
Figure 5.49 Cu Concentration vs. Time in the Freezing and Thawing Test
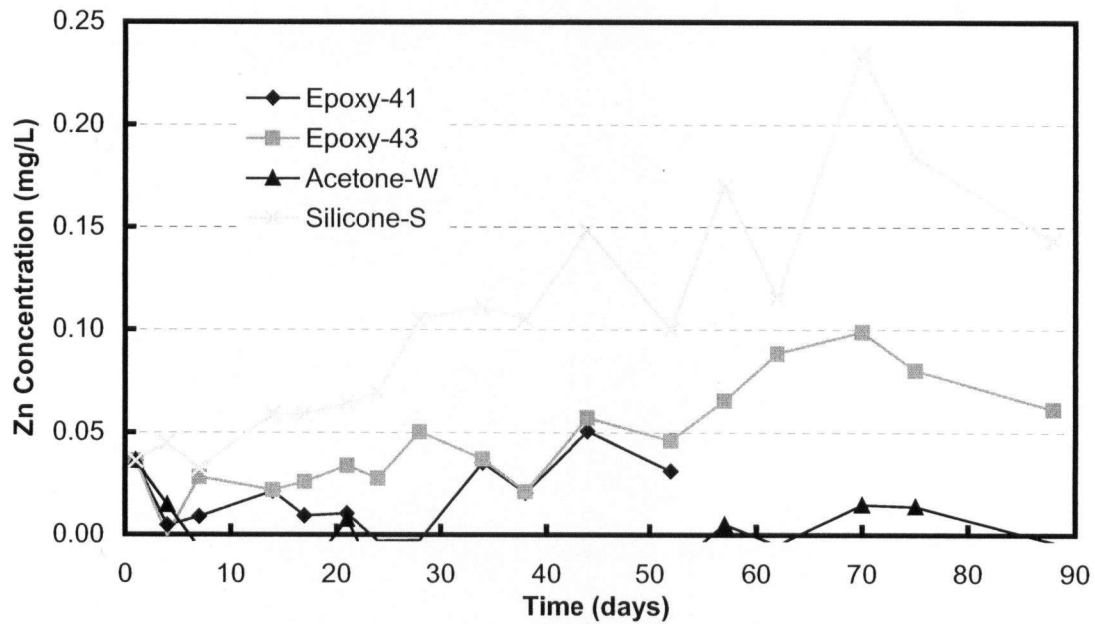
Figure 5.50 Zn Concentration Changes vs. Time in the Freezing and Thawing Test
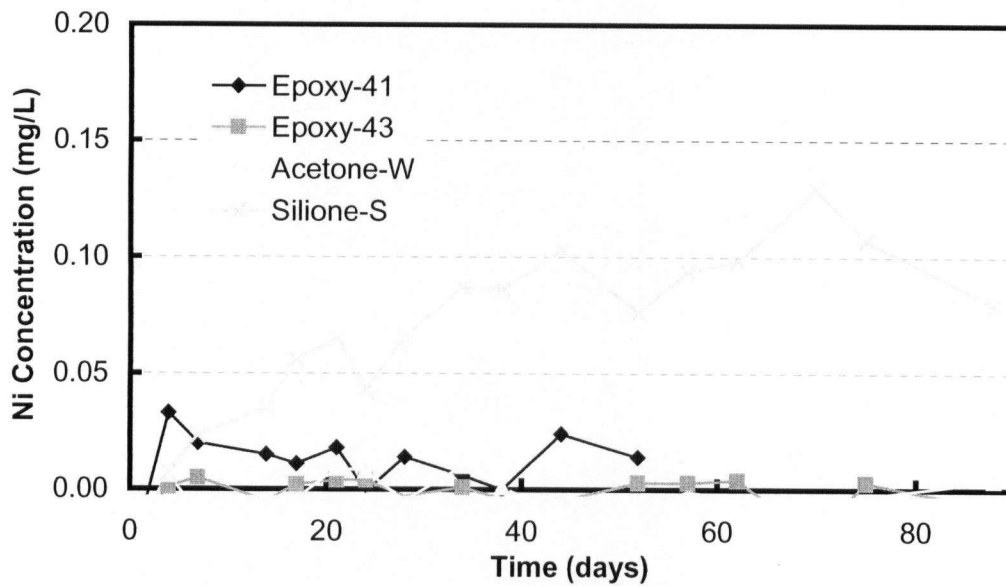
Figure 5.51 Ni Concentration Changes vs. Time in the Freezing and Thawing Test
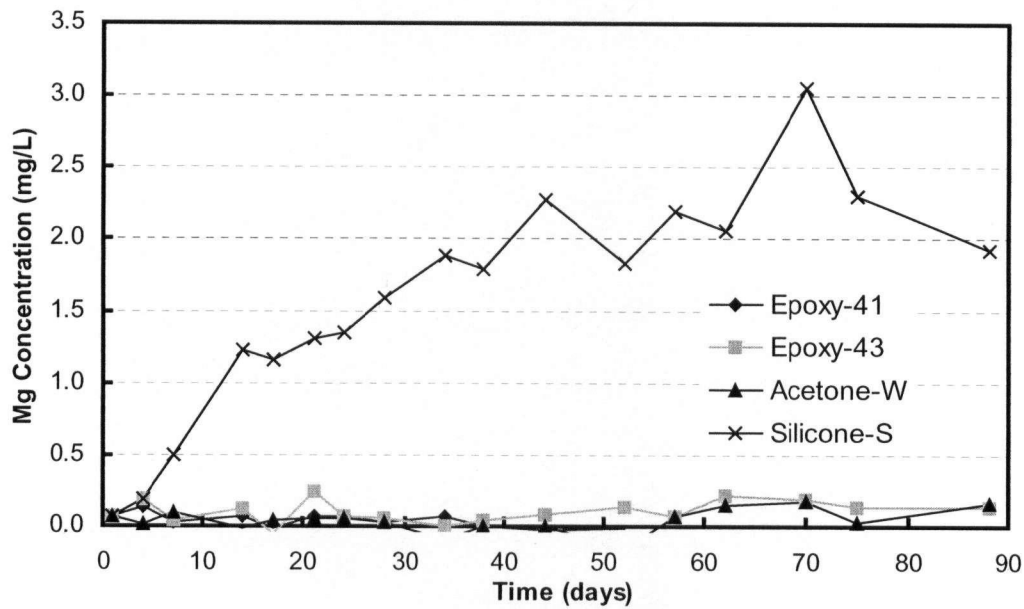
Figure 5.52 Mg Concentration Changes vs. Time in the Freezing and Thawing Test
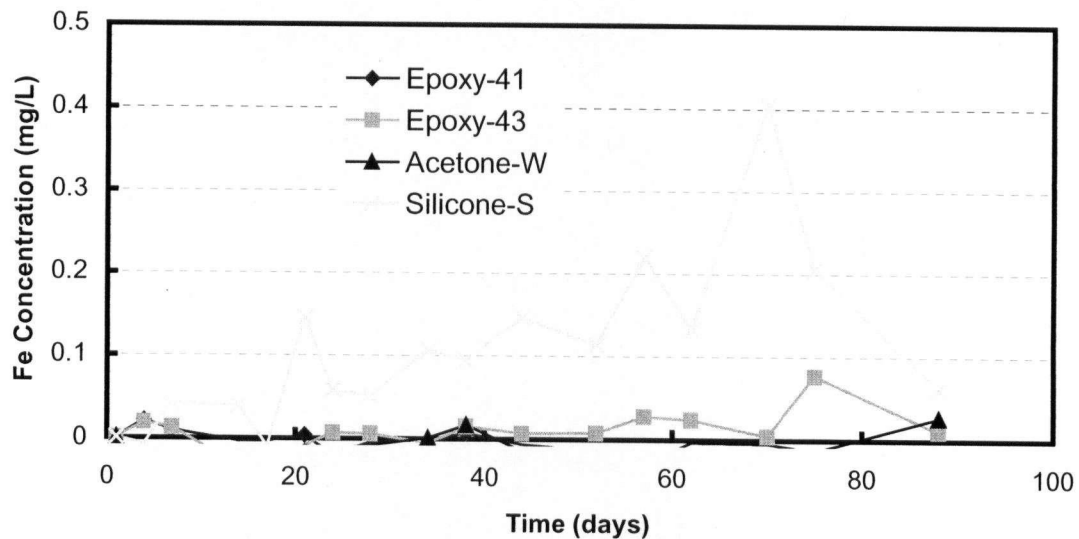
Figure 4.53 Fe Concentration Changes vs. Time in the Freezing and Thawing Test

In general, the result of the freezing and thawing test showed relatively low concentration of primary environmentally concerned metals, Zn, Cu and Ni. Freezing and thawing cycles did not obviously influence the material's capacity of excluding rocks from water.

The pH value of epoxy-41 and silicone-S decreased, approaching the field measurements of 3.8, while the values found for acetone-W and epoxy-43 were much higher. It requires further test to determine the reason of the pH increase. The conductivity of Silicone-S was much higher that these of the rest three samples, but not as high as that of the field measurement.

The Cu concentration of silicone-S approached 1.0 mg/l, which was even higher than that of the field measurement, and greatly exceeded the Aquatic Life Standards of 0.02-0.09 mg/l. To ensure whether it is caused by ARD generation requires further study. Zn and Ni concentrations were lower than the Aquatic Life Standards.

The correlation of pH and Cu concentration is shown in Figures 5.54 to 5.57. Unlike previous tests, only Silicone-S had a strong correlation.
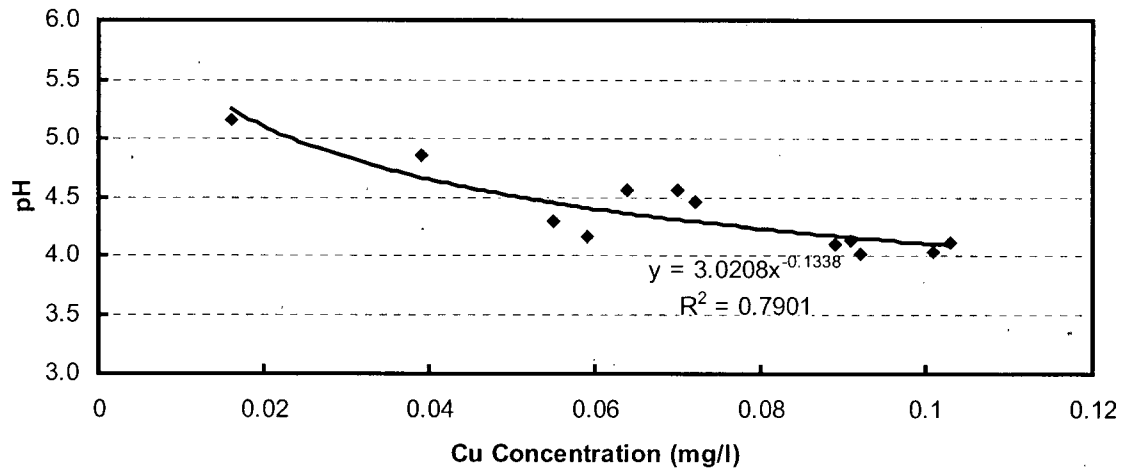
Figure 5.54 pH and Cu Concentration Correlation of Epoxy-41 in Freezing and Thawing Test

$$y = 3.0208x^{-0.1338}$$
$$R^2 = 0.7901$$
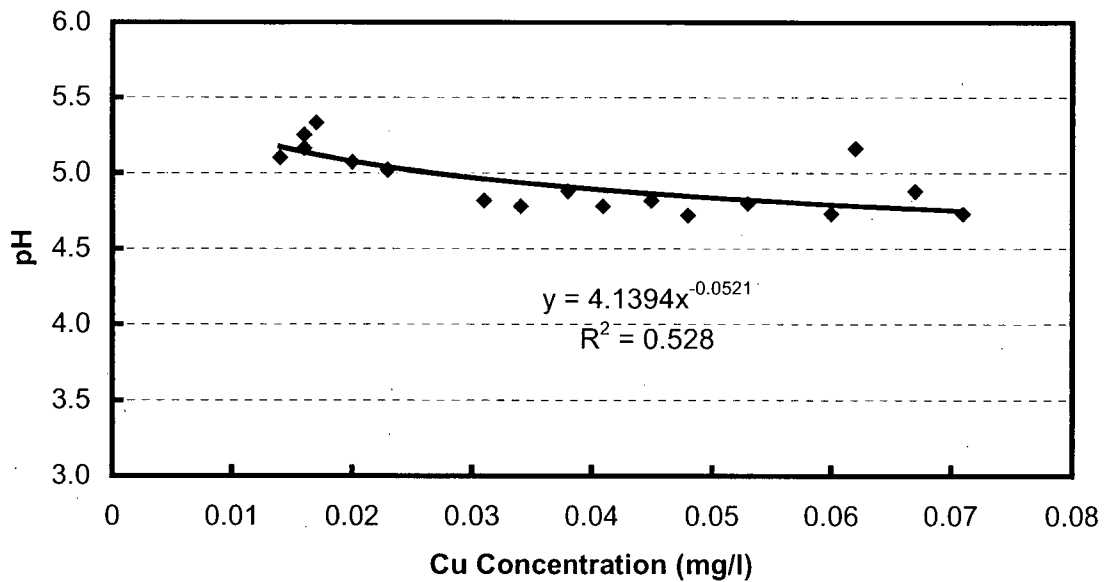
Figure 5.55 pH and Cu Concentration Correlation of Epoxy-43 in Freezing and Thawing Test

$$y = 4.1394x^{-0.0521}$$
$$R^2 = 0.528$$
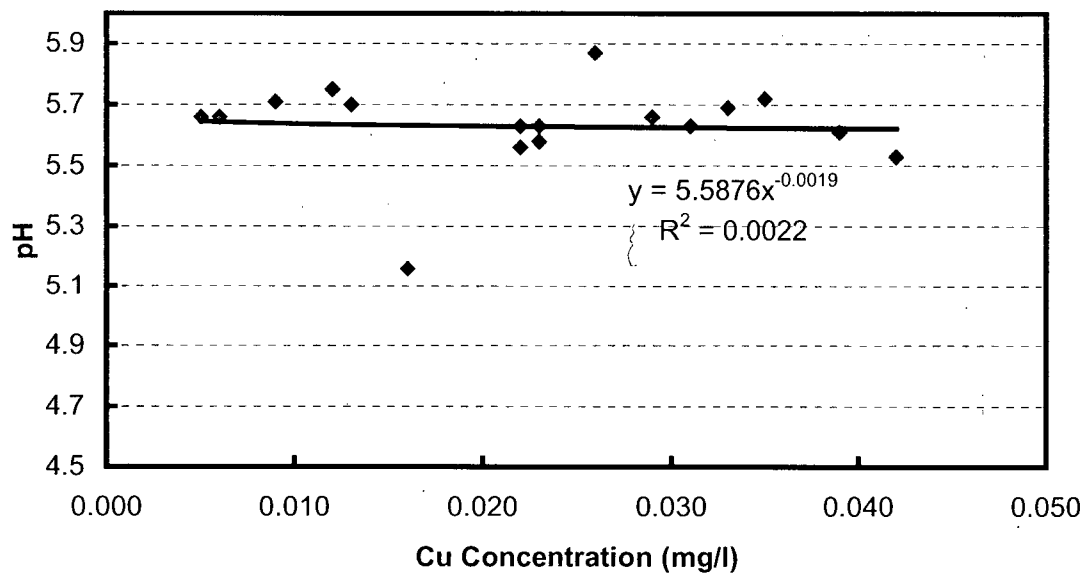
Figure 5.56 pH and Cu Concentration Correlation of Acetone-W in
Freezing and Thawing Test
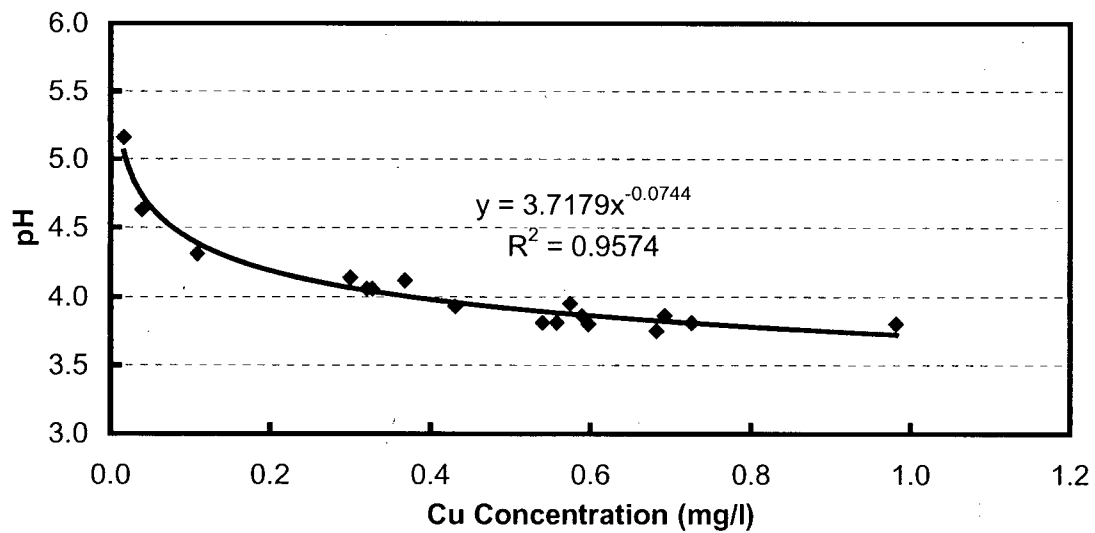
Figure 5.57 pH and Cu Concentration Correlation of Silicone-S in
Freezing and Thawing Test

5.2.5 Heating and Cooling Test

The heating and cooling cycle was repeated 12 times, and each cycle lasted approximately 24 hours. There were no obvious visible changes of the coating surfaces either during or after heating and cooling procedures for any of the coatings.

After the heating and cooling test, samples were air-dried for one month, then set into cells and submerged in distilled water for the coating material capacity test. The test results are shown in Figures 5.58 to 5.63.

The pH changes with time show a different pattern from previous tests. The pH of epoxy-43 increased in the beginning, and then decreased after 30 days. The pH of epoxy-41 continually increased. The pH of Silicone-S decreased sharply during the first 10 days, then increased between 20-50 days and then decreased again. The pH of all samples was no lower than 4.0, which was higher than that of the ARD generation test, coating materials capacity test, and freezing and thawing test. The reason why pH values of epoxy-41 and silicone-S increased is not clearly understood. There are two assumptions: 1) there was a possible chemical reaction happening between the coating layer and water, and 2) there were outside materials, such as dust from other tests in the lab falling into the test cells and reacting with water in the cells.

The conductivity changing with time is shown in Figure 5.59. The conductivity of Silicone-S was much higher than that of the others, which was similar to that of the freezing and thawing test. However, the values were lower than that of the freezing and thawing test and higher than that of the coating capacity test, but only one sixth of that of the field measurement.

The pH and conductivity correlation was not high, except for acetone-W. Therefore, the

results were withdrawn from the discussion.
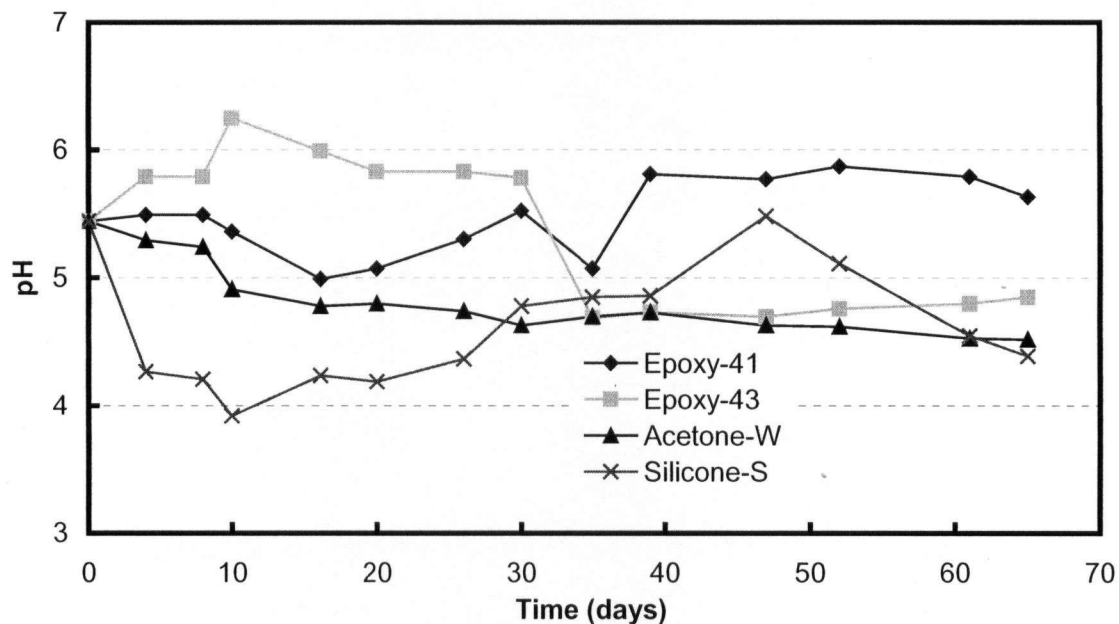
Figure 5.58 pH Changes vs. Time in Heating and Cooling Test
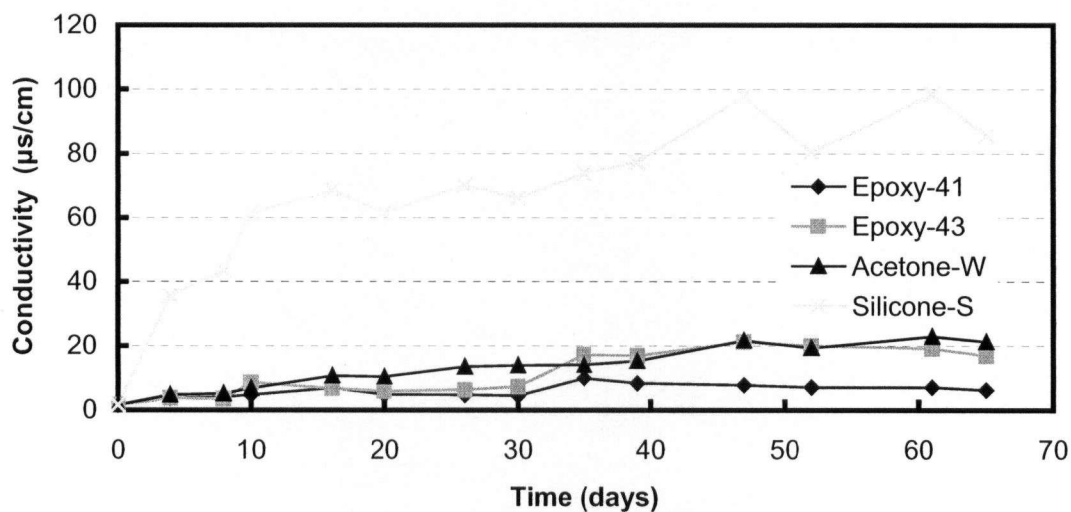
Figure 5.59 Conductivity vs. Time in Heating and Cooling Test

The test results of metal concentrations are given in Figures 5.59 to 5.62. Similar to that of test F, Silicone-S had a much higher value than the others for all metals expect Cu, and the

rapid increase in concentration started from the very beginning. The order of the value of the metal concentration was Mg > Zn > Fe > Cu.

The Cu concentration changes with time (Figure 5.60) had an extremely low value (lower than 0.12mg/l) compared to previous tests, and the values in all four samples had no significant difference. The analysis was repeated, but the results were similar. The reason was unclear.
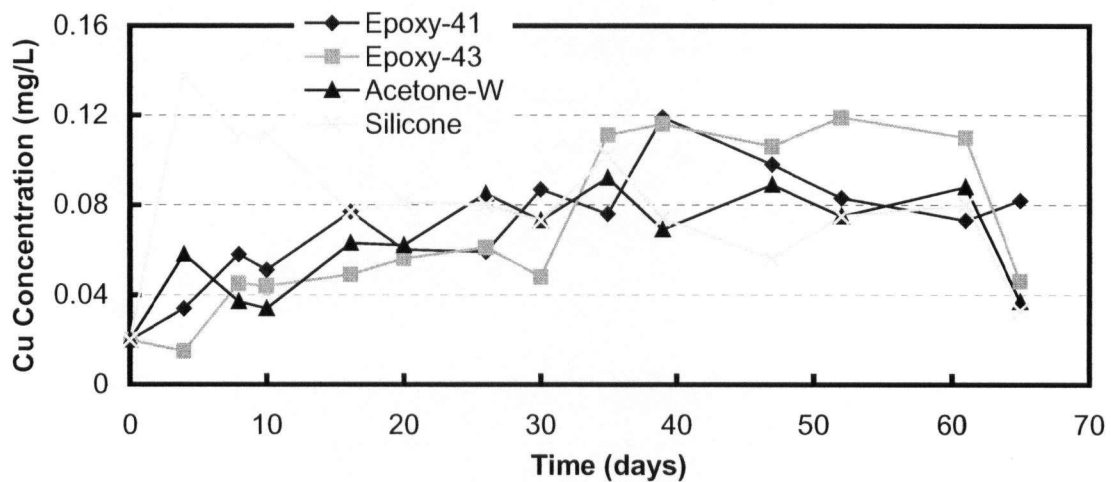
Figure 5.60 Cu Concentration vs. Time in Heating and Cooling Test
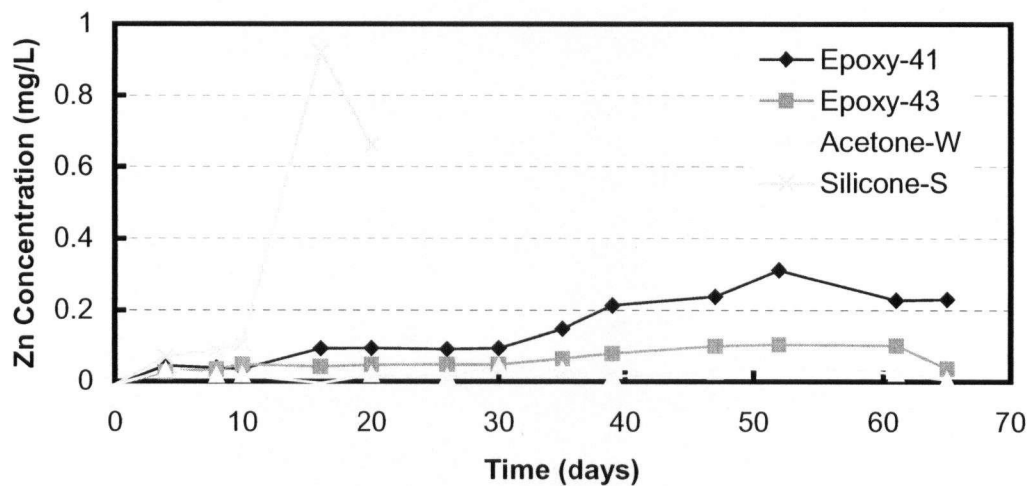
Figure 5.61 Zn Concentration vs. Time in Heating and Cooling Test

Zn concentration (Figure 5.62) was over 1.0mg/l, which was at the limit of the standard liquid prepared for the test. The sample might have been contaminated. For Mg and Fe concentration, Silicone-S showed ten to twenty times greater value than the others.
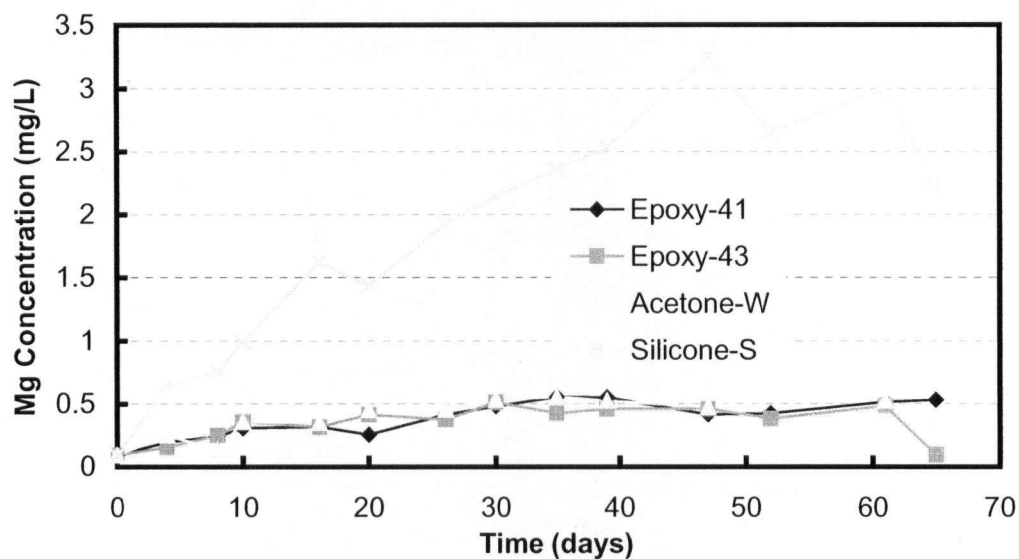
Figure 5.62 Mg Concentration vs. Time in Heating and Cooling Test
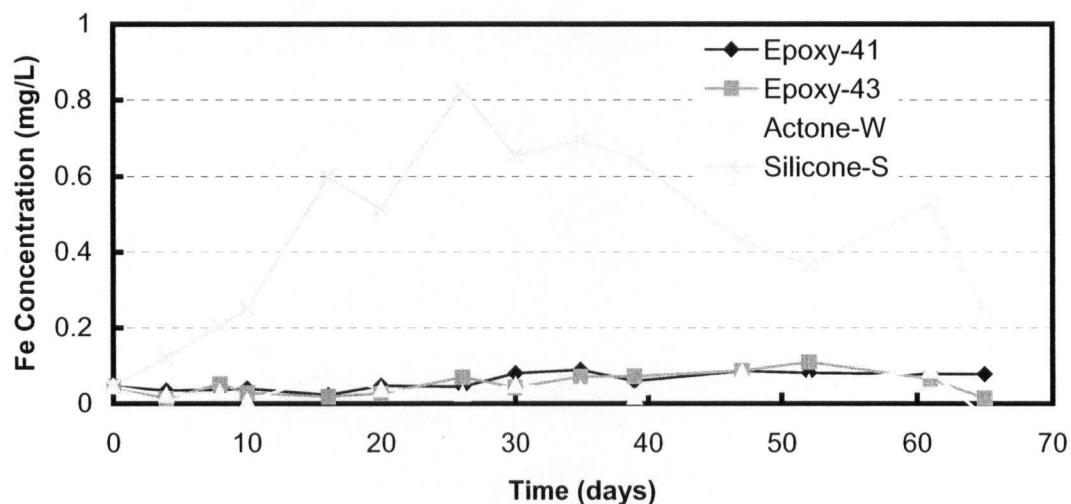
Figure 5.63 Fe Concentration vs. Time in Heating and Cooling Test

Discussion

The minimum values of pH, maximum value of conductivity, and metal concentrations of different tests are provided in Figures 5.64 to 5.69.

The pH values (Figure 5.64) of all tests with coated rock samples were higher than those without. The pH values in the freezing and thawing test were relatively lower, but still higher than those of the ARD generation tests and field measurements (approximately 3.1 to 3.5). The pH of each coating material changed its order according to the test; for example, the pH of epoxy-41 in the coating capacity test was the highest, while it was the second to lowest in the freezing and thawing test. It is suggested that the coating material's reactions with water were different under different testing conditions.
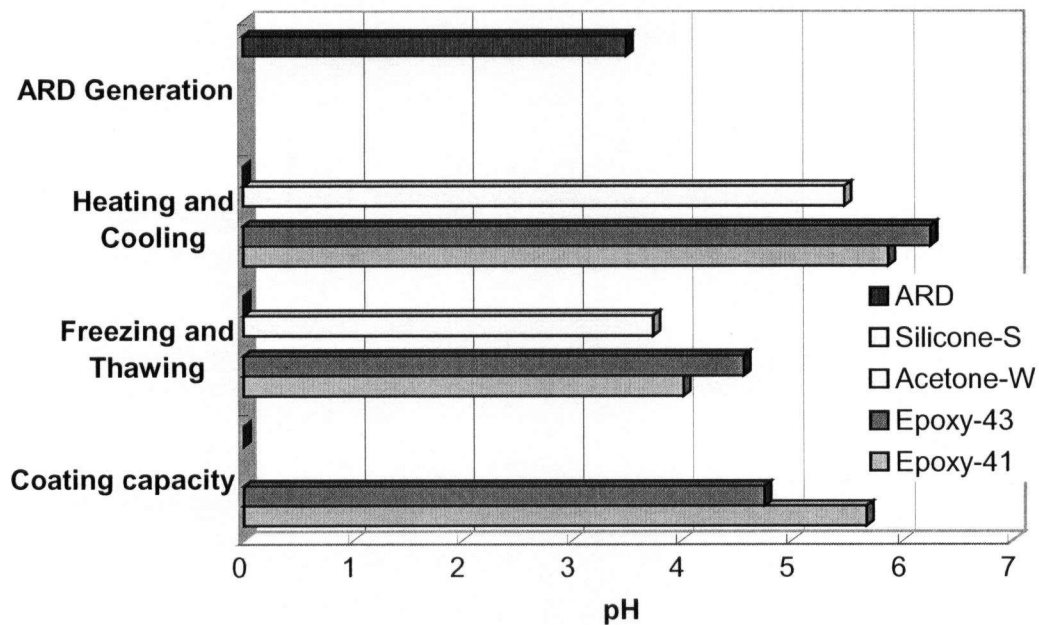
Figure 5.64 The Minumum pH in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)

The conductivity of silicon-S was significantly greater than those of all others in the heating and cooling tests and freezing and thawing tests (Figure 5.64). However, the values of all samples were much less than that of the ARD generation test. All coating materials indicated the ability to reduce the conductivity.
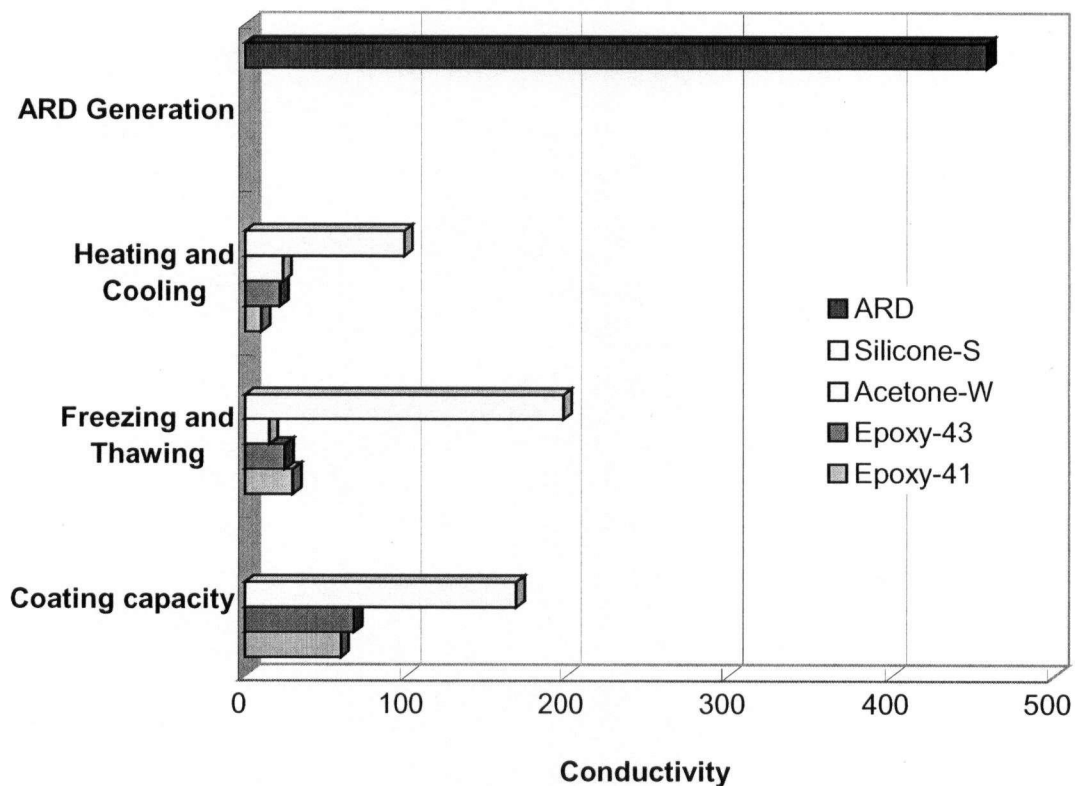
Figure 5.65 The Maximum Conductivity in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)

The maximum metal concentrations of all four materials in all tests are given in Figures 5.66 to 5.69. The values of the coating and capacity test resulted in relatively high values. This might be due to the changes that happened during the storage. Although there were some extremely large values due to the part failure of testing equipment or outside contamination,

in general, the coated rock samples exhibited much lower metal concentrations. This suggested that the coating materials were able to reduce metal concentrations, thus preventing potential ARD generation.
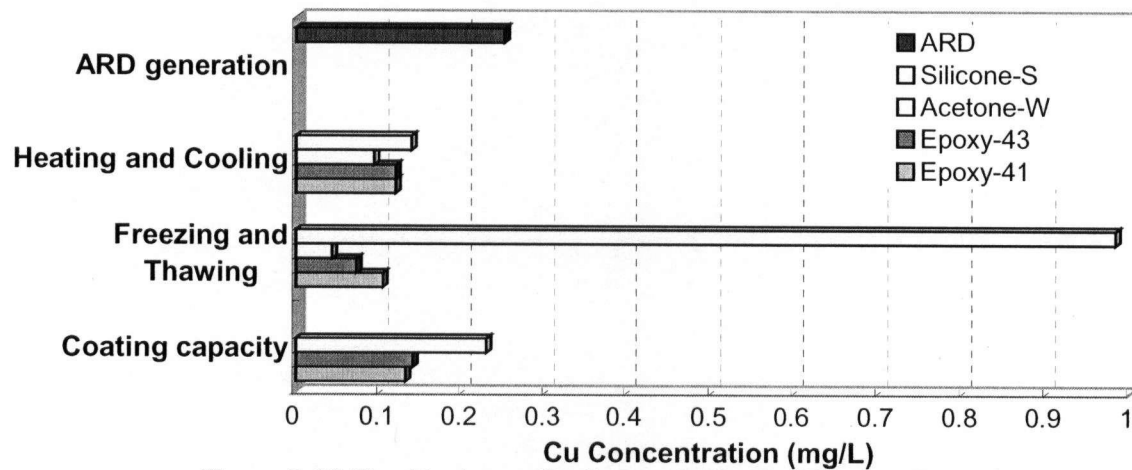
Figure 5.66 The Maximum Cu Concentration in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)
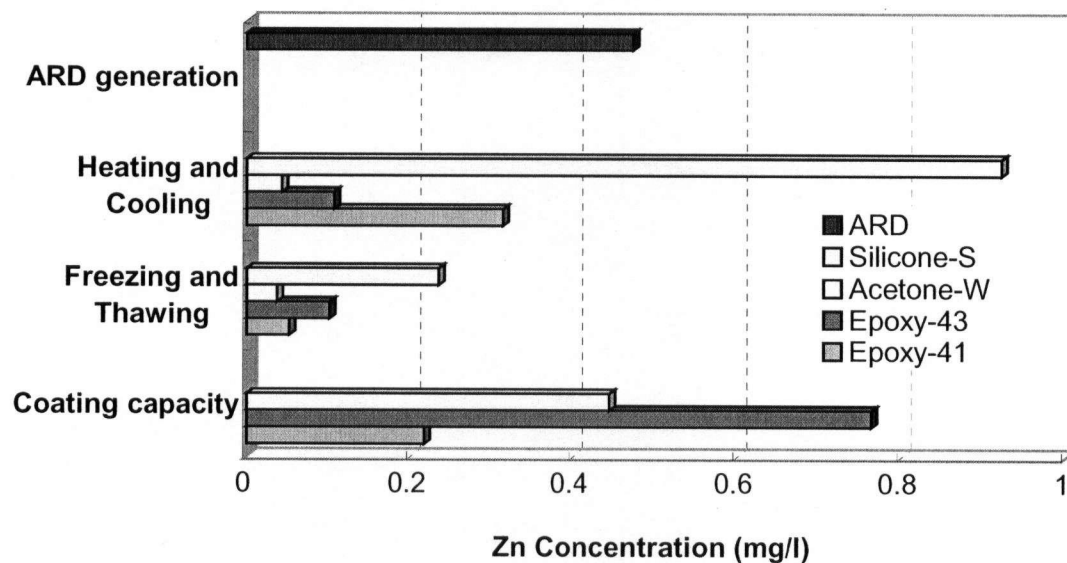
Figure 5.67 The Maximum Zn Concentration in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)
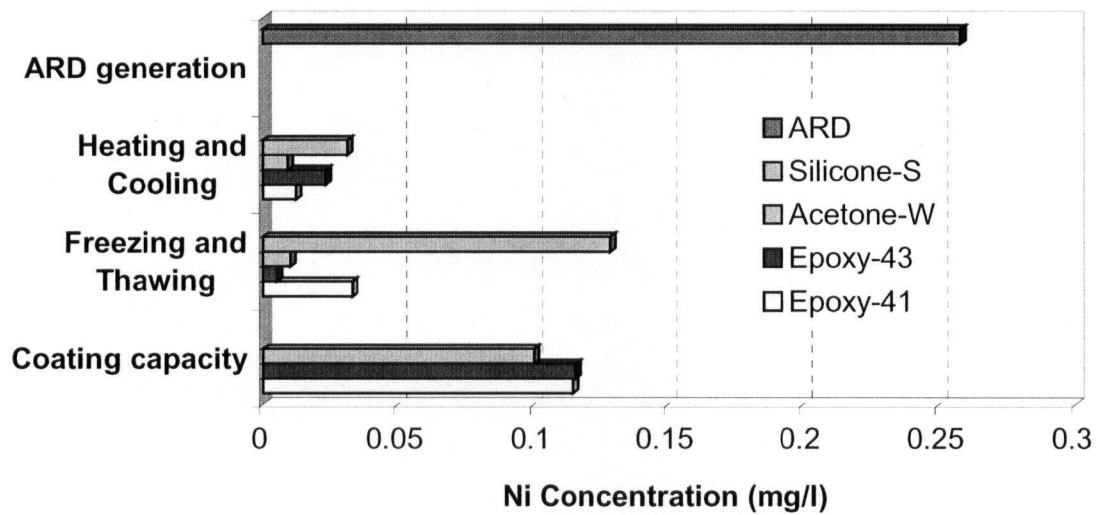
Figure 5.68 The Maximum Ni Concentration in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)
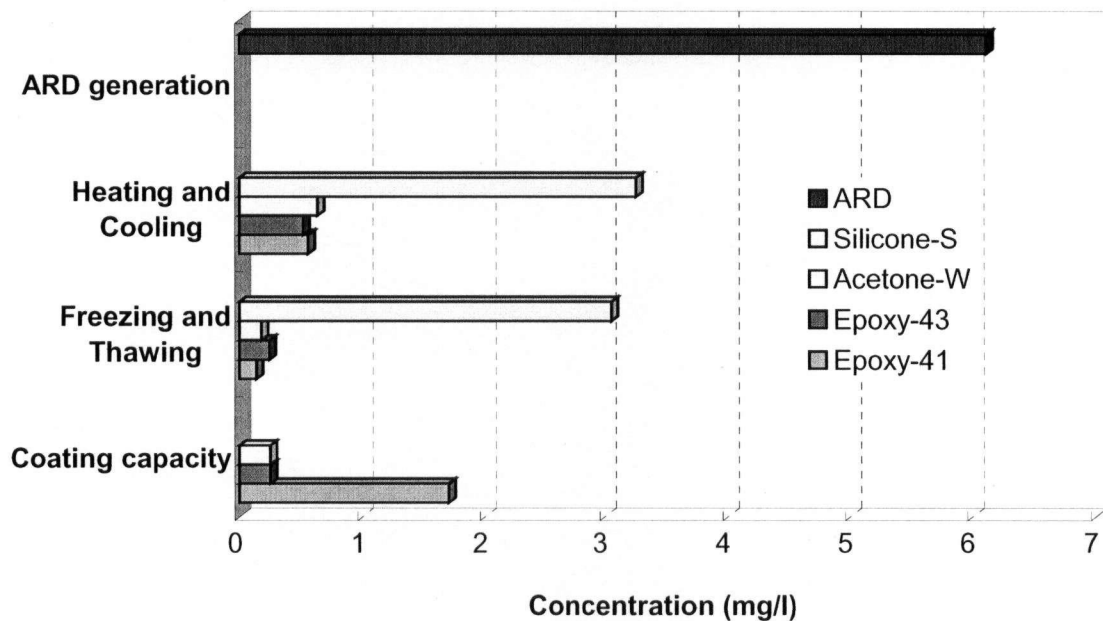
Figure 5. 69 The Maximum of Mg Concentration in Different Tests (ARD Generation Test, Coating Capacity Test, Freezing and Thawing Test, and Heating and Cooling Test)

The metal concentration in ARD generation processing is considered to be the result of the oxidation of rock samples. Therefore, the estimated number of years for rock samples to be 100% oxidized was calculated based on the metal concentration of the ARD generation test and the coating capacity test. The results are presented in Tables 5.3 to 5.4. For each sample, the oxidation rate was calculated by dividing the metal amount, which was the result of the concentration multiplied by the liquid volume, by the weight of rocks in the cell and the testing time. The detailed calculation is listed in Appendix D.

Ca is the easiest element to be released of all measured metals, and requires 7,000 to 14, 000 years to be 100% "ARD generated", while the most difficult element is Fe, which requires 8,900,000 to 27,000,000 years, 2 order (200 times) longer than that of Ca. The years required for Ni and Cu are also in the range of 1,000,000 years, while Mg and Na are about one order less (Table 5.3).

The result of the coating capacity test provides an estimated range of about 100,000 to 1,000,000 years (Table 5.4).

Table 5.3 Estimated years of Rock Samples to be 100% oxidized (Unit: year)

Metal Concentration (mg/l)	Water Rock Ratio		
	2:3	3:3	3:5
Cu	1.8×10^6	2.0×10^6	1.9×10^6
Mg	5.5×10^4	4.9×10^4	3.2×10^4
Ca	1.4×10^4	9.2×10^3	7.1×10^3
Zn	7.1×10^5	8.4×10^5	6.3×10^5
Fe	8.9×10^6	1.1×10^7	2.7×10^7
Na	1.4×10^5	1.4×10^5	5.5×10^4
Ni	1.6×10^6	1.5×10^6	9.0×10^5

Table 5.4 The estimated years of rock samples to be 100% oxidized in the Coating Capacity Test (unit: years)

Metal Concentration (mg/l)	Sample		
	Epoxy-41	Epoxy-43	Acetone-W
Cu	2.0×10^6	1.8×10^6	8.4×10^5
Mg	9.2×10^5	7.7×10^5	1.0×10^5
Ca	2.3×10^5	2.1×10^5	2.1×10^5
Zn	2.9×10^5	5.2×10^5	1.1×10^6
Fe	1.7×10^6	1.5×10^6	5.8×10^4
Na	1.3×10^5	1.1×10^5	4.4×10^5
Ni	2.5×10^6	2.3×10^6	2.2×10^6

Note: Epoxy-41: Tripoxy 41, epoxy based, two components mixture by 1:1

Epoxy-43: Tripoxy 43, epoxy based, two components mixture by 1:4

Acetone-W: Wet Look Lacquer, aromatic acetone based, one component

5.2.6 Bonding Capacity Test

The coating material bonding capacity test followed the ASMT standard. Since Silicon-S showed no capacity for preventing ARD generation and was unable to stick rock samples together strongly enough for testing, it was withdrawn from the test. The bonding capacity test only included epoxy-41, epoxy-43, and acetone-W.

There were two test samples prepared for each coating material. Each test sample consisted of one piece of concrete brick and one piece of rock sample, stuck together by one kind of coating material from epoxy-41, epoxy-43 and acetone-W. After two months of air-drying, test samples were pushed apart by the testing machine to measure the final tensile strength. The load was gradually increased as a constant speed. The testing time of each sample lasted approximately 20 seconds.

When a load was greater than the bonding capacity of the coating materials, the two pieces of test samples were pulled apart from each other. The failure pattern of the test samples varied. Some were completely separated, while the others were still stuck together in some parts. The failure surfaces of all test samples are shown in Figure 5.70.
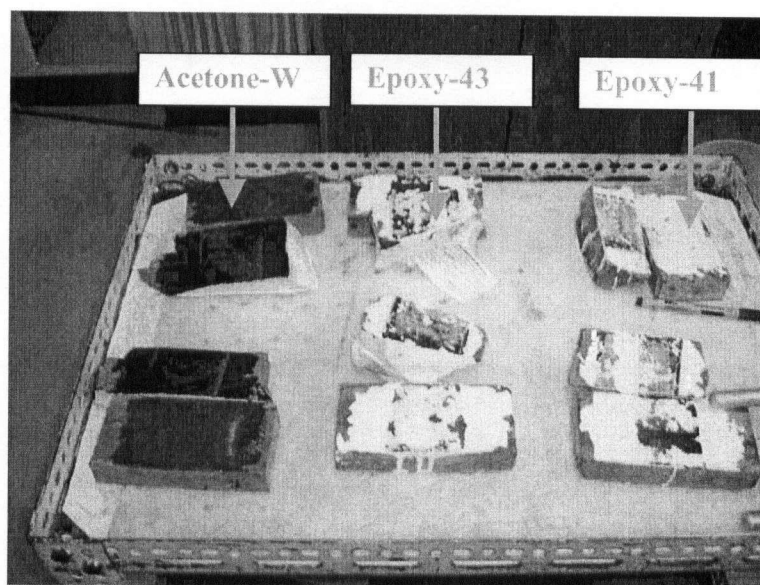
Figure 5.70 The Rock Samples After Bonding Capacity Test (The Rock Samples Were Coated with: Epoxy-41 (left), Epoxy-43 (middle), and Acetone-W (right))

The test results showed that there was no one sample that was 100% covered by coating materials. The reason was probably due to: 1) the uneven surface area, and 2) the un-standardized coating procedure.

The interface areas between rock samples and concrete in each testing sample were carefully measured, and the areas completely coated with coating materials were measured and calculated. The completely coated areas changed from sample to sample, and ranged from 20 % to 95 % of total contacting areas (Table 5.5). Acetone-W had the smallest value with only 20%, while epoxy-41 and epoxy-43 were highest with more than 90% coated.

The bonding capacity was calculated by dividing the final loads by the completely coated area (table 5.5). C2, one of the two test samples of acetone-W, had the largest value, which was almost three times higher than that of the others, but with a lower percentage of completely coated area (15-20%). Epoxy-41 and epoxy-43 both had approximately the same values of 60-70%.

Another important fact was that all destroyed interfaces were on the rock sides; in other words, the results represented the bonding capacity of the rock, instead of the concrete. All samples had a relatively high bonding capacity with concrete, but acetone-W had the highest bonding capacity.

Table 5.5 The Bonding Capacity Testing Results

	Tensile Reading (pounds)	Bonding Area (mm^2)	The Bonding Capacity (N/m^2)	Bonding Coverage occupied in total Area (%)
Epoxy-41				
Test 1	1250	4,186.3	13.3	90-100%
Test 2	1825	4,016.3	20.2	90-100%
Epoxy-43				
Test 1	1825	3,519.0	23.1	90-100% (30% left on rock)
Test 2	1500	3,405.5	19.6	95-100%(5-15% left on rock)
Acetone-W				
Test 1	1650	4,214.1	17.4	15-20%
Test 2	5900	4,363.4	60.2	60-70%

5.2.7 Thin Section

Thin section technique was employed to observe the interface between coating materials and rock samples. Ten thin section samples from the coating capacity test, the freezing and thawing test, and the heating and cooling test and washed rock samples were prepared. In each test, there was one sample coated by coating material of epoxy-41, epoxy 43, and acetone-W separately. One rock sample was prepared for comparison. The pictures taken after observation under the Micropet are shown in Figures 5.71 to 5.80. Each picture consists of three components: 1) the white part is the background color of the glass, 2) the dark part in the middle is the coating layers, and 3) the mixed part of brown with dark dots is rock samples.

Thin section pictures represented the coating layers visually. The pictures show that the thickness of coating layers varied from position to position. Some parts are thicker than other parts, and edges are thinner than the surface. This is due to the coating procedures and curing time. A rock sample was placed on the table and coated with liquid coating materials with a brush. The liquid flowed from the top of the samples down to the table. Therefore, the bottom surfaces and edges of the rock samples on the table became coated more thickly, while the top and slope surfaces had a thinner layer of coating. Thus, in future studies, it is necessary to develop a method to keep the thickness of the materials coating the whole rock samples constant.

The pictures showed that all three coating materials adhered to the rock surface well (Figures 5.71 to 5.80), even with some weathered surfaces. In Figure 5.73, the coating material sealed the cracks in the rock sample. However, because of the limitation of the enlargement of the Micropet, it was not possible to identify the penetration of coating materials into the rock. A Micropet with higher resolution is recommended for further studies.

In general, the outline surface of coating materials was smooth, except in the broken layer of acetone-W from the freezing and thawing test (Figure 5.73).
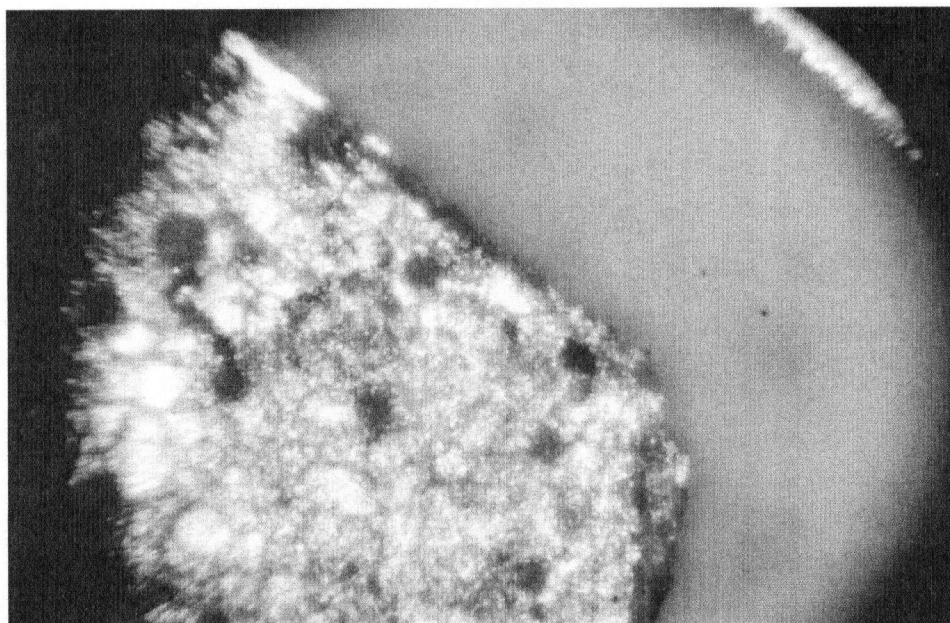
Figure 5.71 Thin Section Picture of Epoxy-41 in Coating Material Capacity Test
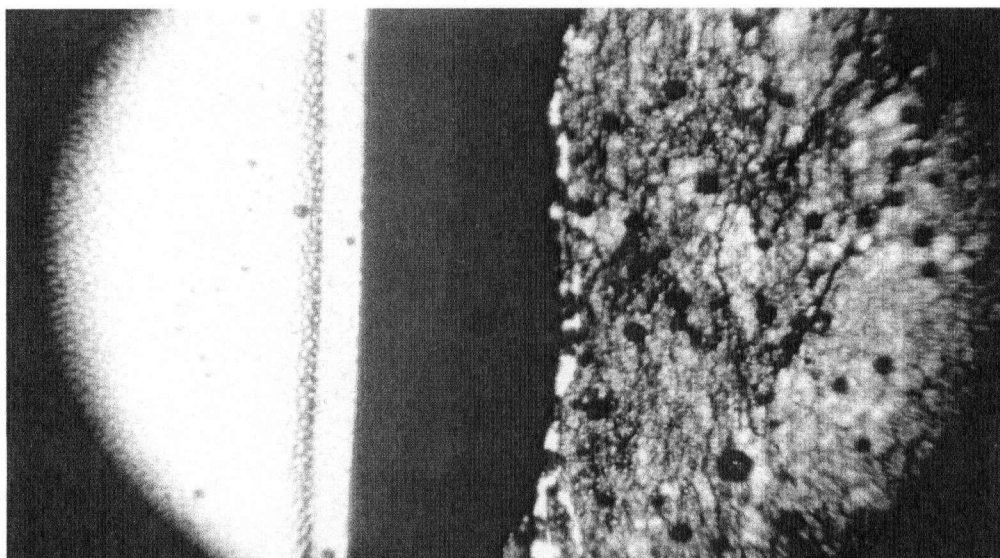
Figure 5.72 Thin Section Picture of Epoxy-43 in Coating Material Capacity Test
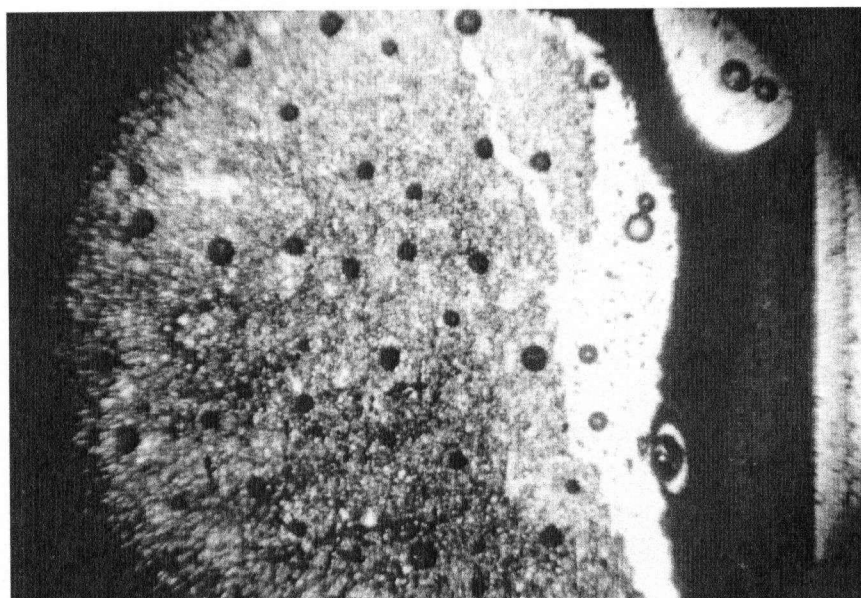
Figure 5.73 Thin Section Picture of Acetone-W in Coating Material Capacity Test

Thin section pictures of epoxy-41, epoxy-43 and acetone-W from the coating materials capacity tests are shown in Figures 5.71 to 5.73. The coating materials adhered to the rock surface well, and the outline of the coating layer of coating materials is smooth.
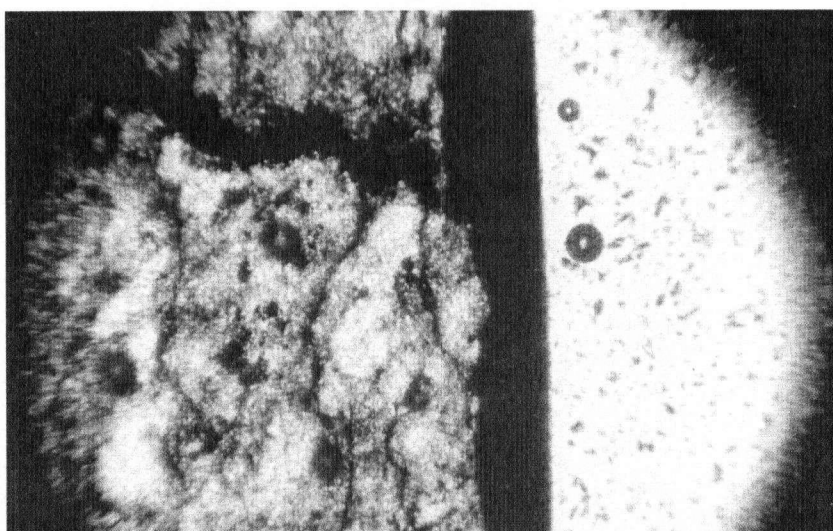
Figure 5.74 Thin Section Picture of Epoxy-41 in Freezing and Thawing Test
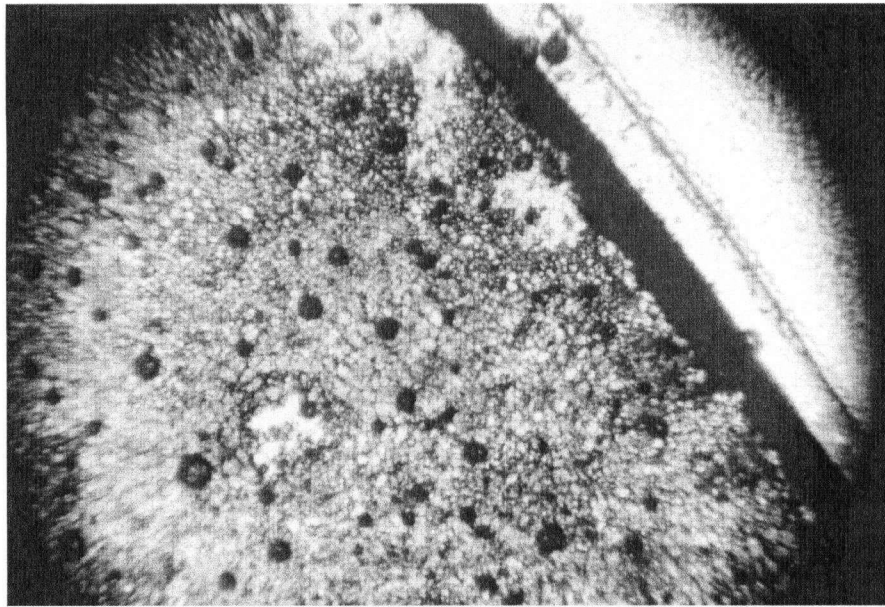
Figure 5.75 Thin Section Picture of Epoxy-43 in Freezing and Thawing Test
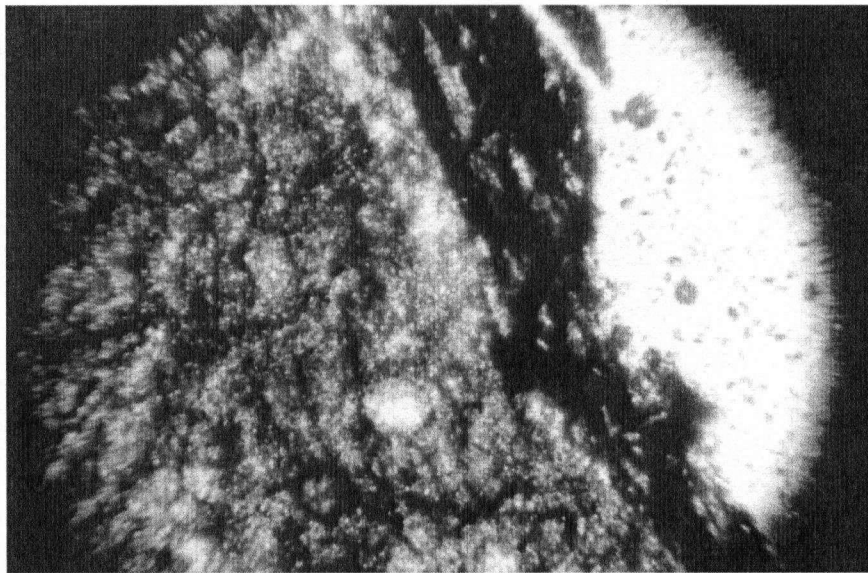
Figure 5.76 Thin Section Picture of Acetone-W in Freezing and Thawing Test

The thin section pictures of samples coated by epoxy-41, epoxy-43 and acetone-W in the freezing and thawing test are shown in Figures 5.74 to 5.76. Epoxy-41 and B showed similar patterns. They exhibit constant thickness, adhere to the rock well, and possess smooth

outlines. Acetone-W stuck to the rock surface well, however with a broken outline. It shows the part of coating layer that was broken by cutting rock the sample to a smaller piece for the thin section sample.
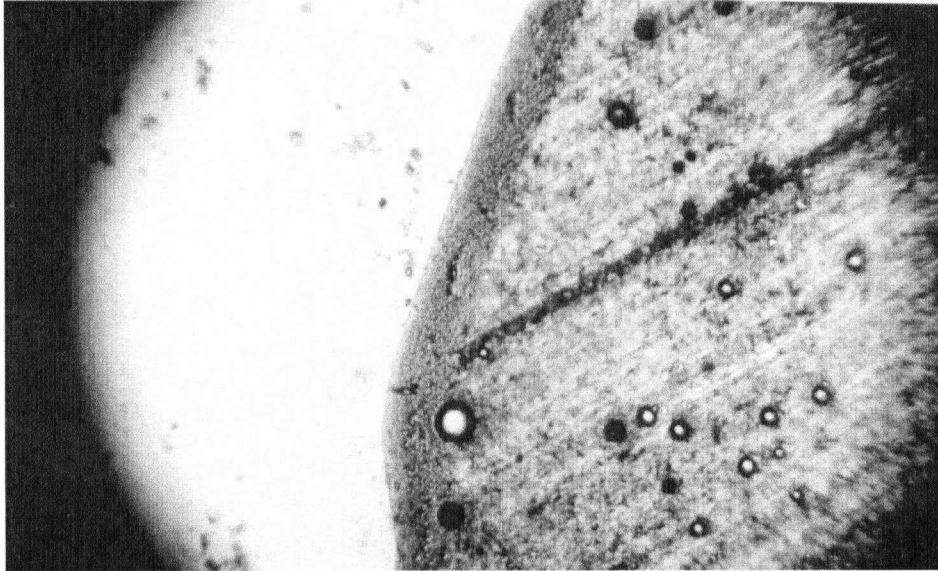
Figure 5.77 Thin Section Picture of Epoxy-41 in Heating and Cooling Test
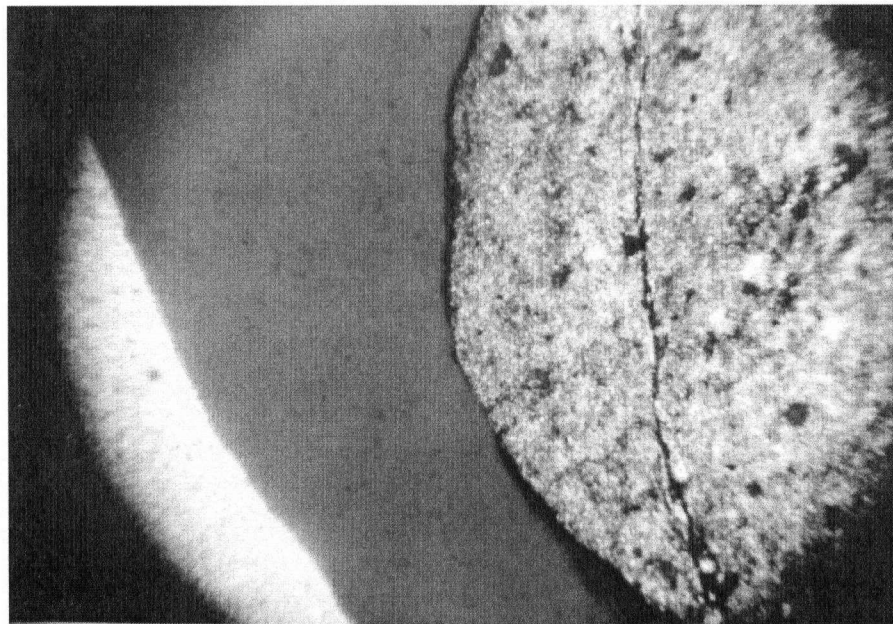
Figure 5.78 Thin Section Picture of Epoxy-43 in Heating and Cooling Test
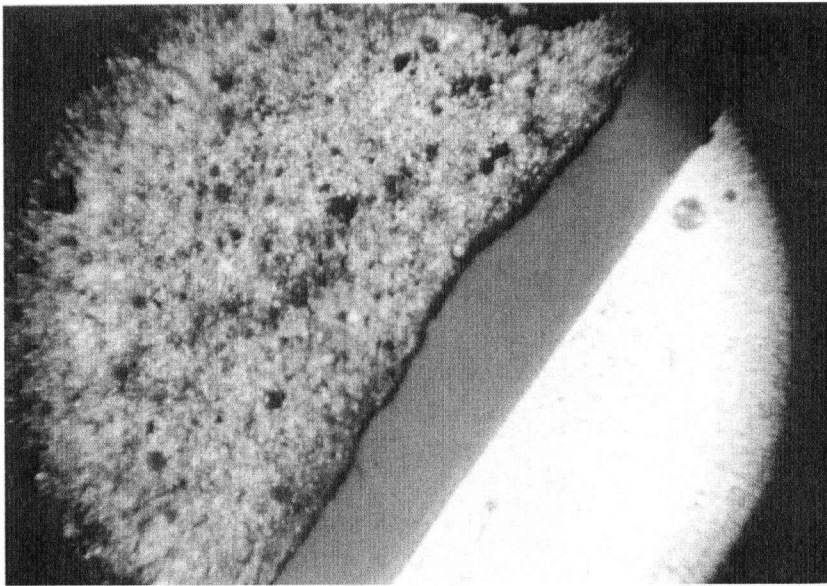
Figure 5.79 Thin Section Picture of Acetone-W in Heating and Cooling Test

Thin section pictures of epoxy-41, epoxy-43, and acetone-W from the heating and cooling test are shown in Figures 5.77 to 5.79. The heating and cooling process did not influence the coating layers. The pictures showed clear adherence of the coating materials to the rock surface.
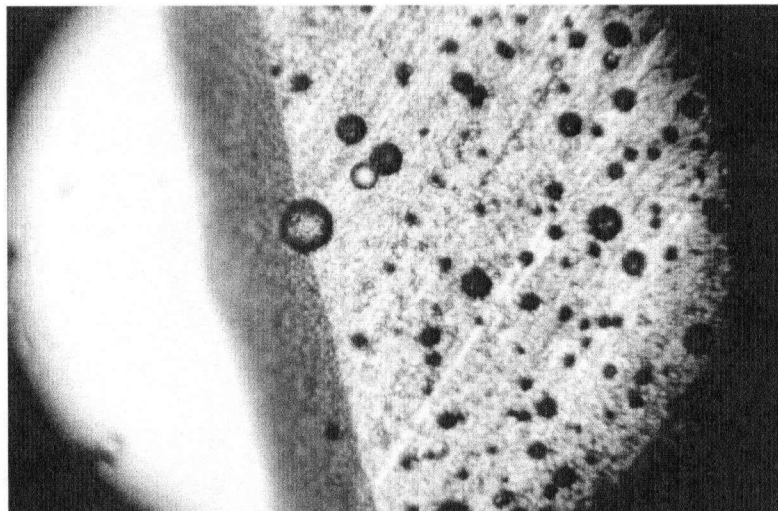
Figure 5.80 Thin Section Picture of Washed Rock Sample

The thin section picture of washed rock sample is shown in Figure 5.80. There was a clear surface layer in the rock sample surface. What the components of the layer are is unclear. This requires further study.

The thin section pictures showed that all three coating materials adhere to the rock surface well, and with a constant layer, as well as with a clear outline. The influence of heating and cooling, freezing and thawing processes to the coating layer was not identified.

The thin section analysis is a useful technique to determine the coating materials performance in different test conditions, however, a higher resolution Micropet, higher performance recording equipment, and analytical software are desirable for future studies.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

6.1.1 ARD Generation

Five sets of tests were carried out to study the ARD generating characteristics of rock samples. The pH value decreased to as low as 3.5 after approximately 90 days, which was near the field measurement in the Pennask Site. Metal concentrations of Cu, Zn and Ni were as high as that of the field measurements, and exceeded Aquatic Life Standards. Therefore, the rock samples from the Pennask Site have ARD generating potential.

The water to rock ratio influenced pH, conductivity, and metal concentrations. The higher the water to rock ratio, the higher the pH, and the lower the conductivity and metal concentrations. The water to rock ratio represents the natural changes due to seasonal weather changes, such as rainfall, floods and snow, etc. Therefore it can be assumed that the ARD generation rate may change seasonally under natural condition.

A simplified estimation of the time for oxidizing100% the rock samples was calculated based on metal concentrations. The majority of elements require more then 1,000,000 years to complete the process. It is assumed that ARD generation would take place continually during this time.

6.1.2 Coating Method and Coating Materials

Five test methods or analyzing techniques were done to preliminarily study the feasibility of using the coating method, and to rate the performance of four candidate coating materials by observing their capacity on preventing ARD generation.

In general, compared to the ARD generation test, all test results of samples coated by coating materials showed lower values in conductivity and metal concentration, and a higher value of pH. This indicated that the coating layer functioned as a barrier to prevent ARD generation. Therefore, it is possible to say that the coating method is an efficient and reliable solution for preventing ARD generation, and that the coating materials tested in this study are appropriate for the coating method discussed here.

Although, four coating materials performed with slight differences under different test conditions, with exception of silicon-S they performed with a higher reliability in preventing ARD generation. Epoxy-41, epoxy-43 and acetone-W were seen to have a high pH and lower metal concentration and conductivity. However, silicon-S was found not to be an appropriate material for the coating method.

The freezing and thawing, and the heating and cooling cycles did not influence the performance of epoxy-41, epoxy-43 and acetone-W as coating materials. Those three have a relatively high bonding capacity, acetone-W was having the highest. This indicated they might be used on slopes to stick rocks together and keep the slope stable in future field applications.

Based on the discussion above, the recommended coating materials for the coating method in order of performance are acetone-W, epoxy-43, and epoxy-41.

6.2 FUTURE STUDY AND RECOMMENDATIONS

This preliminary study was designed to better understand the basic concepts and feasibilities of the coating method and its feasibility in preventing ARD generation. However, the following points are recommended for further study.

1. Since every piece of rock sample was not exactly the same in weight, surface area, shape, and weathering condition, it is impossible to test coating materials under exactly the same conditions. Therefore, developing standardized test procedures and methods is important.

2. Since the rock samples used in the tests were less than 15 cm in size, some tests had very low metal concentrations, and the results were influenced by experimental errors. Therefore, the larger samples should be used in future studies.

3. A UV influence test is suggested for future work to study the performance of coating materials under UV, since coating materials are exposed to sunlight in the field.

4. Coating materials may face acidic conditions in some circumstances; therefore, anti-acidic tests are recommended.

5. A test of the coating materials on a slope is an important issue for future study. The final goal of the coating method is for it to be used on the slope surface in engineering projects.

6. The freezing and thawing test followed by the heating and cooling test to evaluate long-term durability of materials is also an issue that needs to be studied in the future.

7. The setting of rock samples in all tests with candidate materials for comparison is recommended for future study.

8. The higher resolution Micropet, higher performance recording equipment, and analytical software are desirable for future studies.

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Appendix A

Coating Materials Information

1. Epoxy-41

Production name: Tripoxy 41
Producer: Triangle Coatings, Inc.
1930 Fairway Drive
San Leandro, CA 94577-5631

1.1 Tripoxy I White (150)

Composition/Information on Ingredients are listed as following.

Item	Chemical Name	Gas Number	WT/WT % Less Then
01	Xylene	1330-20-7	15.0 %
02	1-Methoxy –2 – propanol (PM)	00107-98-2	15.0 %

1.2 Tripoxy I Curing Agent

Composition/Information on Ingredients are listed in following

Item	Chemical	Gas Number	WT/WT % Less then
01	Isopropyl Alcohol	67-63-0	15.0 %
02	Butyl Alcohol	71-36-0	10.0 %
03	2-Butoxyethanol	111-76-2	10.0 %
04	Xylene	1330-20-7	10.0 %

2. Epoxy-43

Production name: Tripoxy 43
Producer: Triangle Coating, Inc.

2.1 Tripoxy HB White Base

Composition/Information on Ingredients are listed as following.

Item	Chemical Name	Gas Number	WT/WT % Less Then
01	Xylene	1330-20-7	10.0 %
02	1-Methoxy –2 – propanol (PM)	00107-98-2	10.0 %
03	Butyl Alcohol	71-36-3	5.0 %

2.2 Tripoxy HB Curing Agent

Composition/Information on Ingredients are listed in following.

Item	Chemical	Gas Number	WT/WT % Less then
01	Xylene	1330-20-7	35.0 %
02	Butyl Alcohol	71-36-0	5.0 %

3. Aromatic-W

Production name: Wet Look Lacquer 11- 02

Manufacturer:
Triangle Coatings, Inc.
1930 Fairway Drive
San Leandro, CA 94577-5631

Composition/Information on Ingredients are listed in following.

Item	Chemical Name	Gas Number	WT/WT % Less Then
01	AceTONE	67-64-1	40.0 %
02	4-chlorobenzotrifluoride	98-56-6	30.0 %
03	Aromatic Hydrocarbon Mixture	64742-95-6	15.0 %

4. Silicon-S

Production name: Stone Armor

Manufacturer:
Radon Mitigation & Waterproofing Concrete Sealer Co.
Novion Inc., 18 L'Hermitage Drive,
Shelton, CT 06484 USA

Composition/Information on Ingredients are listed in following.

Hazardous Ingredients	%	CAS/PIN	LD50(Species/Route)	LC50 (Species)
Silicates, Bonding catalysts, Gelling agents, Wetting agents, Defoaming agents, Stabilizing agents	18-34 1-5	1344-09-8 Proprietary	(rat)2003-3000 mg/kg	N/A

Appendix B: Whole Rock Analysis Procedure

ACME ANALYTICAL LABORATORIES LTD.

ISO 9001:2000
FM 63007
Vancouver 2003

METHODS AND SPECIFICATIONS FOR ANALYTICAL PACKAGE
GROUP 4B - WHOLE ROCK TRACE ELEMENTS BY ICP-MS

Analytical Process

Receive Samples

↓

Sort and Log Samples

↓

- Soils & Sediments
- Vegetation
- Rock and Core

Soils & Sediments:
Oven Dry at 60°C
↓
Label and Sieve samples to -80 Mesh

Vegetation:
Ash at 475°C

Rock and Core:
Label, Crush & Pulverize to -150 mesh

↓

Weigh out 0.2 g pulp into graphite crucibles. Sample standards and pulp duplicates added to sequence.

↓ *Re-split*

Mix with LiBO2 and fuse at 1050°C

↓

Dissolve molten bead in 0.5% HNO3

↓

Add Calibration standards and reagent blanks to sample sequence.

↓

Sample solutions analysed by ICP-MS   *Re-analyse*

↓

LIMS system corrects data for interferences and drift. Operator reviews raw data

→ Is data of acceptable quality?   *No* → *Re-split*

Yes ↓

ICP-MS data and any other analyses combined as a final Analytical Report

↓

Verification and Certification by a BC Certified Assayer

Comments

Sample Preparation

All samples are dried at 60°C. Soil and sediment are sieved to -80 mesh (-177 μm). Moss-mats are disaggregated then sieved to yield -80 mesh sediment. Vegetation is pulverized or ashed (475°C). Rock and drill core is jaw crushed to 70% passing 10 mesh (2 mm), a 250 g riffle split is then pulverized to 95% passing 150 mesh (100 μm) in a mild-steel ring-and-puck mill.

Sample Digestion

A 0.2 g sample aliquot is weighed into a graphite crucible and mixed with 1.5 g of LiBO2 flux. The flux/sample charge is heated in a muffle furnace for 15 minutes at 1050°C. The molten mixture is removed and immediately poured into 100 mL of 5% HNO3 (ACS grade nitric acid in de-mineralised water). The solution is shaken for 2 hours then an aliquot is poured into a polypropylene test tube. Calibration standards, verification standards and reagent blanks are added to the sample sequence.

Sample Analysis

Sample solutions are aspirated into an ICP mass spectrometer (Perkin-Elmer Elan 6000) for the determination of the basic package consisting of the following 34 elements: Ba, Co, Cs, Ga, Hf, Nb, Rb, Sn, Sr, Ta, Th, Tl, U, V, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. A second sample split of 0.5 g is digested in Aqua Regia and analysed by ICP-MS (see Group 1DX) to determine: Au, Ag, As, Bi, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Se, Tl and Zn.

Quality Control and Data Verification

An Analytical Batch (1 page) comprises 31 samples. QA/QC protocol incorporates a sample-prep blank (SI or G-1) carried through all stages of preparation and analysis as the first sample, a pulp duplicate to monitor analytical precision, a -10 mesh rejects duplicate to monitor sub-sampling variation (drill core only), two reagent blanks to measure background and aliquots of in-house Standard Reference Materials like STD SO-17 to monitor accuracy. STD SO-17 was certified in-house against 38 Certified Reference Materials including CANMET SY-4 and USGS AGV-1, G-2, GSP-2 and W-2.

Raw and final data undergo a final verification by a British Columbia Certified Assayer who signs the Analytical Report before it is released to the client. Chief Assayer is Clarence Leong, other certified assayers are Dean Toye, Jacky Wang and Ken Kwock.

Document: Method and Specifications for Group 4B.doc	Date: Oct 2, 2003	Prepared By: J. Gravel

Appendix C: The Whole Rock Analysis Result

ELEMENT	SAMPLES	P101	P102	P103	P104	P201	P202	STANDARD SO-17/CSB
SiO2	%	71.25	65.32	76.03	60.11	73.75	72.31	61.42
Al2O3	%	12.89	14.64	10.03	17.3	11.26	11.42	13.78
Fe2O3	%	3.82	6.15	4.26	6.08	4.33	4.64	5.82
MgO	%	1.69	2.26	1.25	3.11	1.8	1.89	2.34
CaO	%	0.94	1.29	0.8	2.2	0.91	0.64	4.66
Na2O	%	2.62	3.4	1.98	3.35	2.29	1.64	4.14
K2O	%	2.33	2.42	1.77	1.5	1.96	2.53	1.41
TiO2	%	0.46	0.61	0.48	0.79	0.5	0.52	0.59
P2O5	%	0.03	0.06	0.03	0.07	0.07	0.04	0.98
MnO	%	0.03	0.04	0.03	0.11	0.05	0.04	0.53
Cr2O3	%	0.005	0.008	0.005	0.006	0.007	0.004	0.435
Ba	ppm	2910	3422	2116	933	3022	2764	413
Ni	ppm	25	< 20	< 20	< 20	< 20	< 20	36
Sc	ppm	17	20	13	23	16	18	23
LOI	%	2.9	2.7	2.5	4.6	2.4	3.3	3.4
TOT/C	%	0.75	0.73	0.48	0.76	0.51	0.87	2.41
TOT/S	%	0.08	0.57	0.18	0.06	0.06	0.3	5.31
SUM	%	99.29	99.29	99.4	99.34	99.67	99.29	99.56

ELEMENT	SAMPLES	P101	P102	P103	P104	P201	P202	STANDARD SO-17
Co	ppm	1.9	5.8	2.3	5.3	3	4.7	18.9
Cs	ppm	7.5	5	3.4	2.8	3	8.5	3.9
Ga	ppm	13.8	17.1	10.7	19.9	15.7	15.1	19.8
Hf	ppm	3.3	4.1	3.1	6.6	4	3.3	12.5
Nb	ppm	3	4	3.3	6.4	4.6	3.8	26.5
Rb	ppm	51.9	53.7	41.4	51.3	44.4	60.3	23.2
Sn	ppm	2	2	1	2	1	1	11
Sr	ppm	156.6	211	130.6	210.6	160.6	99.5	307.5
Ta	ppm	0.2	0.3	0.2	0.5	0.3	0.2	4.3
Th	ppm	2.7	2.9	2.1	4.4	3.2	2	12.2
U	ppm	1.6	2.3	2	2.5	1.5	1.9	11.7

V	ppm	67	98	66	117	82	97	127
W	ppm	1.6	1.2	2	8.4	3	1.1	10.3
Zr	ppm	103.6	137.8	99.8	205.3	115	106.1	355
Y	ppm	34	36.1	20.4	38.4	33.8	21.9	27.3
La	ppm	8.8	11.8	9.3	9.3	12	11.1	10.7
Ce	ppm	15.4	22.6	16.9	20.9	21.7	19.8	23.6
Pr	ppm	2.44	3.6	2.43	3.5	3.33	3.03	3.05
Nd	ppm	11.6	17.7	12.1	17.5	16	14	13.6
Sm	ppm	3.4	4.9	3	4.3	4.2	3.4	3.4
Eu	ppm	0.68	1.17	0.74	1.1	0.94	0.69	1.02
Gd	ppm	3.84	5.39	3.15	4.85	4.35	3.2	3.89
Tb	ppm	0.73	0.97	0.54	0.88	0.84	0.61	0.66
Dy	ppm	4.9	5.5	3.28	5.67	5.23	3.46	4.25
Ho	ppm	1.08	1.15	0.67	1.24	1.06	0.73	0.93
Er	ppm	3.65	3.57	2.09	3.99	3.41	2.25	2.85
Tm	ppm	0.56	0.58	0.33	0.66	0.57	0.39	0.42
Yb	ppm	3.66	3.94	2.01	4.81	3.67	2.71	2.83
Lu	ppm	0.56	0.63	0.34	0.79	0.59	0.41	0.44
Mo	ppm	1.4	1	3.4	1.7	1.8	1.5	12.1
Cu	ppm	24.7	18.9	28.8	46.3	31.3	39.7	146.6
Pb	ppm	6.2	5.4	6.2	4.3	3.2	5.6	25.3
Zn	ppm	43	55	51	65	50	62	141
Ni	ppm	8	21.1	8.4	25.7	11.8	13.9	25.6
As	ppm	4.2	8.7	48.8	47.6	18.8	11.1	18.2
Cd	ppm	0.1	0.1	0.1	0.1	0.1	0.2	5.8
Sb	ppm	0.9	0.7	0.8	0.4	0.6	0.6	3.5
Bi	ppm	0.2	0.2	0.2	0.1	0.1	0.2	5.9
Ag	ppm	0.5	0.8	0.6	0.3	0.5	0.4	0.3
Au	ppb	3.1	2.8	3	2.1	2.1	1.8	42
Hg	ppm	< .01	0.01	< .01	< .01	< .01	< .01	0.18
Tl	ppm	0.2	0.6	0.2	0.2	0.2	0.4	1
Se	ppm	1.3	3.4	2.1	0.9	1.1	3	4.8

Appendix D: The Calculation of Estimated Year Needed of 100% Oxidized In ARD Generation Test

	Cu			Mg			Ca			Zn		
	D1	D2	D3	D1	D2	D3	D1	D2	D3	D1	D2	D3
	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5
The metal concentration after 82 days (mg/l)	0.186	0.112	0.07	6.1116	4.5957	4.2387	23.774	24.292	19.088	0.4735	0.2668	0.2145
Initial rock weight (kg)	3	3	3	3	3	3	3	3	3	3	3	3
Water volume (l)	2	3	5	2	3	5	2	3	5	2	3	5
Total dissolved metal (mg)	0.372	0.336	0.35	12.223	13.787	21.194	47.548	72.876	95.44	0.947	0.8004	1.0725
Dissolved metal in total rock (%)	1E-05	1E-05	1E-05	0.0004	0.0005	0.0007	0.0016	0.0024	0.0032	3E-05	3E-05	4E-05
Divided by days (% / day)	2E-07	1E-07	1E-07	5E-06	6E-06	9E-06	2E-05	3E-05	4E-05	4E-07	3E-07	4E-07
Days for 100% oxidation (days)	7E+08	7E+08	7E+08	2E+07	2E+07	1E+07	5E+06	3E+06	3E+06	3E+08	3E+08	2E+08
Years for 100% oxidation (years)	2E+06	2E+06	2E+06	55139	48884	31801	14175	9248.2	7061.7	711692	842045	628413

Appendix D: The Calculation of Estimated Year Needed of 100% Oxidized In ARD Generation Test

	Fe			Na			Ni		
	D1	D2	D3	D1	D2	D3	D1	D2	D3
	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5	Water Rock Ratio 2:3	Water Rock Ratio 3:3	Water Rock Ratio 3:5
The metal concentration after 82 days (mg/l)	0.038	0.02	0.005	2.4731	1.5917	2.4289	0.209	0.151	0.15
Initial rock weight (kg)	3	3	3	3	3	3	3	3	3
Water volume (l)	2	3	5	2	3	5	2	3	5
Total dissolved metal (mg)	0.076	0.06	0.025	4.9462	4.7751	12.145	0.418	0.453	0.75
Dissolved metal in total rock (%)	3E-06	2E-06	8E-07	0.0002	0.0002	0.0004	1E-05	2E-05	3E-05
Divided by days (% / day)	3E-08	2E-08	1E-08	2E-06	2E-06	5E-06	2E-07	2E-07	3E-07
Days for 100% oxidation (days)	3E+09	4E+09	1E+10	5E+07	5E+07	2E+07	6E+08	5E+08	3E+08
Years for 100% oxidation (years)	9E+06	1E+07	3E+07	136261	141143	55496	2E+06	1E+06	898630

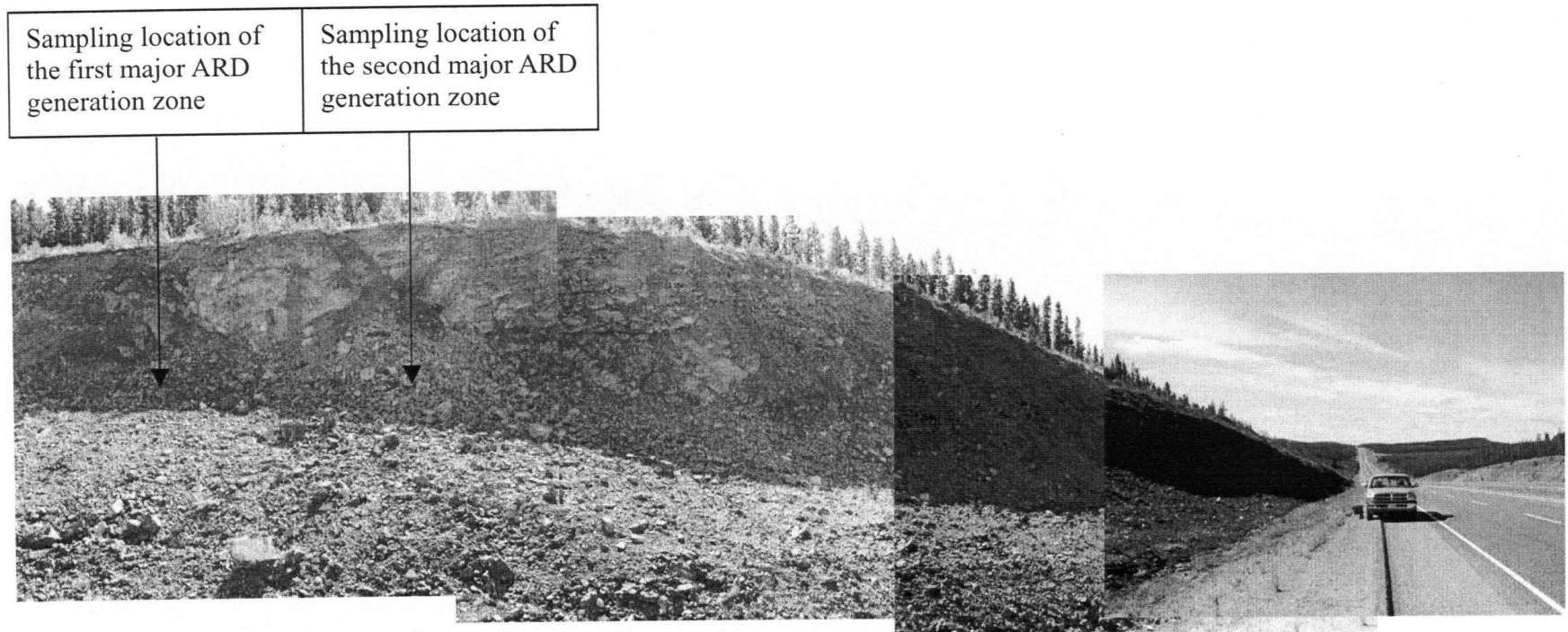## Appendix D: The Calculation of Estimated Year Needed of 100% Oxidized In Coating Capacity Test

	Cu			Zn			Mg			Ca		
	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B
Metal concentration after 90 days (mg/l)	0.177	0.068	0.078	0.141	0.4844	0.2695	1.487	0.1511	0.182	0.713	0.608	0.67
Daily change of metal concentration (mg/l/day)	0.002	0.0008	0.0009	0.0016	0.0054	0.003	0.0165	0.0017	0.002	0.0079	0.0068	0.0074
Initial weight of rock samples (g)	904	845	853	904	845	853	904	845	853	904	845	853
Water volume(l)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total dissolved metals (mg)	0.2655	0.102	0.117	0.2115	0.7266	0.4043	2.2305	0.2267	0.273	1.0695	0.912	1.005
Dissolving ratio (% / day)	3E-09	1E-09	2E-09	3E-09	1E-08	5E-09	3E-08	3E-09	4E-09	1E-08	1E-08	1E-08
The year needed for 100%oxidated	839564	2E+06	2E+06	1E+06	286755	520294	99935	919286	770435	208419	228461	209282

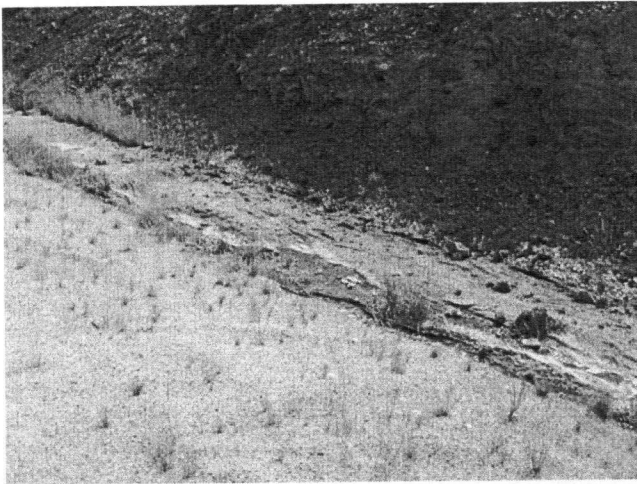## Appendix D: The Calculation of Estimated Year Needed of 100% Oxidized (Continue)

	Ni			Fe			Na		
	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C	Sample A	Sample B
Metal concentration after 90 days (mg/l)	0.068	0.056	0.061	2.564	0.082	0.093	0.3347	1.0346	1.2494
Daily change of metal concentration (mg/l/day)	0.0008	0.0006	0.0007	0.0285	0.0009	0.001	0.0037	0.0115	0.0139
Initial weight of rock samples (g)	904	845	853	904	845	853	904	845	853
Water volume(l)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total dissolved metals (mg)	0.102	0.084	0.0915	3.846	0.123	0.1395	0.5021	1.5519	1.8741
Dissolving ratio (% / day)	1E-09	1E-09	1E-09	5E-08	2E-09	2E-09	6E-09	2E-08	2E-08
The year needed for 100%oxidated	2E+06	2E+06	2E+06	57957	2E+06	2E+06	443988	134259	112229

Site Pictures

| Sampling location of the first major ARD generation zone | Sampling location of the second major ARD generation zone |

E-1.The pictures of the south side of the Pennask site

E-2 The visible drainage in the south ditch

E-3 The south ditch was covered with limestone

E-4 The drainage of the end pond of the south side ditch was brown

E-5 Whole way from the pond to the reservoir was covered by limestone
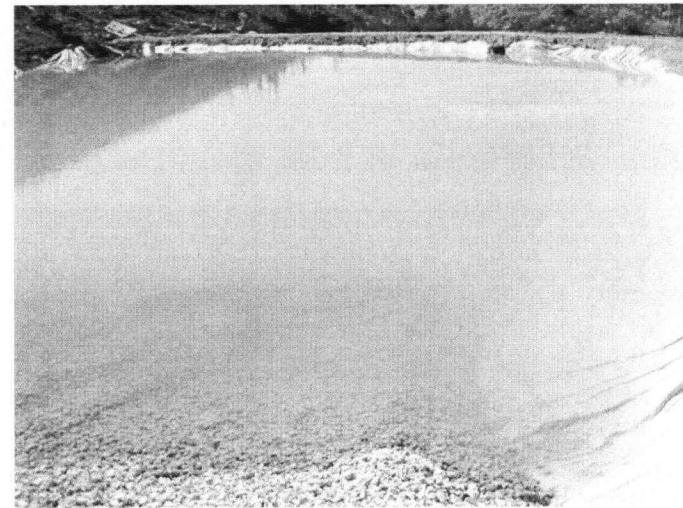
E-6. The newly replaced crushed limestone

E-8 The limestone become brown two months late

E-8 The water flow over limestone to the reservoir

E-9 The water became very clear when entered the reservoir