2000

Iron and acid removal from acid mine drainage in open limestone systems

Qingyun Sun
West Virginia University

Follow this and additional works at: <https://researchrepository.wvu.edu/etd>

Recommended Citation

Sun, Qingyun, "Iron and acid removal from acid mine drainage in open limestone systems" (2000).
Graduate Theses, Dissertations, and Problem Reports. 3185.
<https://researchrepository.wvu.edu/etd/3185>

This Dissertation is protected by copyright and/or related rights. It has been brought to you by the The Research Repository @ WVU with permission from the rights-holder(s). You are free to use this Dissertation in any way that is permitted by the copyright and related rights legislation that applies to your use. For other uses you must obtain permission from the rights-holder(s) directly, unless additional rights are indicated by a Creative Commons license in the record and/ or on the work itself. This Dissertation has been accepted for inclusion in WVU Graduate Theses, Dissertations, and Problem Reports collection by an authorized administrator of The Research Repository @ WVU. For more information, please contact researchrepository@mail.wvu.edu.

**Iron and Acid Removal from Acid Mine Drainage
in Open Limestone Systems**

Qingyun Sun

**Dissertation submitted to the
College of Agriculture, Forestry and Consumer Sciences
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Agricultural Sciences**

**Jeffrey G. Skousen, Ph.D., Chair
Louis M. McDonald, Jr., Ph.D.
Devinder K. Bhumbla, Ph.D.
John C. Sencindiver, Ph.D.
John Renton, Ph.D.**

Division of Plant & Soil Sciences

**Morgantown, West Virginia
2000**

**Keywords: Acid Mine Drainage, Iron Removal, Limestone, Coating,
Water Quality Prediction, Open Limestone System Design**

Copyright 2000 Qingyun Sun

ABSTRACT

Iron and Acid Removal from Acid Mine Drainage in Open Limestone Systems

Qingyun Sun

Passive systems, like wetlands, anoxic limestone drains, and open limestone channels, show promise for treating acid mine drainage (AMD) discharges. Open limestone channels have been developed for over ten years and the treatment effectiveness of AMD by open limestone systems shows wide variation. The variation is due to site conditions (slope and size of the limestone channel) but more importantly to the surface area of the limestone and iron concentrations in the water. Iron in AMD coats the limestone in open limestone systems thereby reducing the surface area available for reaction. Over time, the limestone appears to lose its ability to neutralize acidity and the water quality from open limestone systems is hard to predict.

This study was conducted to understand the effects of limestone surface area, iron concentration of the AMD, and coating thickness of iron on limestone neutralization of AMD. Experiments on limestone surface area showed that the required reaction time to reach a desired final pH is a function of limestone mass specific area, and initial and final acidity of proton acid solutions. The required reaction time, $t = aA_{MS}^k$, can be used to predict the outlet water quality for a hydrogen acid solution in an open limestone system based on a specified limestone particle size and lifetime.

Effects of iron concentration on neutralization of acid solutions by limestone were also researched by batch experiments in the laboratory. The required reaction time for neutralization was modified from previously developed equations by:

$$t(Fe) = t(Fe = 0) + (42 \ln[Fe] + 35.1)pH_f - 176 \ln[Fe] - 143$$

where $t(Fe)$ is the required reaction time for iron acid solutions, $t(Fe=0)$ is the reaction time for hydrogen acid solutions, $[Fe]$ is the iron concentration, and pH_f is the final pH. In addition, equations were established to estimate limestone neutralization of iron acid solutions, $[Ca]_{Fe} = 0.309C_T + 0.27[Fe^{3+}]_i + 0.448$, where $[Ca]_{Fe}$ is the total dissolved Ca in mmol/L, C_T is the total initial acidity (meq/L), and $[Fe^{3+}]_i$ is the initial iron concentration (mmol/L).

Thicknesses of the iron coatings on limestone effects on acid neutralization also were evaluated. By the use of different coating thicknesses on limestone, the required reaction time can be calculated by:

$$t = f(pH_i, pH_f, [Fe^{3+}], A_{MS}, \eta)$$

where t is required reaction time (min), pH_f is the final outlet pH, pH_i is initial pH of the acid solution, A_{MS} is specific surface area of limestone particles, $[Fe^{3+}]$ is ferric iron concentration of the acid solution (mmol/L), and η is the term representing the coating effects on limestone dissolution.

With these equations, open limestone channels can be designed with optimized surface area to meet a specified outlet water pH. Predictions can also be made as to the longevity of the treatment and when channels may need replacement.

ACKNOWLEDGMENTS

A sincere thanks is for Dr. Jeff Skousen. His encouragement, advice, guidance and patience greatly helped me finish this thesis. During my time with him, I attained good experience and knowledge in the practical treatment of acid mine drainage, which will support my future professional career. Due to my English language problems, Dr. Skousen spent large amounts of time in my Ph.D. study and thesis writing. His kindness, patience, and guidance in my thesis writing and field studies not only encouraged me to finish this Ph.D. program, but it also helped me to improve my English. I feel fortunate to have the benefit of his assistance.

A special thanks goes to Dr. Louis McDonald. Without his great help, especially in experimental design, thesis writing, and chemical theory, I could not complete this thesis within such a short period. He also spent a great amount of time in helping my lab research and thesis writing by his knowledge and abundant research experiences. I do appreciate all that he did for me.

I thank Dr. John Sencindiver, who helped me understand soil science and land issues, and who served on my committee. Thanks also to Dr. D. K. Bhumbla for his lectures and laboratory classes. These professors helped me, an engineering student, understand plant and soil sciences.

I especially want to thank Dr. John Renton for his advice and guidance toward limestone coating and mineral research. With his excellent experience and kindness, I completed the last important part of this research.

Last, special thanks go to my family. It is the love and devotion from my wife, Lanjun, and my son, Yipeng, that made this research possible and encouraged me to finish this Ph.D. study.

TABLE OF CONTENTS

TITLE.....	i
ABSTRACT.....	ii
ACKNOWLEDGMENTS.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	v
LIST OF FIGURES.....	vii
Chapter 1. Overview	1
Chapter 2. Introduction.....	6
Chapter 3. Limestone Surface Area and Initial Acidity Effects on AMD Treatment in Open Limestone Channels.....	14
Supporting Information.....	29
Chapter 4. Iron Effects on Limestone Dissolution in Open Systems.....	31
Chapter 5. Coating Effects on Limestone Dissolution	43
Chapter 6 Open Limestone Channel Design Models and the Prediction of Water Treatment	59
Appendixes	68
Vita	112
Approval of Examining Committee	113

LIST OF TABLES

<u>Table</u>	<u>Page</u>
3.1. Limestone specific surface area vs. particle sizes $\bar{d}$	19
3.2. Required retention time in minutes for an initial pH acid solution (pH 2.0, 2.5, 3.0, 3.5, and 4.0) increased to a final pH of 5.5, 6.0, 6.5, and 7.0.....	20
3.3. Regressed equations for retention time function of initial pH and limestone specific surface area.....	21
3.4. Limestone surface area decreases as the limestone mass decreases during the life of the open limestone bed.....	24
4.1. Calculation of total acidity of five iron solutions with pH between 2.4 and 3.0.	38
5.1. Coating thickness as a function of iron solution concentration	47
5.2. Coating effects on outlet water quality.....	55
6.1 Input Spreadsheet.....	61
6.2 Results Spreadsheet.....	62
6.3 Outlet Water Quality Prediction.....	63

<u>Appendix Table</u>	<u>Page</u>
7.1.1 Initial pH 4.0 vs. Particle Sizes.....	69
7.1.2 Initial pH 3.5 vs. Particle Sizes.....	70
7.1.3 Initial pH 3.0 vs. Particle Sizes.....	71
7.1.4 Initial pH 2.5 vs. Particle Sizes.....	72
7.1.5 Initial pH 2.0 vs. Particle Sizes.....	73
7.1.6 Limestone Surface Area Experiment	74
7.1.7 Destination pH 5.5, 6.0, 6.5, 7.0 vs. time of different sizes.....	75
7.2.1 pH changes with the neutralization of acid solution by limestone chips	84
7.2.2 Ca changes with the neutralization of acid solution by limestone chips	86

7.3.1 The neutralization test of proton acid solution (pHi=3) by different limestone chips.....	90
7.3.2 The neutralization of proton acid solution (pHi=2.5) by fresh limestone chips.....	91
7.3.3 The neutralization of proton acid solution (pHi=3.0) by fresh limestone chips.....	92
7.3.4 The neutralization of proton acid solution (pHi=3.5) by fresh limestone chips.....	93
7.3.5 The neutralization of proton acid solution (pHi=4.0) by fresh limestone chips.....	94
7.4.1 The neutralization of 0.0008M iron solutions (FeCl ₃).....	95
7.4.2 The neutralization of 0.0016M iron solutions (FeCl ₃).....	96
7.4.3 The neutralization of 0.003M iron solutions (FeCl ₃).....	97
7.4.4 The neutralization of 0.008M iron solutions (FeCl ₃).....	98
7.4.5 The neutralization of 0.016M iron solutions (FeCl ₃).....	99
7.4.6 The neutralization of 0.03M iron solutions (FeCl ₃).....	100
7.4.7 The neutralization of 0.0M iron solutions (FeCl ₃).....	101
7.4.8 The neutralization of 0.0005M iron solution by saran coated limestone...	102
7.4.9 The neutralization of 0.001M iron solution by saran coated limestone...	103
7.4.10 The neutralization of 0.002M iron solution by saran coated limestone..	104
7.4.11 The neutralization of 0.004M iron solution by saran coated limestone..	105
7.4.12 The neutralization of 0.008M iron solution by saran coated limestone...	106
7.5.1 The neutralization iron solution by 0.0M Fe coated limestone.....	107
7.5.2 The neutralization iron solution by 0.002M Fe coated limestone.....	108
7.5.3 The neutralization iron solution by 0.004M Fe coated limestone.....	109
7.5.4 The neutralization iron solution by 0.006M Fe coated limestone.....	110
7.5.5 pH changing rate.....	111
7.5.6 Coating thickness vs. iron concentration.....	111

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1.1. World Fossil Fuel Reserves (IEA,1999).....	2
1.2. CO ₂ Contribution by countries (IEA,1999).....	2
2.1 Limestone particle size.....	8
2.2. Qualitative interpretation of surface roughness and oblateness of a particle.....	9
3.1. Representation of orthogonal axes.....	16
3.2. Ellipsoid limestone particle size classes effects on neutralization of 0.001 M acid solution.....	19
3.3. The outlet water quality changes with time at different particle size and an initial pH 3.....	25
3.4. The outlet water quality changes with time at different initial pH and optimal particle size (d=0.6mm) or larger particle size (d=10mm).....	25
3.5. The specific surface area vs. the size of sieved limestone.....	28
3.6. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 5.5.....	28
3.7. Reaction constant k and a vs. the initial pH.....	29
3.8. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 6.0.....	29
3.9. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 6.5.....	30
3.10. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 7.0.....	30
4.1. Fe concentration of various iron solutions being neutralized by limestone	35
4.2. pH vs. time in iron acid solutions	35
4.3. Dissolved Ca vs. time in iron acid solution	36
4.4. The reaction time difference of pH reaching 5.5, 6.0 and 6.5 vs. ferric concentration by 6.3-11 mm ellipsoid limestone	36
4.5. Dissolved Ca concentrations vs. the acidity in solutions with and	

without iron.....	39
5.1. Schematic representation of coating method	46
5.2. The coating layer structure.....	48
5.3. Cracking on the coating layer.....	48
5.4. The micro-pits on the surface of the coating layer.....	49
5.5. The CO ₂ gas bubbles cover limestone surface.....	49
5.6. Pit formation in limestone coating layer.....	50
5.7. Coating thickness effects on iron removal.....	51
5.8. Coating thickness effects on calcium concentration vs. time at initial iron concentration 0.001M	51
5.9. Coating thickness effects on neutralization rate at initial iron concentration 0.001M.....	52
5.10. X-ray diagram of FeCl ₃ coated layer.....	57
5.11. X-ray diagram of Fe ₂ (SO ₄) ₃	57
5.12. The X-ray diagram of the coating layer in field limestone systems	58
6.1 Prediction of required time to reach final pH 5.5 vs. different limestone particles and coated limestone square chips.....	64
6.2 Prediction of required time to reach final pH 6.0 vs. different limestone particles.....	64
6.3 Prediction of required time to reach final pH 6.5 vs. different limestone particles.....	65
6.4 Prediction of required time to reach final pH 7.0 vs. different limestone particles.....	65
6.5 Prediction of required time to reach a final pH in iron acid solutions.....	66
6.6 Prediction of required time to reach a final pH with coated limestone.....	67
 <u>Appendix Figure</u>	 <u>Page</u>
7.1.1 pH in proton acid solution (pH _i =2.0) with ellipsoid limestone particles...	76
7.1.2 Ca in proton acid solution (pH _i =2.0) with ellipsoid limestone particles...	76
7.1.3 pH in proton acid solution (pH _i =2.5) with ellipsoid limestone particles...	77

7.1.4 Ca in proton acid solution ($\text{pH}_i=2.5$) with ellipsoid limestone particles...	77
7.1.5 pH in proton acid solution ($\text{pH}_i=3.0$) with ellipsoid limestone particles...	78
7.1.6 Ca in proton acid solution ($\text{pH}_i=3.0$) with ellipsoid limestone particles...	78
7.1.7 pH in proton acid solution ($\text{pH}_i=3.5$) with ellipsoid limestone particles...	79
7.1.8 pH in proton acid solution ($\text{pH}_i=4.0$) with ellipsoid limestone particles...	79
7.1.9 Surface area vs. required reaction time at pH_f 5.5.....	80
7.1.10 a and k vs. pH_i at pH_f 5.5.	80
7.1.11 Surface area vs. required reaction time at pH_f 6.0.....	81
7.1.12 a and k vs. pH_i at pH_f 6.0.	81
7.1.13 Surface area vs. required reaction time at pH_f 6.5.....	82
7.1.14 a and k vs. pH_i at pH_f 6.5.	82
7.1.15 Surface area vs. required reaction time at pH_f 7.0.....	83
7.1.16 a and k vs. pH_i at pH_f 7.0.	83
7.2.1 pH changes as time.....	88
7.2.2 Modeling pH changes as time.....	88
7.2.3 Ca changes as time.....	89
7.2.4 Modeling Ca changes as time.....	89

Chapter 1. Overview

People have called coal “black gold” or “buried sunshine” as it contains the energy from sunlight that fell on the vast forests and swamps covering large areas of the world at various times in the geologic past. Trees and other plants in primeval forests decayed, forming peat bogs that were buried by soil and rock over millennia. The peat converted into coal over time by pressure and heat generated under the ground.

Coal is the world’s most abundant fossil fuel. The total mineable deposit is estimated to be about 1.15 trillion tons (Figure 1.1), which may last over 200 years at the current rates of world consumption. Compared to the reserves of other fossil fuels, coal can last much longer than oil (a supply of about 45 years) and natural gas (a supply for 70 years). In addition, coal is widely distributed in the world, unlike oil and gas reserves which tend to be concentrated in specific regions. In some regions, such as China, coal is the main energy source due to availability and economics. Today, about 40% of the world’s electricity is generated by coal, which accounts for about 70% of the world’s coal production. The second largest use of coal is coke production and it accounts for about 12% of world coal production, which produces 70% of the world’s steel. The remaining 18% of the world’s coal is used for other industrial and domestic purposes.

Although coal is an important resource and a critical component of our energy supply, the whole process of coal extraction, transportation and use is often accompanied by environmental pollution. Coal combustion produces heat, sulfur and nitrogen oxides, and a particulate residue. Atmospheric nitrogen and sulfur oxides cause acid rain. Atmospheric carbon dioxide from fossil fuel combustion has been implicated in global warming. Heavy metals from the particulate residue (ash) are a potential threat to soil and surface waters.

Figure 1.1. World Fossil Fuel Reserves (International Energy Agency, 1999).

Figure 1.2. CO₂ Contribution by country (International Energy Agency, 1999).

Coal transportation systems often cause dust problems and contaminate the air and roads. Coke production is also a major source of air pollution and the released toxic

gases contaminate the air more than coal combustion. Coal mining operations always produce wastes, some of which may contaminate streams and land. During the mining process, it is necessary to excavate large quantities of waste rock in order to extract the coal, so it often results in subsidence and waste spoil problems. The mine drainage from either active or abandoned mines and wastewater from coal processing plants can be a threat to ground and surface waters. The low pH and metal ions in acid mine drainage are toxic to aquatic life. Acid mine drainage (AMD) from many mines requires the addition of expensive chemicals for treatment, and this treatment may continue for decades.

Today, AMD pollution has become a worldwide environmental problem, and has contaminated many rivers and water sources in North American mining areas. According to statistics from the U.S. Bureau of Mines, the abandoned coal mines, metal mines and other mining waste have contaminated over 19,000 km of rivers and over 73,000 hectares of lakes and reservoirs in the United States. About 8,000 km of streams have been seriously contaminated by acid mine drainage in Pennsylvania, West Virginia, Ohio and Maryland. Every year, USA and Canada spend > \$400 million for AMD control and treatment projects, and West Virginia alone annually spends > \$75 million for AMD treatment (USEPA, 1995).

Acid mine drainage has become the biggest environment problem for coal mining in northern West Virginia and south central Pennsylvania due to high sulfur minerals in the rock layers. In these areas, isolation and containment of the potentially toxic parts of the waste is a big challenge. Isolating waste products from water and air prevents, or at least slows down, the onset of AMD. Containing the waste material and runoff (with liners, impervious pads, diversion and collection ditches, etc.) sometimes keeps the pollutants from running off the mine site into groundwater or surrounding streams. Thus, AMD treatment and prevention in this region have become the most urgent tasks for coal operators.

Methods for AMD treatment have been developed based on the site conditions, environmental conditions, and the AMD's chemical composition. Three major approaches have been used to control and treat acid mine drainage: 1) mechanical systems, 2) active (chemical) treatment systems, 3) passive treatment systems. Mechanical systems are an effective way to reduce the formation of AMD by backfilling

and covering of acid-producing materials, alkaline addition, and limiting the exposure of acid-producing materials to air and water by barriers. Active methods use chemicals such as soda ash, ammonia, caustic soda, hydrated lime, and quicklime to raise pH and precipitate metals. Although effective, active treatment is best suited for short-term AMD treatment because of its high chemical and maintenance costs.

Passive treatment systems incorporate the use of aerobic and anaerobic wetlands, anoxic limestone drains, successive alkalinity producing systems, and open limestone channels to treat water. While all function in a slightly different way, they all rely on exchange and precipitation reactions and the dissolution of limestone for AMD treatment. The open limestone channel (OLC) is the newest approach to treat AMD. It relies on limestone dissolution for acid neutralization, and even when the limestone is armored with iron, it continues to dissolve based on AMD flow and quality and other site conditions (Ziemkiewicz et al., 1997). Because of the importance of open limestone channels (OLC) in neutralizing AMD, the goal of this research was to understand the iron armoring process and to model the effect of iron on limestone dissolution in open systems.

Reference:

IEA. 1999. World energy outlook. IEA Publications, London, UK.

Skousen, J. G., and P. F. Ziemkiewicz. 1996. Acid Mine Drainage Control & Treatment. 2nd Edition. West Virginia University and the National Mine Land Reclamation Center. Morgantown, West Virginia.

USEPA. 1995. Streams with fisheries impacted by acid mine drainage in MD, OH, PA, VA and WV. Region III, Wheeling, WV.

Ziemkiewicz, P.F., J.G. Skousen, D.L. Brant, P.L. Sterner, and R.J. Lovett. 1997. Acid mine drainage treatment with armored limestone in open limestone channels. *J. of Environ. Quality*. 26(4):1017-1024.

Chapter 2. Introduction

2.1 Limestone Dissolution

Limestone is an alkaline material that neutralizes acid. Over the years, limestone has been widely used for acid mine drainage (AMD) treatment in the mining industry due to its low cost and worldwide distribution. West Virginia has a great reserve of limestone that makes it an easy and cheap resource for treating AMD and acidic spoils.

Limestone can dissolve in water to produce alkalinity and neutralize acids. The following reactions describe a solution in equilibrium with excess limestone,

Where all species are represented as activities, and K_{sp} , k_H , K_1 , and K_2 are the equilibrium constants.

In open systems, limestone neutralization of acid water involves three ranges based on pH changes (Berner and Morse, 1974). At low pH (<4.5), limestone dissolution causes the pH of the solution to increase exponentially. The second region occurs from pH 4.5 to 7, where pH of the solution increases linearly with time. In the last region, the reaction is approaching equilibrium, so the pH increases very slowly until equilibrium is reached.

In nature, many factors influence the limestone dissolution rate and its equilibrium in solutions. Temperature, CO₂ partial pressure, acidity, ion strength, limestone, flow rate, hydrology, land geography and particle coating are common factors in the study of limestone dissolution in the field. Environmental conditions such as P_{CO2} and temperature have a strong influence on limestone dissolution, and its net dissolution rate (R) is affected by each species' activity and their reaction constants (Plummer and Wigley, 1978).

$$R = k_1\alpha_{H^+} + k_2\alpha_{H_2CO_3} + k_3\alpha_{H_2O} - k_4\alpha_{Ca^{2+}}\alpha_{HCO_3^-} . \quad (2.5)$$

Where k₁, k₂ and k₃ are first order rate constants, k₄ is the function of temperature and P_{CO2}.

Hydrology, geography and water flow rates vary at AMD sources and treatment sites, and their effects on limestone dissolution should be studied independently. Therefore, the key factors that effect limestone neutralization of acid solutions in open limestone systems should be determined. Four of the key factors are: 1) the surface area of the limestone, 2) the initial and final acidity of the solution, 3) the iron concentration of the AMD, and 4) the coating or armoring of the limestone surface.

2.2 Surface Area Effects on CaCO₃ Dissolution

One of the most important factors influencing limestone neutralization is limestone surface area. To quantitatively estimate the surface area effects, the specific surface area of limestone must be determined. Due to different limestone shapes and sizes in real world AMD treatment facilities, it is difficult to quantitatively measure limestone surface area.

One way of determining the surface area of rock particles is to calculate it based on shape. Bowman (1961) derived an equation to calculate the surface area of an ellipsoid particle:

$$S = \frac{\pi c^2}{2} + \frac{\pi b}{2\sqrt{a^2 - c^2}} \left[(a^2 - c^2)E(\theta, k) + c^2 F(\theta, k) \right] \quad (2.6)$$

where S is the surface area; θ is given by inverting the expression; $F(\theta, k)$ and $E(\theta, k)$ are the incomplete elliptic integrals; a , b and c are three orthogonal lengths of limestone particle ($a \geq b \geq c$) (Fig. 2.1).

Figure 2.1 Limestone particle size

A second method of calculating surface area of angular rock particles uses shape and roughness factors. Here the surface area is determined by measuring the three orthogonal axes of each rock particle. By the developed curves relating the mean radius to specific rock sizes, Garga et al. (1991) introduced the surface area by the statistical analysis of a rock:

$$V_e = \frac{\pi}{6} abc \quad (2.7)$$

where V_e is the volume of an ellipsoid particle. For spherical-shaped particles, the surface area can be calculated by:

$$S = \pi[(a + b + c)/3]^2 \quad (2.8)$$

By estimating a particle shape factor with mathematical approximation for the surface area of an ellipsoid, the effect of particle shape and surface roughness on the

hydraulic mean radius can be quantitatively evaluated (Figure 2.2). In fact, the surface roughness has stronger influences than the shapes of crushed rocks (Sabin and Hansen, 1994), where the shape coefficient contains both the shape factor of a perfect ellipsoid and the roughness coefficient for the deviation of a real rock shape from the perfect ellipsoid (Eq.2.9):

$$r_e = R_{oblate} R_{rough} \quad (2.9)$$

where r_e is the general shape coefficient, R_{oblate} and R_{rough} are the factors of a perfect ellipsoid particle and a rough rock different from a perfect ellipsoid, respectively.

$$R_{oblate} = \frac{A_{vs}(\text{for a perfect ellipsoid})}{A_{vs}(\text{for a sphere with a diameter } b)} \approx \frac{S}{\pi a c} \quad (2.10)$$

Figure 2.2. Qualitative interpretation of surface roughness and oblateness of a particle.

Although the shape of a limestone particle affects its surface area, Garga et al. (1991) have shown that the mass-specific surface area (A_{MS}) of a limestone sample can be estimated by:

$$A_{MS} = \frac{3.89}{b^{1.08}} \quad (2.11)$$

Where A_{MS} is specific surface area and b is the average length of the intermediate orthogonal axes (Figure 2.1).

2.3 Iron and coating effects on limestone neutralization

In coal mining areas, iron is commonly found in acid mine drainage as a result of the oxidation of pyrites. The limestone neutralization of acid solutions containing iron is very different from that of hydrogen acid solutions. Iron not only increases acidity of an acid solution and consumes more limestone, but it also forms a coating on limestone surfaces to hinder limestone dissolution.

Studies show that iron precipitation on limestone surfaces forms fine ferric hydroxide particles (Schwertmann and Murad, 1983). These ferric hydroxide particles accumulate and form a coating layer on the limestone surface. X-ray diffraction analysis showed the components and composition of coating minerals that is dependent on the pH of solutions. Poorly crystalline ferrihydrite (FeO-OH) was the predominant solid product in the neutralization of acid solutions by calcite (Schwertmann and Murad, 1983). Loeppert et al. (1984) found that lepidocrocite ($\gamma\text{FeO-OH}$) and goethite ($\alpha\text{FeO-OH}$) dominated the iron coating of limestone in solutions containing ferrous iron. In the $\text{Fe}(\text{ClO}_4)_3$ system, crystalline iron oxides partially coated the calcite surface, and simple iron species subsequently precipitated on existing FeOOH nuclei on the limestone surface (Loeppert et al., 1984).

Past assumptions have held that armored limestone (limestone covered or coated with Fe or Al hydroxides) ceased to dissolve, but experiments showed that coated limestone continues to dissolve at about 20% of the rate of unarmored limestone (Pearson

and McDonnell, 1977). More work has demonstrated that the rate for armored limestone may be even higher (Ziemkiewicz et al., 1997), but continued dissolution probably depends on pH, thickness of coating, and other variables.

Ziemkiewicz et al. (1994) set up the first order dissolution model to describe limestone dissolution rate:

$$\ln \frac{C_F}{C_0} = -kt \quad (2.13)$$

Where t is the retention time, the initial acid concentration is C_F and final acidity is C_0 , and k is the first order reaction constant. Ziemkiewicz et al. (1997) found armored limestone in a series of laboratory experiments was 50 to 90% as effective as unarmored limestone in neutralizing acid. Ziemkiewicz et al. (1994) suggested that armored limestone was only 50% as effective as unarmored limestone. The length of the channel and the channel gradient, which affects turbulence and the buildup of coatings, are design factors that can be varied for optimum performance. Ziemkiewicz et al. (1997) also indicated that optimum performance was attained on slopes exceeding 20%, where flow velocities keep precipitates in suspension and, during high flow events containing high amounts of sediment, clean precipitates from limestone surfaces. In appropriate situations, OLCs are being implemented for long term acid mine drainage treatment. Utilizing OLCs with other passive systems can maximize treatment and metal removal.

2.4 Open Limestone System Design Criteria

Open limestone channel design and sizing criteria are currently based on the length of time required for armored limestone (20% as effective as unarmored limestone) to neutralize the acidity in the AMD. The total amount of limestone in a channel is solely based on acid load (flow x acid concentration) and this number is multiplied by 5 to correct for the armoring effect. This amount of limestone is then configured into a channel where AMD flows along its length for a specified residence time to neutralize the acid. Based on channel lengths and cross sectional areas that together dictate residence

time for acid neutralization, Ziemkiewicz et al. (1994) developed an AMD/Time Spreadsheet to estimate AMD treatment effect and cost for open limestone channels, which has been widely used in AMD treatment estimation. In this model, there is no quantitative consideration of channel slope, limestone particle sizes, flow rate, or the effects of various coating thickness on the limestone. Thus, it is difficult to accurately predict the outlet water quality in both fresh and armored open limestone channels, and it is impossible to estimate the effective lifespan of a limestone channel.

2.5 Objectives

The objectives of this research were:

- 1) to determine acid neutralization by different-sized limestone particles and to evaluate the effects of surface area on limestone dissolution;
- 2) to evaluate the effects of initial and final acid concentrations (pH and iron concentration) on limestone dissolution;
- 3) to assess the effects of iron coating thickness and mineralogy on limestone dissolution;
- 4) to develop a model (spreadsheet) incorporating these variables to more accurately design open limestone channels for acid drainage treatment.

References

- Berner, R. A. and J. W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water. *Am. J. of Sci.* 274:108-134.
- Bowman, F. 1961. *Introduction to Elliptic Functions with Applications*. Dover, New York.
- Garga, V. K., R. Townsend, and D. Hansen. 1991. A method for determining the surface area of quarried rocks. *Geotech. Testing J.* 14(1):35-45.

- Loeppert, R. H., L. R. Hossner, and P. K. Amin. 1984. Formation of ferric oxyhydroxides from ferrous and ferric perchlorate in stirred calcareous systems. *Soil Sci. Soc. Am. J.* 48:677-683.
- Pearson, F. H. and A. J. McDonnell. 1977. Characterization of coarse porous media. *J of the Env. Eng. Div., ASCE*, Vol. 103:615-624.
- Plummer, L. N. and T. M. L. Wigley. 1978. The kinetics of calcite dissolution in CO₂-water systems at 5° to 60° and 0 to 1.0 atm CO₂. *American Journal of Science*, Vol.278:179-216.
- Sabin, G. C. W., and D. Hansen. 1994. The effects of particle shape and surface roughness on the hydraulic mean radius of a porous medium consisting of quarried rock. *Geotech. Testing J.* 17(1): 43-49.
- Schwertmann, U., and E. Murad. 1983. Effect of pH on the formation of goethite and hematite from ferrihydrite. *Clays and Clay Minerals*. Vol. 31(4):277-28.
- Ziemkiewicz, P.F., J.G. Skousen, and R. Lovett. 1994. Open limestone channels for treating acid mine drainage: a new look at an old idea. *Green Lands* 24(4):36-41.
- Ziemkiewicz, P.F., J.G. Skousen, D.L. Brant, P.L. Sterner, and R.J. Lovett. 1997. Acid mine drainage treatment with armored limestone in open limestone channels. *J. of Environ. Quality*. 26(4):1017-1024.

Chapter 3. Limestone Surface Area and Initial Acidity Effects on Acid Treatment in Open Limestone Channels

Abstract

The neutralization rate of acid solutions with limestone is controlled by initial acidity of the solution, reaction time, and limestone surface area. Limestone surface area depends on the shape and roughness of the particles. Despite the importance of surface area in the acid neutralization process, surface area is not a consideration when designing open limestone channels for the neutralization of acid mine drainage, principally because there is no simple way to measure the surface area of coarse media. The objective of this study is to model the relationship between surface area, reaction time and solution acidity in a simplified system, and to demonstrate the importance of surface area when designing acid treatment systems. The required reaction time is directly related to the surface area according to the power function, $t = aA_{MS}^k$; where A_{MS} is the limestone's mass specific surface area, a and k are constants based on initial acidity and final acidity. By use of the derived equation, the outlet water acidity in an open limestone channel can be determined when only proton acidity is present. In addition, open limestone channels can be designed with specified limestone particle sizes and channel length to optimize solution acidity leaving the channels.

Introduction

It has been recognized for years that the dissolution rate of limestone is controlled by surface area (Berner, 1974). Although several investigators have measured the effect of particle size on neutralization rate in the laboratory (Maree et al., 1992, Economou et al., 1996) or speculated on the role of surface area in real systems (Evangelou et al., 1998), surface area effects are seldom considered in the design of acid neutralizing systems. For example, open limestone channels for AMD treatment are typically designed by calculating the mass of limestone needed to neutralize a given quantity of acid, and multiplying by a correction factor (e.g. 10–20 times the annual acid load). The reason for this is that there is no simple method to calculate the surface area of a limestone sample.

For coarse materials, surface area can be estimated using a shape factor and some representative length or from statistical derivation based on some representative length (Allen, 1975). Different methods may give different results for the same-sized materials (Allen, 1975). The physical or chemical adsorption methods based on the well-known Brunauer, Emmett and Teller (B.E.T.) equation used to measure the surface area of fine particles are not appropriate because of the low specific surface area of coarse particles. Coating methods such as the use of nickel or saran ignore surface roughness (Garga et al., 1991). Though microscopes can observe every surface of macro particles, statistical methods must be used to determine the particle size distribution. For example, industry often uses the shape coefficient to estimate the surface area for large (1-50 mm) mineral particles, especially for coal, dolomite, silica, diamonds, etc (Allen, 1975).

Although the shape of a particle affects its surface area, Garga et al. (1991) have shown that the mass-specific surface area of a limestone sample can be estimated by:

$$A_{MS} = \frac{3.89}{b^{1.08}} \quad (1)$$

Where, b is the average length of the intermediate orthogonal axis (Figure 3.1). Sabin and Hansen (1994) used the diameter ($\bar{d}$) and surface area (S) of a sphere of

equivalent volume, and a shape factor (r_e) to determine the volume and specific surface area of crushed rock. The shape factor was given as:

$$r_e = R_{oblate} R_{rough} \quad (2)$$

Figure 3.1. Representation of orthogonal axis.

where r_e is the general shape coefficient; R_{oblate} represents deviations of an ellipsoid rock from a perfect sphere and R_{rough} represents the deviations of an actual rock from an ellipsoid. The surface area of an actual rock was then calculated as (Sabin and Hansen, 1994):

$$S_A = r_e S \quad (3)$$

Previous studies on limestone neutralization primarily focused on a single parameter such as surface area, temperature, P_{CO_2} , or water acidity; the interaction among these factors was not reported. For fresh limestone, no effective models have been developed to describe the interaction of limestone surface condition, water retention time, and water acidity during the neutralization process. So, it is difficult to quantitatively predict limestone consumption and assess the treatment effects at AMD treatment sites using limestone for acid neutralization. Therefore, it is difficult to accurately predict the outlet water quality after passage through limestone treatment systems.

Quantitatively defining the effects of limestone particle size and water retention time on acidity changes is a potentially useful contribution to the design of an effective AMD limestone treatment system. By modeling optimal limestone size based on its surface area, hydrogen ion concentration, and the reaction time, a limestone treatment

system such as an open limestone channel can be designed with the optimal length (retention time) and limestone particle size distribution to optimize its outlet water quality or final acid concentration. Based on this derived relationship, when any three of the four factors (initial acidity, limestone particle sizes, retention time and final pH) are known, the fourth can be calculated. The objective of this research was to model these relationships by using data from laboratory experiments.

Materials and Methods

Laboratory experiments were conducted using different sized and shaped limestone to neutralize acid solutions. All limestone came from Germany Valley, West Virginia, which has a CaCO_3 equivalent of about 98.5% (Zurbuch, 1996). Ellipsoidal limestone from the Blackwater River Limestone Drum Station, which were originated from Germany Valley, was sieved into five diameter classes (2.0~4.75, 4.75~6.3, 6.3~11, 11~19 and 19~25 mm) and washed with dilute HCl acid and deionized water.

The volume (V), number of particles (n), and exact mass (m) of an approximately 100 g sample of each size class was determined. The average equivalent spherical diameter ($\bar{d}$) was calculated as,

$$\bar{d} = \sqrt[3]{\frac{6V}{n\pi}} \quad (4)$$

and the shape factor was calculated using Equation 2. Because the limestone particles were smooth and ellipsoidal, R_{rough} was set to 1 and R_{oblate} was estimated to be 1.90. The total surface area of the sample was calculated as:

$$S_A = \pi \bar{d}^2 n \quad (5)$$

and the spherical limestone mass-specific surface area (A_{MS}) is:

$$A_{MS} = \frac{n\pi\bar{d}^2}{m} \quad (6)$$

Considering the actual rock factor (R_{oblate} 1.90), the mass specific area (A_{MS}^0) of limestone particles may be estimated by the following:

$$A_{MS}^0 = \frac{n\pi\bar{d}^2}{m} R_{oblate} \quad (7)$$

Batch experiments were designed to use the ellipsoidal limestone to neutralize 400 mL of a stirred HCl acid solution in a 600-mL beaker. During the experiment, small solution samples (0.9 mL) were taken at predetermined time intervals and analyzed. The pH of the solution was measured at the time of extraction (Accumet 25 pH meter, Fisher Scientific Company, Accu-pHast Electrode), and the withdrawn samples were analyzed for Ca concentration with either Inductively Coupled Plasma (Perkin Elmer P4000) or Atomic Absorption Spectroscopy (Perkin Elmer 5000).

Results and Discussion

The smaller-sized particles had larger mass-specific surface area and, since mass was constant, larger total surface area (Table 3.1). Based on a correspondence between average sieve size (d) and average diameter ($\bar{d}$), an equation similar to Equation 1 was derived:

$$A_{ms} = 3.6635d^{-0.9828} \quad (8)$$

where A_{ms} is mass-specific surface area of ellipsoid limestone, and d is the average sieve size. In comparing Equations 1 and 8, the only difference is that the average sieve size (d) replaces b , the average length of intermediate axis.

Table 3.1. Limestone specific surface area vs. particle sizes $\bar{d}$.

Sieve Sizes	n	V	Mass	$\bar{d}$	Total S	Specific A_{MS}
mm		cm ³	g	mm	cm ²	cm ² /g
2.0~4.75	820	37.0	100.0	4.4	507.8	9.7
4.75~6.3	270	37.0	99.9	6.4	349.6	6.7
6.3~11.0	74	36.9	99.7	9.9	226.9	4.3
11.0~19.0	15	37.2	100.6	16.9	134.3	2.5
19.0~25.0	4	37.2	100.6	26.2	86.4	1.6

n = the number of 100 g limestone particles; V=volume of 100 g limestone particles;
 $\bar{d}$ =average diameter of particles; Total S= total surface area of limestone particles.

The importance of surface area is illustrated in Figure 3.2. Both systems have the same initial pH (3.0) and the same equilibrium pH (8.2), but the paths to that equilibrium are very different. For example, it takes 2.3 times longer to reach pH 7 when average sieve size increased from 3.4 to 22 mm (or 9.7-1.6 cm²/g). Table 3.2 contains the observed reaction time required to reach a specific destination pH for several initial pH and surface area combinations.

Figure 3.2. Ellipsoid limestone particle size classes effects on neutralization of 0.001 M acid solution.

Table 3.2. Required retention time in minutes for an initial acid solution of pH 2.0, 2.5, 3.0, 3.5, and 4.0 to be increased to a final pH of 5.5, 6.0, 6.5, and 7.0.

Specific A_{MS} cm^2/g	Final pH 5.5				
	pHi=2.0	pHi=2.5	pHi=3.0	pHi=3.5	pHi=4.0
	-----		min	-----	
9.7	40	23	14	8	3
6.7	48	30	16	10	4.5
4.3	65	40	21	15	5.5
2.5	100	60	50	25	6
1.6	130	90	58	42	17
a	183.2	125.7	94.2	62.6	19.2
k	-0.68	-0.76	-0.89	-0.94	-0.83
Final pH 6.0					
9.7	77	37	22	13	4
6.7	93	55	24	15	7
4.3	130	75	43	20	8
2.5	175	95	54	33	10
1.6	180	125	75	52	22
a	256.2	178.7	108.4	71.1	27.9
k	-0.51	-0.65	-0.72	-0.79	-0.83
Final pH 6.5					
9.7	220	90	37	24	7
6.7	255	110	44	26	9
4.3	255	140	58	31	12
2.5	265	160	83	47	14
1.6	270	190	105	75	24
a	281.1	273.9	142.3	91.3	29.8
k	-0.09	-0.41	-0.60	-0.64	-0.64
Final pH 7.0					
9.7	400	240	75	36	11
6.7	410	240	84	37	15
4.3	420	250	95	45	16
2.5	415	260	125	70	17
1.6	440	270	155	100	30
a	443.6	278.1	184.2	123.9	32.6
k	-0.04	-0.07	-0.41	-0.60	-0.47

The initial acidity of the solution also showed a strong influence on the required reaction time. High acidity or low pH solutions required more time than did high initial pH or lower acidity solutions. By regressing reaction time against initial pH and limestone specific surface area, we attained the general equation:

$$t = aA_{MS}^k \quad (9)$$

where t is reaction time (min), k is the regressed exponential constant for every initial pH_i , a is the regressed coefficient constant for every initial pH_i , and A_{MS} is limestone specific surface area (cm^2/g).

Tabulated values for a and k are listed in Table 3.2, and Equations 10 and 11 are general functions for k and a :

$$k = k_1 pH_i + k_2 \quad (10)$$

$$a = a_1 pH_i + a_2 \quad (11)$$

where a_1 and a_2 are the constants related to the final pH ; k_1 and k_2 are the constants corresponding to the final pH ; and pH_i is the initial pH .

Combining equations 9, 10 and 11, the general equation of the reaction time for acid neutralization by limestone to attain each of four destination pH values was determined (Table 3.3). Thus, the increase of specific surface area of limestone results in shorter reaction time, translating into a faster reaction rate. As the initial acidity increases (or pH decreased), the reaction time to reach pH 5.5 increases. Even though low pH solutions reacted faster with limestone, the increase in the amount of acid to be neutralized required more time.

Table 3.3 Regressed equations for retention time function of initial pH and limestone specific surface area.

Final pH	Regressed function $a=a_1pH_i + a_2$	Regressed k function $k=k_1pH_i + k_2$	General Equation $t = aA_{MS}^k$
5.5	$a = -78.234pH_i + 331.7$ ($R^2=0.987$)	$k = -0.0952pH_i - 0.5343$ ($R^2=0.53$)	$t = (331.7 - 78.234pH_i)A_{MS}^{-0.0952pH_i-0.5343}$
6.0	$a = -112.82pH_i + 466.92$ ($R^2=0.975$)	$k = -0.1535pH_i - 0.2415$ ($R^2=0.946$)	$t = (466.92 - 112.82pH_i)A_{MS}^{-0.1535pH_i-0.2415}$
6.5	$a = -137.06pH_i + 574.84$ ($R^2=0.947$)	$k = -0.2642pH_i + 0.314$ ($R^2=0.795$)	$t = (574.84 - 137.06pH_i)A_{MS}^{-0.2642pH_i+0.314}$
7.0	$a = -195.25pH_i + 798.22$ ($R^2=0.965$)	$k = -0.2758pH_i + 0.5081$ ($R^2=0.767$)	$t = (798.22 - 195.25pH_i)A_{MS}^{-0.2758pH_i+0.5081}$

From Table 3.3, we derived the general equation (Eq. 12) for the required reaction time to neutralize the acidity from an initial to final pH.

$$t = aA_{MS}^k = (a_1 pH_i + a_2) A_{MS}^{k_1 pH_i + k_2}$$

$$a_1 = -75.058 pH_f + 338.27$$

$$a_2 = 0.8053 pH_f^{3.5346}$$

$$k_1 = -0.1305 pH_f + 0.6185$$

$$k_2 = 0.7365 pH_f - 4.5918$$

$$t = \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} \quad (12)$$

Where pH_f is the final pH and pH_i is initial pH, and A_{MS} is mass specific surface area.

So, whenever the outlet acidity (or pH_f) and inlet water acidity (or pH_i) of an acid solution is fixed, the required reaction time can be determined for specified limestone particle sizes. Once we know the limestone particle sizes, the length, width and depth of a limestone bed can be determined for an open limestone channel by Equation 12.

Example

To show how Equation 12 can be used to optimize a limestone treatment system, the following example is given. Suppose an acid source has 1000 L/min of effluent with an initial pH of 3.0 and no iron (acidity 10^{-3} M or 50 mg/L as $CaCO_3$). If the final pH is designated as 7.0, the open limestone channel is designed for 10 years and the retention time is 60 minutes, the final pH and the limestone consumption can be predicted at any time during the life of the open limestone channel.

Acid load:

$$A = 10^{-\text{pH}_0} \left(\frac{\text{eq}}{\text{L}} \right) Q \left(\frac{\text{L}}{\text{min}} \right) * 365 \left(\frac{\text{days}}{\text{year}} \right) * 24 \left(\frac{\text{hr}}{\text{day}} \right) * 60 \left(\frac{\text{min}}{\text{hr}} \right) * 50 \left(\frac{\text{g}}{\text{eq}} \right)$$

$$= 26,280,000 \text{ g CaCO}_3/\text{year}.$$

The total required limestone for 10 years is:

$$W_0 = 10 * A = 262,800,000 \text{ g} = 262,800 \text{ kg}.$$

Optimized limestone surface area is (Eq. 12):

$$A_{MS0} = \left(\frac{t(\text{min})}{(-75.08 \text{pH}_f + 338.27) \text{pH}_i + 0.8053 \text{pH}_f^{3.5346}} \right)^{\frac{1}{(-0.1305 \text{pH}_f + 0.6185) \text{pH}_i + 0.7365 \text{pH}_f - 4.5918}}$$

$$= 55.91 \text{ cm}^2/\text{g}$$

The optimal sieve size of limestone particles is (Eq. 8):

$$d_0 = \left(\frac{A_{MS} \left(\frac{\text{cm}^2}{\text{g}} \right)}{3.6635} \right)^{\frac{1}{0.9828}} = \left(\frac{59.91}{3.6635} \right)^{\frac{1}{0.9828}} = 0.0614 \text{ cm}$$

Total surface area:

$$S_0 = A_{MS0} \left(\frac{\text{cm}^2}{\text{g}} \right) * W_0(\text{g}) \approx 1.57 * 10^{10} \text{ cm}^2$$

After running for one year, the limestone loss is A and limestone remaining is W_1 :

$$A = (10^{-\text{pH}_i} - 10^{-\text{pH}_1}) Q * 365 * 24 * 60$$

$$W_1 = W_0 - A$$

$$\text{Since } 10^{-\text{pH}_i} \gg 10^{-\text{pH}_1}, W_1 \approx W_0 - A = \left(1 - \frac{1}{10} \right) W_0.$$

So, one tenth of the limestone mass is lost in the first year, which results in a volume decrease of 1/10. Thus, the average diameter and the total surface area in the end of the first year are:

$$d_1 = \left(1 - \frac{1}{10}\right)^{\frac{1}{3}} d_0 = 0.059 \text{ cm}$$

$$S_1 = \left(1 - \frac{1}{10}\right)^{\frac{2}{3}} S_0 = 1.46 * 10^{10} \text{ cm}^2$$

In the second year, limestone loss will again be about 1/10 or 52560000g ($10^{-pH_i} \gg 10^{-pH_1}$), so the remaining limestone will be only about 80% of the original mass. $W_2 \approx (1 - 2 * 10\%) W_0$.

For any year n, the mass, diameter and surface area is given as:

$$W_n \approx (1 - n * 10\%) W_0$$

$$d_n = \left(1 - 10\% * n\right)^{\frac{1}{3}} d_0$$

$$S_n = \left(1 - 10\% * n\right)^{\frac{2}{3}} S_0$$

Calculations for years 0 to 10 are given in Table 3.4.

Table 3.4. Limestone surface area decreases as the limestone mass decreases during the life of the open limestone channel.

Time	Mean Diameter	LS Mass	Total surface area	Surface area changes S/So
Year	cm	kg	$\times 10^{10} \text{ cm}^2$	%
0	0.061	262800	1.57	100
1	0.059	236520	1.46	93
2	0.057	210240	1.35	86
3	0.055	183960	1.24	79
4	0.052	157680	1.12	71
5	0.049	131400	0.99	63
6	0.045	105120	0.85	54
7	0.041	78840	0.70	45
8	0.036	52560	0.54	34
9	0.029	26280	0.34	22
10	0.000	0	0.00	0

As limestone is continually removed from the system, the particle size and total surface area remaining must decrease. Given the relationship between neutralization rate

and particle size for a fixed reaction time (Figure 3.2 and Eq. 12), the outlet pH must decrease (Figure 3.3).

Figure 3.3. The outlet water quality changes with time at different particle size and an initial pH 3.

Figure 3.4. The outlet water quality changes with time at different initial pH value and optimal particle size ($d=0.6\text{mm}$) or larger particle size ($d=10\text{mm}$).

Since AMD treatment systems must discharge water at $\text{pH} > 6$, the expected life of the optimized system would be 7 years. Note that this is less than the original calculated 10 years based only on limestone mass. The effect of larger particle size and lower influent pH on this system are given in Figures 3.3 and 3.4. If larger limestone particles (sieve size 10 mm) are used in this example to build an open limestone channel, its effective lifetime for acid neutralization is about 4 years.

Conclusion

The neutralization of acid solutions by limestone is a surface-controlled reaction and limestone dissolution rate primarily depends on the limestone surface area and initial pH of the solution. Limestone particle size and shape determine the limestone mass specific surface area, which in turn affects limestone reaction surface in an open limestone treatment system. The required contact time between limestone and the acid solution is determined by the initial and final pH of the solution and the limestone specific surface area, $t = aA_{MS}^k$; where k and a are determined by the initial and final acidity of the acid solution.

These equations, incorporating reaction time, limestone surface area, and initial and final pH, can be used to design an open limestone channel. If the initial pH and final pH of an AMD are known, the optimal limestone particle size and the dimensions of an open limestone channel can be selected. The effective life and the final pH of an open limestone channel can be predicted at any time from these equations. On the other hand, if we know the initial acidity of an acid mine drainage passing through an open limestone channel of specified length and particle size, the outlet water pH can be predicted based on the retention time. However, the economic factors of limestone size and amount should be considered when designing a limestone treatment system, as fine particles cost more to crush and prepare.

All these calculations and estimations can only be used for fresh open limestone channels. If a coating develops over limestone surfaces (like iron armoring), these equations should be corrected because the effective surface area changes.

References

- Allen, T. 1975. Particle Size Measurement. 2nd Edition. John Wiley & Sons, New York.
- Berner, R. A., and J. W. Morse. 1974. Dissolution kinetics of calcium carbonate in sea water. *American J. of Sci.* 274:108-134.
- Economou, E. D., N. P. Evmiridis, and A. G. Vlessidis. 1996. Dissolution kinetics of CaCO_3 in powder form and influence of particle size and pretreatment on the course of dissolution. *Ind. Eng. Chem. Res.* 35:465-474.
- Evangelou, V. P. 1998. *Environmental Soil and Water Chemistry: Principles and Applications*. Wiley, New York.
- Garga, V.K., R. Townsend, and D. Hansen. 1991. A method for determining the surface area of quarried rocks. *Geotech. Testing J.* 14(1):35-45.
- Maree, J. P., P. D. Plessis, and C. J. Van der Walt. 1992. Treatment of acidic effluents with limestone instead of lime. *Wat. Sci. Tech.* 26(1-2):345-355.
- Pearson, F. H., and A. J. McDonnell. 1977. Characterization of coarse porous media. *J. of the Environ. Eng. Division, ASCE.* 103:615-624.
- Sabin, G. C. W., and D. Hansen. 1994. The effects of particle shape and surface roughness on the hydraulic mean radius of a porous medium consisting of quarried rock. *Geotech. Testing J.* 17(1): 43-49.
- Zurbuch, P. E. 1996. Early results from calcium carbonate neutralization of two West Virginia rivers acidified by mine drainage. p. L1-L9. In *Proc. of the Seventeenth Annual West Virginia Surface Mine Drainage Task Force Symposium*. Morgantown, WV.

Supporting Information

Figure 3.5. The specific surface area vs. the size of sieved limestone.

$$\begin{aligned} \text{pHi } 2.0: t &= 183.21 A_{\text{MS}}^{-0.6867} \quad R^2 = 0.9952 \\ \text{pHi } 2.5: t &= 125.74 A_{\text{MS}}^{-0.7583} \quad R^2 = 0.9965 \\ \text{pHi } 2.0: t &= 94.232 A_{\text{MS}}^{-0.8928} \quad R^2 = 0.9432 \\ \text{pHi } 2.0: t &= 62.598 A_{\text{MS}}^{-0.9405} \quad R^2 = 0.9911 \\ \text{pHi } 2.0: t &= 19.196 A_{\text{MS}}^{-0.8277} \quad R^2 = 0.8484 \end{aligned}$$

Figure 3.6. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 5.5.

Figure 3.7. Reaction constant k and a vs. the initial pH.

Figure 3.8. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 6.0.

Figure 3.9. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 6.5.

Figure 3.10. The reaction time required for various acid solutions (pHi 2.0~4.0) neutralized by different limestone surface areas to attain pH of 7.0.

Chapter 4. Iron Effects on Limestone Dissolution in Open Systems

Abstract

The chemical composition and metal concentrations of acid solutions have a significant influence on limestone dissolution rate. Metals, like iron, in water can be neutralized by limestone, but the limestone surface may be coated, thereby limiting its surface area for reaction. This study reports the relationships between limestone neutralization of acid solutions containing iron and without iron in order to set up empirical limestone neutralization models. In open air systems, the required reaction time (t) for a proton-only acid solution to be neutralized to a destination pH is predicted by $t = aA_{MS}^k$, where t is the function of initial pH, final pH and limestone mass-specific surface area. However, the batch experiments showed that the neutralization reactions with iron-containing water required more time. The required reaction times were modified with the function, $t(Fe) = t(Fe = 0) + (42 \ln[Fe] + 35.1)pH_f - 176 \ln[Fe] - 143$, where $t(Fe)$ is the required reaction time for iron acid solution; $t(Fe=0)$ is the reaction time for proton-only acid solutions, $[Fe]$ is iron concentration, and pH_f is the final pH. In addition, the limestone requirement to neutralize iron acid solutions is calculated by $[Ca]_{Fe} = 0.309C_T + 0.27[Fe^{3+}]_i + 0.448$, where $[Ca]_{Fe}$ is total dissolved Ca in mmol/L, C_T is total initial acidity (meq/L), and $[Fe^{3+}]_i$ is initial iron concentration (mmol/L).

Introduction

Limestone neutralization of acid solutions in an open-air system may be summarized by the following Equations 1 and 2. Each plays a different role during the neutralization process, which is mainly controlled by acidity (or pH), limestone surface area, temperature, ionic strength, and ion species and concentration.

When the solution has low pH, almost all the dissolved CO_3^{2-} forms H_2CO_3 , which may quickly change into CO_2 gas and be released from solution. During this period, Equation 2 dominates limestone dissolution. As pH rises, CO_3^{2-} begins to form HCO_3^- and CO_2 gas is released less and less. At high pH, Equation 1 becomes dominant where almost no CO_2 gas is released.

Limestone dissolution is a solid-liquid reaction, so many factors, such as diffusion, temperature, ionic strength, and CO_2 partial pressure may affect its reaction. The ion species and their activities effects on the dissolution of $CaCO_3$ were presented by the net dissolution rate (Plummer and Wigley, 1978):

$$R = k_1\alpha_{H^+} + k_2\alpha_{H_2CO_3} + k_3\alpha_{H_2O} - k_4\alpha_{Ca^{2+}}\alpha_{HCO_3^-} \quad (3)$$

where R is net dissolution rate, k_1 , k_2 and k_3 are first order rate constants, k_4 is the function of temperature and P_{CO_2} , α_{H^+} , $\alpha_{Ca^{2+}}$, $\alpha_{H_2CO_3}$, α_{H_2O} , and $\alpha_{HCO_3^-}$ are activities of species.

Dissolved metals have significant influences on limestone neutralization of acid solutions, and dissolved aluminum and iron may increase acidity of AMD (Broshears et al., 1996). Iron is the most common dissolved metal in AMD. Acid solutions containing

iron consume more limestone than proton acid solutions because of iron hydrolysis and precipitation (Eq. 4 or 5).

Iron hydrolysis reactions are pH buffered near pH 3.5. Therefore, the concentrations of ferric ion in acid solutions may affect limestone dissolution rate as well as the increase of pH with neutralizing time. Loeppert et al. (1984) showed iron effects on the neutralization of acid solutions. Solution pH decreased slightly initially due to iron hydrolysis and then gradually increased to its equilibrium during the neutralization of iron acid solutions by limestone.

Iron not only increases the acidity of solutions and neutralization time, but it also can armor the surface of limestone. Once limestone is coated with iron hydroxides, limestone dissolution rate decreases from 20% to 90% of its fresh uncoated state (Pearson and McDonnell, 1977; Ziemkiewicz et al., 1994). Thus, the neutralization of iron acid solutions by limestone will require more reaction time due to iron effects on reaction surfaces and reaction rate.

The objective of this study was to model the neutralization of iron acid solutions by limestone particles. By comparing the neutralization of proton acid solutions with iron acid solutions, the interactions among acid levels, limestone particle sizes, and iron concentration were quantitatively accounted for. The desired equation will allow more accurate limestone requirements to neutralize iron containing acid solutions. This will help design of limestone amount and particle sizes for the treatment of AMD containing iron in open limestone systems

Materials and Methods

All limestone for our laboratory experiments came from Germany Valley, West Virginia, which has a CaCO_3 equivalent of 98.5% (Zurbuch, 1996). Crushed limestone

was prepared by crushing separate samples of limestone with a Jaw Crusher and sieving into the same size classes (6-11 mm). Flat, square limestone blocks (38 x 38 x 8 mm) were prepared by cutting large blocks of limestone with a rock saw. A single 35x35 mm surface was isolated by dipping the block in liquid Saran and drying at 105°C.

Batch experiments were designed to use 100 g of the crushed limestone chips or eight pieces of square limestone blocks to neutralize 400 mL of the stirred acid solution with iron and without iron in a 600-mL beaker. A series of ferric acid solutions (pH ranged between 2.0 and 3.0) were made with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and de-ionized water. The pH, calcium, and iron concentrations were measured over time as the neutralization experiments progressed. At each time interval, a 0.9-ml sample was taken, filtered with a 0.45- μm syringe-operated filter (Millipore), and diluted with 4.1ml of 2% HNO_3 . These acidified samples were analyzed for Ca and Fe concentrations with either Inductively Coupled Plasma (Perkin Elmer P4000) or Atomic Absorption Spectroscopy (Perkin Elmer 5000). The pH of the solution was measured by an Accumet pH meter 25 (Fisher Scientific Company, Accu-pHast Electrode).

Results and Discussion

During the neutralization of iron acid solutions, the increase of pH led ferric ion to form iron hydroxides and precipitate from solution. Since iron hydrolysis and complexation occur simultaneously, it is impossible to separate iron hydroxide formation from hydrolysis or limestone neutralization. Thus, the results show that total iron concentration changes with time (Figure 4.1). The total iron concentration in the solution remained unchanged during an initial period but then suddenly declined rapidly, where iron precipitation time depended on the initial iron concentrations and pH.

Figure 4.1. Fe concentration of various iron solutions being neutralized by limestone.

Figure 4.2. pH vs. time in iron acid solutions.

Figure 4.3. Dissolved Ca vs. time in iron acid solution.

Figure 4.4. The reaction time difference of pH reaching 5.5, 6.0 and 6.5 vs. ferric concentration by 6.3-11 mm ellipsoid limestone.

The results of pH changing with time in iron acid solutions presented different trends from proton acid solutions (Figure 4.2). During the neutralization of proton acid

solutions, pH increases continually with time until reaching the equilibrium. In iron acid solutions, pH increase was caused by limestone dissolution during the first 10-20 minutes. Then, pH began decreasing but limestone was still dissolving (Figure 4.3). The length of this period depended on the iron concentration. The higher the iron concentration, the longer the period and the lower the pH went. These buffering processes were caused by iron hydroxide. After these lag periods with decreasing pH, pH began increasing again until its equilibrium. Thus, the required reaction time of pH increasing to a final pH should be corrected for iron concentration.

The experimental data (Figure 4.4) showed that a linear relationship existed between the required time for neutralization of iron acid solutions and hydrogen acid solutions with identical initial pH as Equation 6.

$$\Delta t = t(Fe) - t(Fe = 0) = (42 \ln[Fe] + 35.1)pH_f - 176 \ln[Fe] - 143 \quad (6)$$

$$t(Fe) = t(Fe = 0) + (42 \ln[Fe] + 35.1)pH_f - 176 \ln[Fe] - 143 \quad (7)$$

where Δt is the difference of the retention time between iron acid solution neutralization, $t(Fe)$ is the required reaction time for iron acid solutions, $t(Fe=0)$ is reaction time for hydrogen acid neutralization, and pH_f is the final outlet pH.

According to the previous derived equations $t = aA_{MS}^k$ (Chapter 3, Eq. 12) for hydrogen acid solution neutralization, the required reaction time for iron acid solutions to be neutralized to a certain specified pH is:

$$t(Fe = 0) = \left[(-75.08pH_f + 338.27)pH_i + 0.8053pH_f^{3.5346} \right] A_{MS}^{(-0.1305pH_f + 0.6185)pH_i + (0.7365pH_f - 4.5918)} \quad (8)$$

So, the required reaction time that limestone particles with a mass specific surface area to neutralize iron acid solutions to a final pH is:

$$t(\text{Fe}) = \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} + (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 \quad (9)$$

where pH_f is the final outlet pH, t is the required reaction time (min), pH_i is initial pH of the acid solution, A_{MS} is the mass specific surface area of limestone particles, and $[Fe]$ is ferric iron concentration of the acid solution (mmol/L).

Iron hydrolysis and precipitation generated more hydrogen, so iron acid solutions need more time to neutralize the acidity. Generally speaking, higher iron concentration causes an increase in limestone dissolution due to the increase of hydrogen acid from iron hydrolysis and precipitation. The presence of iron makes limestone dissolution more complicated, so the limestone dissolution can be derived from the total dissolved calcium concentration (Figure 4.3).

With limestone neutralization of acid solutions without iron, the total dissolved Ca should relate linearly to the total initial acidity of a solution. The total acidity of iron acid solutions (Table 4.1) was calculated by Equation 10.

$$C_T = [H^+] + 3[Fe^{3+}] \quad (10)$$

Where C_T is total acidity (meq/L); $[H^+]$ is initial hydrogen concentration (mmol/L); and $[Fe^{3+}]$ is ferric ion concentration (mmol/L). A plot of the total dissolved calcium concentration vs. the total acidity shows the difference between the required limestone for proton acid solution and iron acid solutions (Figure 4.5).

Table 4.1. Calculation of total acidity of five iron solutions with pH between 2.4 and 3.0.

pH_i	$[H^+]_i$	$[Fe]_i$	$[Ca]$ Final	C_T
	-----	mmol/L	-----	meq/L
3.00	1.00	0	0.96	1.00
2.97	1.06	0.55	1.42	2.70
3.01	0.99	1.07	1.82	4.19
2.99	1.03	2.16	3.56	7.50
2.70	2.02	4.46	6.10	15.40
2.44	3.64	9.87	13.50	33.25

Figure 4.5. Dissolved Ca concentrations vs. the acidity in solutions with and without iron.

The experimental data revealed that the concentration of dissolved calcium at equilibrium is lower than the theoretical value (Figure 4.5), where one mole limestone can neutralize two equivalents of acidity. The total dissolved Ca is the function of initial iron concentration and total acidity as Equation 12.

$$[\text{Ca}]_{\text{Fe}} = 0.309C_T + 0.27[\text{Fe}^{3+}]_i + 0.448 \quad (11)$$

where $[\text{Ca}]_{\text{Fe}}$ is total dissolved Ca in mmol/L; C_T is total initial acidity (meq/L); and $[\text{Fe}^{3+}]_i$ is initial ferric ion concentration (mmol/L).

Thus, more limestone is required to neutralize the same amount of acidity in hydrogen acid solutions than iron acid solutions. One reason for iron acid solutions consuming less limestone may be that some iron forms complexes, which may be absorbed to the surfaces of $\text{Fe}(\text{OH})_3$ or co-precipitate with iron hydroxides, thereby reducing the total alkalinity needed for neutralization. In addition, ionic strength effects may decrease the limestone amount needed for neutralization.

Example

To show how iron affects a limestone treatment system, the following example is given.

Suppose an acid mine drainage source has 1000 L/min of flow and the water has an initial pH of 3.0 (acidity 10^{-3} M or 50 mg/L as CaCO_3), but also contains 55 mg/L of iron. If the outlet pH is specified to be 7.0 and the open limestone channel is designed for 10 years, the retention time based on an optimal limestone particle size ($d = 10$ mm for hydrogen acid solution) should be increased and limestone requirement should increase due to the increased iron acidity concentration.

According to previous optimal calculation based on hydrogen acid (pH 3.0 without iron), the optimal limestone size is about 10 mm and the lifetime is about 5 years.

Considering the effect of iron, the acid load is:

$$A = (10^{-pH_0} + 3[Fe]/55/1000)Q * 365 * 24 * 60 * 50 = 105,120,000 \text{ g CaCO}_3/\text{year}.$$

Theoretical amount of limestone required for 10 years is:

$$W = 10 * A = 1,051,200 \text{ kg CaCO}_3/\text{year}$$

The real limestone required for 10 years is:

$$\begin{aligned} W_0 &= 10 * (0.309C_T + 0.27[Fe^{3+}]_i + 0.448)Q * 365 * 24 * 60 * 50 * 100 \\ &= 1,027,022,400 \text{ g} = 1,027,022.4 \text{ kg} \end{aligned}$$

To make the outlet pH 7.0, the retention time should be:

$$\begin{aligned} t &= \left[\left(-75.08 pH_f + 338.27 \right) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} \\ &\quad + (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 = 245 \text{ min} \end{aligned}$$

If the reaction time is only 60 minutes, the outlet water pH can be estimated to be 4.95.

Conclusion

Iron in acid solution has significant influences on limestone dissolution, and iron removal by precipitation depends on initial iron concentration and pH of the solutions. Neutralization of iron acid solutions is different from that of hydrogen acid solutions. There is a lag period (in fact a slight decrease) for pH that gradually increases with time as the neutralization of iron acid solutions continues, so it may need more reaction time to reach a final pH. The previous model to predict the reaction time needed for proton acid solutions to be neutralized by limestone should be corrected for iron concentration. Iron effects on required reaction time for acid to be neutralized are a function of the final pH and iron concentrations, $t(Fe) = t(Fe = 0) + (42 \ln[Fe] + 35.1)pH_f - 176 \ln[Fe] - 143$. Therefore, the retention time needed for neutralization can be corrected by including a term for initial iron concentration. Thus, once the initial pH and iron concentration are known and the final pH is specified, the surface area and residence time can be estimated.

The amount of limestone needed to neutralize the acidity of iron solutions is less than the amount need for the same acidity of hydrogen solutions due to iron co-precipitation and complex such as $Fe(OH)^{+2}$ and $Fe(OH)_2^+$, being precipitated with $Fe(OH)_3$. Therefore, when iron concentration is high, the limestone requirement may be less than the theoretical amount calculated by the acid load.

References

- Broshears, R. E., R.L. Runkel, E. A. Kimball, D. M. Mcknight, and K. E. Bencala. 1996. Reactive solute transport in an acid stream: experimental pH increase and simulation of controls on pH, aluminum, and iron. *Environ. Sci. & Tech.* 30(10):3016-3024.
- Loeppert, R. H., L. R. Hossner, and P. K. Amin. 1984. Formation of ferric oxyhydroxides from ferrous and ferric perchlorate in stirred calcareous systems. *Soil Sci. Soc. Am. J.* 48:677-683.

- Pearson, F. H. and A. J. McDonnell. 1977. Characterization of coarse porous media. J. of the Environ. Eng. Division, ASCE. 103: 615-624.
- Plummer, L. N. and T. M. L. Wigley. 1978, The kinetics of calcite dissolution in CO₂-water systems at 5 ° to 60 ° and 0 to 1.0 atm CO₂. Am. J. of Sci. 278:179-216.
- Ziemkiewicz, P.F., J.G. Skousen, and R. Lovett. 1994. Open limestone channels for treating acid mine drainage: a new look at an old idea. Green Lands 24(4):36-41.
- Zurbuch, P. E. 1996. Early results from calcium carbonate neutralization of two West Virginia rivers acidified by mine drainage. p. L1-L9. In Proc. of the Seventeenth Annual West Virginia Surface Mine Drainage Task Force Symposium. Morgantown, WV.

Chapter 5. Coating Effects on Limestone

Dissolution

Abstract

The use of limestone in treating AMD is limited because metals, particularly iron, develop a coating, thereby armoring the limestone surface and inhibiting its dissolution. Previous studies have shown that coated limestone does not completely stop dissolving, but its dissolution can be slowed from 20% to 90% of uncoated limestone. This study evaluated the thickness of the coating materials, and examined the effect of these factors on limestone dissolution rates. Electron photomicrographs showed the effects of moisture and iron concentration on the coating formation. Differences in drying methods influenced the number and depth of cracks in the coating. The composition of the coatings did not vary with iron concentration, and X-ray diffraction patterns revealed that the coatings were primarily composed of iron hydroxides and calcium sulfates. The thicker coatings reduced the limestone neutralization rate. Comparing the neutralization of acid solutions by limestone with different coating thicknesses, we developed a general function, $t=f(\text{pH}_i, \text{pH}_f, [\text{Fe}^{3+}], A_{\text{MS}}, \eta)$, to predict the treatment of AMD containing iron in armored limestone treatment systems, where t is required reaction time (min); pH_f is the final outlet pH; pH_i is initial pH of acid solution; A_{MS} is specific surface area of limestone particles; $[\text{Fe}^{3+}]$ is ferric iron concentration of the acid solution (mmol/L); and η is the coefficient representing coating effects on limestone dissolution.

Introduction

Open limestone channels or ditches introduce alkalinity to acid water (Ziemkiewicz et al., 1997). Where metals such as iron are dissolved in the water, a coating forms on the limestone surface. Initial assumptions held that armored limestone (limestone covered or coated with Fe or Al hydroxides) did not dissolve. However, Pearson and McDonnell (1977) showed that coated limestone continues to dissolve at about 20% of the rates of unarmored limestone. Recent work has demonstrated that the dissolution rate for armored limestone may be even higher than the 20% (Ziemkiewicz et al., 1997), but continued dissolution likely depends on solution pH, thickness of the coating, and other variables. Field experiments have shown that the length of the channel and the channel gradient, which affect turbulence and the buildup of coatings, are design factors that can be varied for optimum performance (Ziemkiewicz et al., 1994). Optimum performance was attained on slopes exceeding 20%, where flow velocities kept precipitates in suspension and clean precipitates from limestone surfaces during high flow events containing high amounts of sediment (Ziemkiewicz et al., 1994).

The acidity (or pH) of the solution, limestone surface area, and metal ions are primary factors that affect the neutralization rate of acid solutions. Surface area and calcium concentration effects on the limestone dissolution were presented by the first order reaction rate (Maree et al., 1992), where reaction rate is linearly related to the surface area of limestone. The initial pH and iron concentration of an acid solution also have direct influences on the neutralization of acid solutions, so reaction time for fresh limestone to neutralize acid solutions will vary with initial pH, iron concentration, and limestone surface area in the following manner (Chapter 4):

$$t = aA_{MS}^k + (42\ln[Fe] + 35.1)pH_f - 176\ln[Fe] - 143 \quad (1)$$

Where t is the time for acid solutions to be neutralized to a designed final pH, A_{MS} is limestone mass specific surface area, a and k are surface and pH effect constants, $[Fe]$ is iron concentration, and pH_f is the final pH.

The generation of coating materials on limestone surfaces primarily results from metal hydroxide precipitation. In eastern U.S. coal mining areas, most coating material is composed of ferric hydroxides since iron is the most common metal in AMD. In open air systems, iron exists primarily as the oxidized ferric iron, and limestone neutralization results in the formation of ferric hydroxide. When limestone neutralizes AMD containing both ferric and ferrous ions, many iron compounds can exist and co-precipitation can occur. Under such conditions, the ferrous iron may be oxidized to ferric iron in acid solution (Sung, 1981).

The suspended neutralized iron compounds, as fine solid particles, may absorb onto limestone surfaces to form layers of iron hydroxide (Christiansen and Nielson, 1951). The coating crystal growth rate can be expressed as (Snoeyink and Jenkins, 1980):

$$\frac{dC}{dt} = -kS(C - C^*)^n \quad (2)$$

Where C and C* are actual and saturation concentrations, k is a rate constant, S is surface area available for precipitation, and n is a constant. In the Fe(ClO₄)₃ system, Loeppert et al. (1984) found that crystalline iron oxides partially coated the calcite surface, and simple iron species subsequently precipitated on existing FeOOH nuclei on the limestone surface.

Because of the complicated mineral composition, X-ray diffraction was introduced to study coating mineral structure. Loeppert and Hossner (1984) found that lepidocrocite (γFeO-OH) and goethite (αFeO-OH) dominated the iron coating of limestone with a ferrous iron system, while poorly crystalline ferrihydrite (FeO-OH) was the only product in ferric systems. X-ray diffraction analysis showed the mineral's formation that is dependent on the pH values of the solutions (Schwertmann and Murad, 1983), where ferrihydrite resulted in the formation of goethite and hematite (Fe₂O₃).

While some research has been done on iron hydroxide formation and growth on limestone, no models have been developed to quantitatively assess the coating layer growth and its effects on coated limestone dissolution rate. This research was conducted to identify the composition of coating materials and to evaluate coating growth and

layering. By comparing the neutralization rates of uncoated and coated limestone, the effects of coating thickness on reaction rate were determined and predictions were made as to proper sizing and design of limestone systems that will be coated with iron.

Materials and Methods

Limestone (from Germany Valley, West Virginia, which is about 98.5% CaCO_3), was cut into square chips (30 x 30 x 5~8mm). The square chips were washed with dilute acid water and smoothed with fine sandpaper. To control the reaction surface area, five of the six surfaces of each square limestone chip were coated with saran, and then dried for about three hours in an oven (105°C) for sealing. Recoat this limestone chips three times with the same method. Thus, each square limestone chip only had one available top surface to react with an acid solution, and all square chips had very similar surface areas.

Figure 5.1. Schematic representation of coating method.

Eight square limestone chips were placed in a 1000 ml container filled with 400 ml of iron acid solution. Four different iron containing acid solutions were allowed to react with individual limestone squares. As the limestone chips neutralized the acid solution, ferric hydroxide precipitated on the limestone surface. The iron solutions (Figure 5.1) were placed in a ventilated hood until the solution evaporated (usually 3 days). The different concentrations of iron in solution caused a slightly different thickness of iron coating on the limestone.

Once the limestone chips were coated with various thicknesses of iron hydroxide and dried, the coating layers were observed and photomicrographs were taken. The

coating thickness was measured from the ruler in the microscope. The duplicate coating layers were sent for X-ray diffraction, which was usually 1-3 days after microscope observation. The dry, coated limestone chips were then placed into a 400 ml iron acid solution ($[\text{Fe}^{3+}] = 0.001 \text{ M}$, $\text{pH} \sim 3.0$) and allowed to react. The ferric acid solutions were made with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and deionized water. During the experiment, small solution samples (about 2 mL) were taken at predetermined time intervals, and filtered with a $0.45\text{-}\mu\text{m}$ syringe-operated filter (Millipore) for chemical analysis. The pH of the solution was measured at the time of extraction (Accumet pH meter 25, Fisher Scientific Company, Accu-pHast Electrode) and the withdrawn water samples were analyzed for Ca and Fe concentration with either Inductively Coupled Plasma (Perkin Elmer P4000) or Atomic Absorption Spectroscopy (Perkin Elmer 5000).

Results and Discussion

Because of the small amount of surface area of the limestone chips, iron acid solutions were neutralized very slowly. But due to the different acid concentrations, more concentrated iron solutions created thicker coatings (Table 5.1).

Table 5.1. Coating thickness as a function of iron solution concentration.

Fe Concentration Mol/L	Coating Thickness	
	Range μm	Average μm
0.010	40~50	45
0.006	25~35	30
0.004	15~25	20
0.002	10~15	12.5
0.001	5~10	7.5

The photomicrographs of the coatings on the limestone chip's top surface are shown in Figures 5.2 through 5.4. The moisture of the coating layer controlled the shape and binding strength of the coating materials. When the moisture was high, the coating layer appeared smooth and even. When dried, the coating cracked so seriously that some of it stripped off. The number and width of cracks in the coating not only depended on the coating thickness and moisture content, but also depended on the drying rate. When

dried under room conditions, cracks were fewer and less deep than when dried under a ventilated hood (Figure 5.3).

Figure 5.2. The coating layer structure.

Figure 5.3. Cracking on the coating layer.

Figure 5.4. The micro-pits on the surface of the coating layer.

One of the intriguing findings of this study was the observation of small pits forming in the coating (Figure 5.4). From microscopic observation, the bottom of the small cone-shaped pits directly connected to the limestone surface. The generation and release of CO_2 gas from the limestone surface may cause the formation of these pits.

Figure 5.5. The CO_2 gas bubbles cover limestone surface.

Figure 5.6. Pit formation in limestone coating layer.

At the very beginning of the neutralization process when the solution pH was near 3.0, the fresh limestone surface was covered by numerous, fine gas bubbles (Figure 5.5). As the gas bubbles enlarged, they eventually overcame the adsorption forces and the force of the solution holding them down, and rose in the solution and were released to the air. As the pH rose to about 5.0, no more gas bubbles were evident. As iron hydrolysis, neutralization, and precipitation began, iron hydroxides formed around the gas bubbles (Figure 5.4) leaving a sparkled appearance. These gas pits became the available reaction surfaces for limestone with acid, and the coated surface hindered the reaction rate (Figure 5.6).

Since dissolved iron concentration never increased (Figure 5.7), iron hydroxide dissolution is not considered a significant H^+ consuming reaction. The overall neutralization rate increased as the thickness of the coating layer decreased (Figure 5.8). The time required to reach pH 5.5 is 120% longer with 12.5 μm coating and 275% longer with a 20 μm coating, compared to no coating. Figure 5.9 indicates that the rate of calcium release to the solution is reduced by a coating, but is independent of coating thickness.

Figure 5.7. Coating thickness effects on iron removal.

Figure 5.8. Coating thickness effects on neutralization rate at initial iron concentration 0.001M.

Figure 5.9. Coating thickness effects on calcium concentration vs. time at initial iron concentration of 0.001M.

If the general function for acid neutralization by fresh limestone is given by $pH_{fresh} = f(t)$, then an efficiency factor to account for the effect of a coating, K , can be introduced such that:

$$pH = K * f(t) = K * pH_{fresh} \quad (3)$$

Regressing the pH difference between the neutralization by coated limestone and fresh limestone with the coating thickness (Figure 5.7), an empirical equation for K was determined as:

$$K = -0.0098b + 1.003 \quad (4)$$

where b is the coating thickness (μm). The overall function is then given as:

$$pH = (-0.0098b + 1.003) pH_{fresh} \quad (5)$$

The required reaction time for fresh limestone particles neutralizing iron acid solutions was given in Chapter 4 as:

$$t(\text{Fe}) = \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} + (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 \quad (6)$$

where: $t(\text{Fe})$ = required reaction time (min);

pH_f = the final outlet pH;

pH_i = initial pH of acid solution;

A_{MS} = specific surface area of limestone particles (cm^2/g);

$[Fe]$ = ferric iron concentration of the acid solution (mmol/L).

For coated limestone particles, limestone surface area is not as effective as fresh surfaces, so it should take longer to reach the desired final pH. Thus, the general required retention time should be corrected by an efficiency constant, η :

$$t = \eta * t(\text{Fe}) \quad (7)$$

where t is the required retention time for coated limestone, $t(\text{Fe})$ is the required retention time for fresh limestone. From the required reaction time to reach pH 5.0, 5.5 and 6.0, an empirical equation for η was determined from Figure 5.7 as:

$$\eta = e^{0.0654b} \quad (8)$$

where b is again the thickness (μm) of the coating layer. The overall equation for the effect of armoring on the neutralization of acid solutions containing iron is then:

$$t = e^{0.0654b} \left\{ \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} + (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 \right\} \quad (9)$$

The coating layer directly influenced the removal rate of iron from solution. The time required (Figure 5.8) to completely remove 0.001 M Fe from solutions was a linear function of the coating thickness:

$$t (\text{Fe removal}) = 4.1404 b + 126.67 \quad (10)$$

where t is the time of iron totally removed from the solution (min) and b is the thickness of coating layer (μm).

Example:

To show how the coating affects limestone treatment systems, the following example is given.

Suppose an AMD source has 1000 L/min of effluent and the water has an initial pH of 3.0 (acidity 10^{-3} M or 50 mg/L as CaCO_3), but also contains 55 mg/L of iron. If the outlet pH is specified to be 7.0 and the open limestone channel is designed for 10 years, the retention time based on an optimal limestone particle size ($d = 9.18$ mm for hydrogen acid solution) should be increased to 245 minutes (Example II). Assume the coating growth rate is 4 μm per year, we can predict the final pH and the lifetime of the limestone treatment system.

Limestone required for 10 years is:

$$W_0 = 10 * (0.309 C_T + 0.27 [\text{Fe}^{3+}]_i + 0.448) Q * 365 * 24 * 60 * 50 * 100$$

$$= 1,027,022,400 \text{ g} = 1,027,022.4 \text{ kg}$$

From Figure 5.7, the final pH for the reaction time of 245 minutes is a function of coating thickness (Eq. 5) :

$$\text{pH} = K * \text{pH}_{\text{fresh}} = (-0.0098b + 1.003) \text{pH}_{\text{fresh}}$$

So the final pH of each year can be predicted and is shown in Table 5.2. The effective lifespan (outlet pH over 6.0) of the limestone treatment system is only about 3.5 years.

Table 5.2. Coating effects on outlet water quality.

Year	Outlet pH in fresh limestone system	Coating Thickness μm	Outlet pH in coated limestone system
1	7.00	0	7.00
2	6.92	4	6.67
3	6.74	8	6.24
4	6.48	12	5.74
5	6.15	16	5.20
6	5.77	20	4.66
7	5.37	24	4.12
8	4.97	28	3.62
9	4.58	32	3.16
10	4.24	36	3.00

Conclusion

In coal mining areas, iron hydroxides and other iron minerals are the predominate coating materials on limestone surfaces in AMD treatment systems. The water flow rate and iron concentration have a great influence on the coating layer growth, so higher iron concentration and air exposure will enhance the coating layer formation in open limestone channels. The thickness of the coating layer is a function of iron concentration. As concentrations of iron in solution increase, the coating layer becomes thicker.

The thickness of the coating layer and the micro pits on the coating surface may greatly affect the neutralization rate of acid solutions by limestone. A general equation to estimate the required reaction time is derived for an open limestone system using empirically determined efficiency factors. An efficiency constant, η , was introduced to correct the reaction time required for neutralization of iron containing acid solutions with coated limestone. By knowing the water chemistry (acidity, pH, and iron) and the type and size of a limestone treatment system (amount and size of limestone), we can more accurately predict the treatment efficiency and longevity of the system for treating a specified AMD flow.

References

- Christiansen, J. H., and A. E. Nielson. 1951. Acta Chem. 2nd Edition 5: 673.
- Loeppert, R. H., L. R. Hossner, and P. K. Amin. 1984. Formation of ferric oxyhydroxides from ferrous and ferric perchlorate in stirred calcareous systems. Soil Sci. Soc. Am. J. 48:677-683.
- Loeppert, R. H., and L. R. Hossner. 1984. Reactions of Fe^{2+} and Fe^{3+} with calcite. Clays and Clay Minerals. Vol.32(3):213-222.
- Maree, J. P., P. D. Plessis, and C. J. Van der Walt. 1992. Treatment of acidic effluents with limestone instead of lime. Wat. Sci. Tech. 26(1-2):345-355.
- Pearson, F. H. and A. J. McDonnell. 1977. "Characterization of Coarse Porous Media," J of the Env. Eng. Div., ASCE, Vol. 103:615-624.
- Schwertmann, U., and E. Murad. 1983. Effect of pH on the formation of goethite and hematite from ferrihydrite. Clays and Clay Minerals. Vol. 31(4):277-28.
- Snoeyink, V. L., and D. Jenkins. 1980. Water Chemistry. John Willey & Sons, New York.
- Sung, W., and J. J. Morgan. 1981. Oxidative removal of Mn(II) from solution catalysed by the γ -FeOOH (lepidocrocite) surface. Geochimica et Cosmochimica Acta. 45:2377-2383.
- Ziemkiewicz, P.F., J.G. Skousen, and R. Lovett. 1994. Open limestone channels for treating acid mine drainage: a new look at an old idea. Green Lands 24(4):36-41.

Ziemkiewicz, P.F., J.G. Skousen, D.L. Brant, P.L. Sterner, and R.J. Lovett. 1997. Acid mine drainage treatment with armored limestone in open limestone channels. J. of Environ. Qual, 26(4):1017-1024.

Supporting information

Figure 5.10. X-ray diagram of FeCl₃ coated layer.

Figure 5.11. X-ray diagram of Fe₂(SO₄)₃ coated layer.

Figure 5.12. The X-ray diagram of the coating layer in field OLCs.

Chapter 6. Open Limestone Channel Design

Models and the Prediction of Water Treatment

Today's design for open limestone systems is based solely on the acid load of an acid mine drainage outflow, which does not consider the chemical composition of the water, nor the slope of the land. Our research on the neutralization rate of acid mine drainage by limestone showed that the iron concentration, water flow rate, and limestone properties have great influences on limestone coating and acid removal, which determines the outlet water quality. Therefore, there is a need to design optimal limestone systems for field AMD treatment and to predict water quality in the future.

This spreadsheet model optimizes open limestone system design and predicts water treatment effects during the life of the system based on previous research on required reaction time for iron acid solutions and coating formation. Because the coating thickness depends on the flow rate (flushing force) and iron concentration, land slope and its effect on water flow velocity have been incorporated into the model. Iron concentrations of the AMD and its influence on coating growth have also been included in the model. Based on the required reaction time and land slope, we can design the length of an open limestone channel as well as the limestone particle size to optimize its performance.

For fresh open limestone systems, we can predict the outlet water pH based on the field design. By considering the limestone surface area decreasing and estimating iron concentration effects on coating growth rate, the outlet water pH in an old limestone system can be predicted by this spreadsheet model. Therefore, we can predict the system's effectiveness for treating AMD over time and make modifications or replace the system once the outlet pH becomes too low.

Table 6.1 Input Spreadsheet

STREAM	VALUE	UNITS	SYMBOL
pHi	3		pHi
Expected Final pH	7		pHf
[Fe3+]	50	mg/L	[Fe3+]
[Fe2+]	0	mg/L	[Fe2+]
[Al3+]	0	mg/L	[Al3+]
[Mn2+]	0	mg/L	[Mn2+]
[Zn2+]	0	mg/L	[Zn2+]
[Cu2+]	0	mg/L	[Cu2+]
[Cu+]	0	mg/L	[Cu+]
Others	0	mmol/L	[M]
Flow Rate	500	GPM	Qo
Final Acidity	10	mg/L	Af
Total Calculated Acidity	3.68	meq/L	$Ac = 10^{3-pH} + \sum C_i / M_i Z_i$
	184.2	mg/L	$Acid_t = 50Ac$
		CaCO3	
Total Measured Acidity(as CaCO3)	150.0	mg/L	Ai
		CaCO3	
CHANNEL'S CHARACTER			
Depth	3	ft	D
Top Width	10	ft	W1
Bottom Width	6	ft	W2
Void Ratio	35	%	R
Slope	20.00	%	k
Hydraulic Conductivity K	0.10	cm/s	K
LIMESTONE			
Average Particle Size	2.0	in.	d
Shape Factor	0.20		r
Cost of Limestone/Placement	15	\$/ton	P
Limestone Density	2.2	Mg/m ³	ρ

Table 6.2 Results Spreadsheet

STREAM	VALUE	UNITS	EQUATION
Flow Rate	1.11	ft ³ /sec	$Q=0.1137/60*Q_o$
Outlet pH	7		Expected final pH
Final Acidity	10	mg/L	Measured
Final Acid Load	11	tons/year	$A_f*Q_o*0.0022$
Original Acid Load	164.5	tons/year	$Acid\ load=A_i*Q_o*0.0022$
Acid Removal	93.33	%	$(A_i-A_f)/A_i$
Coating Growth Rate	5	um/year	$B=2[Fe^{3+}]/k$
Stream Cross Section	24	ft ²	$So=(W1+W2)/2*D$
Stream Initial Velocity	0.1326	ft/sec	$Vo=Q/(So*R)$
Residence Time			
Retention Time(Fe=0)	107.50	min	$t = \left[\left(-75.08 pH_f + 338.27 \right) pH_i + 0.8053 pH_f^{3.5346} \right] * A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)}$
Retention Time(Fe)	234	min	$t=t(Fe=0)+(42\ln Fe+35.1)*pH_f-176\ln Fe-143$
Total Required Reaction Time	3.90	hours	$T=t/60$
Limestone Channel			
Specific Surface Area	9.3	cm ² /g	$A_{MS} = 3.6635d^{0.9828} / r$
Slope Caused dH/dl	0.20		$dH/dl = k / \sqrt{1+k^2}$
Slope Caused Velocity	0.0021	ft/Sec.	$V_x = K/R * dH/dl$
Required Length	1890	ft	$L= t(Vx+Vo)$
Construction Required LS	2021	tons	$LS=So*L*\rho$
Cost of Channel	30310	\$	$\$=P*LS$
Limestone Consumption Rate	99	tons/Year	$RLS= (A_i-A_f)Q$
Life of Drain	20	years	$Y=LS/RLS$

Table 6.3 Outlet Water Quality Prediction

Year	Limestone Remains Tons	Fresh Limestone System			Coated Limestone System			
		Outlet pH	Outlet Fe	Final Acidity	Coating Thickness	Outlet pH	Outlet Fe	Final Acidity
			ppm	ppm	μm		ppm	ppm
1	2020.7	7.00	0	10.0	0	7.00	0	10.0
2	1922	6.97	0	10.0	2	6.86	0	10.0
3	1823.3	6.89	0	10.0	4	6.64	0	10.0
4	1724.6	6.77	0	10.0	6	6.39	0	10.0
5	1625.9	6.61	0	10.0	8	6.11	0	10.0
6	1527.2	6.40	0	10.0	10	5.80	0	10.1
7	1428.6	6.17	0	10.0	12	5.46	0	10.2
8	1329.9	5.92	0	10.1	14	5.12	0	10.4
9	1231.2	5.65	0	10.1	16	4.78	0	10.8
10	1132.5	5.37	0	10.2	18	4.44	20	29.7
11	1033.8	5.09	0	10.4	20	4.11	20	31.8
12	935.17	4.82	0	10.8	22	3.80	20	35.9
13	836.49	4.56	0	11.4	24	3.50	20	43.5
14	737.81	4.32	20	30.2	26	3.23	20	57.0
15	639.13	4.10	20	31.8	28	3.00	20	77.9
16	540.45	3.91	20	34.1	30	3.00	20	77.9
17	441.77	3.73	20	37.1	32	3.00	20	77.9
18	343.08	3.59	20	40.8	34	3.00	20	77.9
19	244.4	3.46	20	45.2	36	3.00	20	77.9
20	145.72	3.36	20	49.9	38	3.00	20	77.9
21	47.044	3.27	20	54.7	40	3.00	20	77.9
22	0	3.00	20	59.1	42	3.00	20	77.9

Based on derived models, we calculated the errors between the theory values and experimental data by the following statistics functions:

$$R^2 = 1 - \frac{SSE}{SST} \quad (1)$$

$$SSE = \sum (Y_i - \hat{Y}_i)^2 \quad (2)$$

$$SSE = \sum Y_i^2 - \frac{(\sum Y_i)^2}{n} \quad (3)$$

1. For proton acid solution, the required reaction time is:

$$t = \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} \quad (4)$$

Where t is reaction time required to reach a final pH, pH_f is the final pH and pH_i is initial pH, and A_{MS} is mass specific surface area.

[illegible]

pH _i	R ²
2.0	0.77466
2.5	0.98265
3.0	0.9584
3.5	0.98922
4.0	0.77714

pH _i	R ²
2.0	0.73462
2.5	0.99167
3.0	0.94538
3.5	0.98508
4.0	0.61836

[illegible]

$$\begin{aligned} \text{t(Fe)} = & \left[(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346} \right] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} \\ & + (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 \end{aligned} \quad (5)$$

Where: $t(\text{Fe})$ = required reaction time (min);

pH_f = the final outlet pH;

pHi = initial pH of acid solution;

$$A_{MS} = \text{specific surface area of limestone particles (cm}^2\text{/g)};$$

[Fe] = ferric iron concentration of the acid solution (mmol/L).

Figure 6.5 Prediction of required time to reach a final pH in iron acid solutions.

$$t = e^{0.0654b} \{ [(-75.08 pH_f + 338.27) pH_i + 0.8053 pH_f^{3.5346}] A_{MS}^{(-0.1305 pH_f + 0.6185) pH_i + (0.7365 pH_f - 4.5918)} (42 \ln[Fe] + 35.1) pH_f - 176 \ln[Fe] - 143 \} \quad (6)$$

Where t is the required retention time for coated limestone, b is again the thickness (μm) of the coating layer.

Figure 6.6 Prediction of required time to reach a final pH with coated limestone.

Appendix

Experimental Data Sheet and Figures

Appendix Table 7.1.1 Initial pH 4.0 vs. Particle Sizes

1.1-4.0 pH vs. Particle Sizes							
pH=4.0 8-26-1998							
		Soil Size	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
		Weight (g)	99.448	99.536	99.53	99.648	99.515
		Last Wt.	99.439	99.53	98.682	99.638	99.499
			pH	pH	pH	pH	pH
	Time	React t	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
1	10:05	0	3.98	3.99	3.99	3.98	4.00
2	7	2	4.87	4.31	4.22	4.14	4.15
3	9	4	6.01	5.42	4.60	4.37	4.28
4	13	8	6.66	6.34	6.08	5.80	4.65
5	19	14	7.45	6.94	6.76	6.50	5.14
6	24	19	8.66	8.63	8.30	7.66	5.79
7	30	25	9.07	9.04	8.88	7.86	6.67
8	37	32	9.21	9.24	9.15	8.10	7.10
9	45	40	9.26	9.30	9.23	8.80	7.30
10	11:05	60	9.35	9.31	9.30	9.13	7.59
	12:20	135	9.28	9.33	9.32	9.32	9.23

Appendix Table 7.1.2 Initial pH 3.5 vs. Particle Sizes

1.1-3.5 pH vs. Particle Sizes							
pH=3.5; 9:40, 8-17-1998							
		Soil Size	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
		Weight (g)	99.566	99.545	99.542	99.652	99.523
		Last Wt.	99.448	99.536	99.53	99.648	99.515
Each beaker filled with 400 ml water solution pH = 3.448, 3.45, 3.452							
	Time	React t	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
1	9:40	0	3.45	3.45	3.45	3.45	3.45
2	41	1	3.61	3.51	3.45	3.45	3.46
3	43	3	3.89	3.87	3.60	3.58	3.49
4	46	6	5.19	4.39	4.00	3.68	3.58
5	49	9	5.64	5.38	4.26	3.87	3.64
6	52	12	5.98	5.76	5.13	4.02	3.76
7	56	16	6.16	6.10	5.62	4.37	3.85
8	10:00	20	6.38	6.28	6.00	4.76	4.03
9	5	25	6.53	6.44	6.23	5.48	4.20
10	10	30	6.84	6.80	6.50	5.81	4.60
11	17	37	7.08	7.01	6.67	6.19	5.07
12	25	45	7.79	7.28	7.04	6.40	5.75
13	35	55	8.29	7.91	7.34	6.74	6.05
14	45	65	8.32	8.02	7.73	6.94	6.30
15	11:00	80	8.44	8.42	8.12	7.32	6.66
16	20	100	8.46	8.49	8.46	7.62	7.00
17	55	135	8.44	8.49	8.55	8.43	7.51
18	12:25	165	8.45	8.55	8.51	8.43	7.87
19	15:00	320	8.42	8.47	8.61	8.56	8.49

Appendix Table 7.1.3 Initial pH 3.0 vs. Particle Sizes

1.1-3.0 pH vs. Particle Sizes										
24.3 oC; pH=3.0; 10:00, 8-10-1998										
Soil Size	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25					
Weight (g)	99.598	99.583	99.567	99.68	99.555					
Last Wt.	99.566	99.545	99.542	99.652	99.523					
Each beaker filled with 400 ml water solution pH = 3.046, 2.993, 2.989										
React t	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
0	3	3	3	3	3	0	0	0	0	0
1	3.12	3.08	3.02	3.00	3.02	19.50	-0.12	11.93	6.52	5.46
5	3.37	3.42	3.25	3.13	3.07	28.41	25.73	25.40	9.66	8.54
8	4.05	3.96	3.75	3.23	3.16	24.37	23.56	22.56	14.20	12.41
12	5.19	4.86	4.14	3.38	3.29	26.86	27.41	22.83	17.16	13.72
15	5.54	5.44	4.67	3.60	3.40	27.53	28.06	25.47	19.39	16.16
19	5.83	5.74	5.32	3.76	3.50	29.83	29.01	24.70	21.98	17.27
23	6.07	5.98	5.65	4.11	3.69	31.00	29.29	26.38	22.65	20.93
28	6.20	6.10	5.83	4.53	3.79	32.48	31.14	29.86	24.08	20.57
33	6.35	6.26	6.01	5.10	3.94	37.57	33.64	30.72	26.80	25.37
39	6.51	6.40	6.20	5.49	4.30	36.54	35.54	32.19	27.94	24.18
47	6.66	6.54	6.31	5.83	4.68	38.76	33.31	34.40	28.05	25.18
55	6.82	6.66	6.48	6.03	5.38	38.92	36.73	31.98	30.01	25.24
65	7.02	6.83	6.61	6.21	5.71	41.86	35.95	36.47	28.05	28.42
75	7.13	6.92	6.76	6.39	6.01	38.43	35.32	31.39	26.62	23.99
85	7.27	7.06	6.81	6.51	6.20	41.62	35.72	33.41	27.20	27.22
100	7.51	7.24	7.05	6.73	6.45	44.07	40.72	34.20	29.87	26.55
125	7.84	7.51	7.35	7.04	6.75	41.16	36.19	37.76	33.28	26.61
155	8.02	7.79	7.67	7.33	7.04	35.59	38.13	32.38	31.07	-0.20
185	8.05	8.02	7.94	7.62	7.34	46.29	39.26	40.84	32.28	26.59
230	8.07	8.05	8.09	8.02	7.83	40.51	40.38	37.04	33.42	27.96
290	8.17	8.17	8.21	8.29	8.22	38.39	37.38	35.82	37.78	28.34
350	8.26	8.21	8.25	8.35	8.35	-0.20	-0.20	43.68	51.32	55.09
1365	8.01	8.03	8.12	8.17	8.03					

Appendix Table 7.1.4 Initial pH 2.5 vs. Particle Sizes

1.1-2.5 pH vs. Particle Sizes											
24.3 oC; pH=2.5; 9:40, 7-23-1998											
Soil Size	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25						
Weight (g)	99.499	99.593	99.398	99.776	99.653	Each beaker filled with 400 ml water solution pH = 2.431, 2.432					
Last Wt.	99.387	99.104	99.573	99.682	99.555	Ca in the solution without diluted					
React t	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25		2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
0	2.43	2.43	2.43	2.43	2.43	4.3	76.7	24.7	85.8	30.7	18.6
2	2.55	2.47	2.45	2.44	2.43	7.2	93.3	67.4	64.6	42.2	31.1
5	3.08	2.68	2.79	2.56	2.52	9.5	97.0	80.6	79.5	56.4	41.0
9	3.67	2.98	2.85	2.68	2.58	12.5	113.3	99.1	89.7	74.4	54.0
12	4.29	3.21	2.99	2.74	2.66	15.3	108.8	106.7	96.1	81.7	66.2
15	5.00	3.47	3.19	2.90	2.72	14.9	111.5	96.0	101.5	88.4	64.5
18	5.29	3.93	3.54	3.03	2.80	17.2	120.0	109.3	109.2	96.8	74.5
21	5.40	4.56	3.80	3.21	2.87	17.8	118.1	109.2	107.1	109.4	77.1
24	5.56	5.04	4.32	3.35	2.99	20.3	118.8	101.8	105.5	159.5	87.9
28	5.75	5.36	4.77	3.60	3.08	21.7	117.6	113.0	107.5	103.6	93.9
33	5.90	5.58	5.18	3.89	3.30	22.3	120.0	115.2	108.3	111.9	96.4
38	6.01	5.72	5.32	4.39	3.41	23.2	126.2	121.9	111.7	109.1	100.4
44	6.12	5.86	5.56	4.88	3.70	23.7	128.9	117.6	109.0	106.1	102.5
50	6.16	5.92	5.68	5.18	4.03	23.5	127.1	117.7	116.6	110.5	101.7
57	6.26	6.01	5.77	5.37	4.33	24.1	124.2	121.1	110.8	107.7	104.5
65	6.35	6.18	5.89	5.56	4.72	23.7	135.9	127.4	121.8	116.5	102.6
75	6.45	6.25	6.02	5.72	5.17	24.2	149.9	130.9	117.2	115.0	104.8
85	6.49	6.35	6.09	5.89	5.48	27.9	157.4	149.2	132.2	135.5	121.0
100	6.58	6.45	6.19	6.01	5.67	27.6	153.2	150.4	140.3	135.6	119.5
120	6.64	6.60	6.38	6.21	5.97	27.8	164.0	150.3	134.5	135.1	120.4
145	6.79	6.72	6.53	6.41	6.19	27.2	159.0	155.2	142.1	131.1	117.8
173	6.84	6.81	6.69	6.59	6.42	27.2	160.0	154.7	145.3	127.8	117.9
240	7.04	7.05	6.92	6.90	6.81	28.6	155.4	153.1	142.2	141.6	123.8
315	7.31	7.30	7.21	7.28	7.38	31.8	224.2	170.3	176.9	176.6	137.6
485	7.46	7.53	7.50	7.59	7.73	4.3	76.7	24.7	85.8	30.7	18.6

Appendix Table 7.1.5 Initial pH 2.0 vs. Particle Sizes

1.1-2.0 pH vs. Particle Sizes ^{pH=2.0 20-7-1998}												
			Sample 1	Sample 2	Sample 3	Sample 4	Sample 5					
		Particle Size	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25					
		Weight (g)	100.053	100.054	100.094	100.161	100.055					
		Last Wt.	99.499	99.593	100.005	99.776	99.653	Each beaker filled with 400 ml water solution pH = 1.974;1.938.				
			pH	pH	pH	pH	pH		Ca in the solution without diluted			
	Time	React t	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25	2.0-4.65	4.75-6.3	6.3-11	11.0-19.0	19-25
1	9:50	0	1.93	1.94	1.92	1.93	1.93	0.0	0.0	0.0	0.0	0.0
2	9:51	1	2.08	1.94	1.95	1.92	1.92	206.0	318.7	140.9	70.9	57.1
3	54	4	2.17	1.98	1.97	1.97	1.96	473.8	69.0	238.0	192.6	99.4
4	57	7	2.41	1.99	2.24	2.10	2.00	469.4	457.6	415.6	235.7	138.7
5	10:00	10	2.80	2.29	2.48	2.17	2.06	441.9	348.1	491.4	304.1	172.4
6	10:03	13	2.63	2.51	2.66	2.28	2.10	478.3	398.5	475.9	336.5	217.5
7	6	16	3.16	3.12	2.87	2.37	2.18	536.2	-0.1	483.3	378.8	241.8
8	10	20	3.41	2.78	3.02	2.51	2.22	497.0	479.0	459.3	471.0	261.5
9	13	23	4.31	3.14	3.31	2.67	2.27	549.0	545.9	554.4	436.9	320.6
10	17	27	4.75	3.80	3.64	2.78	2.38	517.0	525.2	540.5	446.8	328.5
11	20	30	5.10	4.57	3.99	2.90	2.45	504.3	534.7	541.3	467.0	361.1
12	24	34	5.26	5.00	4.42	3.07	2.56	523.2	520.5	549.7	553.7	393.8
13	28	38	5.48	5.22	4.85	3.28	2.69	550.8	550.9	547.8	466.3	391.8
14	33	43	5.58	5.38	5.03	3.50	2.81	515.2	527.2	510.0	456.0	411.7
15	37	47	5.67	5.47	5.19	3.69	2.94	591.3	601.4	584.7	539.5	474.7
16	40	50	5.71	5.58	5.28	3.90	3.06	606.4	589.5	578.4	538.3	462.8
17	45	55	5.79	5.65	5.38	4.19	3.24	587.6	565.0	2.0	499.9	494.2
18	50	60	5.86	5.71	5.46	4.62	3.41	561.0	584.3	838.3	503.8	483.2
19	55	65	5.90	5.78	5.52	4.82	3.53	568.2	593.4	569.3	514.2	511.3
20	11:00	70	5.95	5.82	5.58	4.99	3.72	584.2	644.6	578.9	532.3	488.1
21	8	78	6.02	5.91	5.67	5.17	4.12	651.2	662.0	572.7	528.4	477.3
22	17	87	6.07	5.96	5.73	5.30	4.51	581.9	620.0	582.6	499.8	482.6
23	25	95	6.13	6.01	5.81	5.42	4.88	576.1	593.3	574.3	495.3	486.9
24	36	106	6.18	6.09	5.88	5.56	5.21	614.1	663.8	623.8	533.0	523.3
25	50	120	6.26	6.15	5.96	5.67	5.40	667.0	665.5	614.4	549.9	510.9
26	12:10	140	6.33	6.21	6.07	5.81	5.68	610.5	650.9	654.5	589.5	509.9
27	35	165	6.40	6.31	6.17	5.93	5.89	619.1	666.8	625.1	568.7	499.6
28	13:05	195	6.47	6.36	6.27	6.14	6.17	629.7	684.7	588.1	569.0	513.5
29	40	230	6.53	6.46	6.39	6.30	6.39	660.4	678.5	665.7	584.9	519.7
30	14:30	280	6.69	6.55	6.54	6.52	6.54	650.1	693.7	630.5	559.9	538.4
31	16:50	420	7.01	6.78	6.84	7.07	6.83	642.4	639.4	620.9	579.7	520.5

Appendix Table 7.1.6 Limestone Surface Area Experiment

Limestone Surface Area Experiment.21-Jun-99											
	Surface Area vs. Mean Diameter				As 100g Limestone Particle				r=1	r=0.7*0.9	r=0.5*0.9
Limestone Size	No. of Particle	Weight (g)	Volume (ml)	Sieve Size (cm)	No. of Particles	Mean Dia.	Volume (ml)	Mean D (cm)	Ams (cm2/g)	MinAms (cm2/g)	MaxAms (cm2/g)
19~25	4	100.6	37.7	2.2	4.0	26.2	37.5	2.6	0.9	1.4	1.9
12.5~19	15	100.6	38.7	1.5	14.9	16.9	38.5	1.7	1.3	2.1	3.0
6.3~12.5	40	53.9	19.5	0.9	74.2	9.9	36.1	1.0	2.3	3.6	5.1
4.75~6.3	40	14.8	5.7	0.5	270.4	6.4	38.5	0.6	3.5	5.6	7.8
2~4.75	119	14.5	5.4	0.4	819.8	4.4	37.0	0.4	5.1	8.1	11.3

Appendix Table 7.1.7 Destination pH 5.5, 6.0, 6.5, 7.0 vs. time of different sizes

Destination pH 5.5, 6.0, 6.5, 7.0 vs. time of different sizes												
					Destination pH=5.5					t=a*Ams^k		
	# Particle	A _{MS}	Size(mm)	lgAms	pHi=2.0	pHi=2.5	pHi=3.0	pHi=3.5	pHi=4.0	pHi	a	k*(-100)
2~4.75	820	9.7	4.44	0.99	40	23	14	8	3	2	183.2	68.1
4.75~6.3	270	6.7	6.42	0.82	48	30	16	10	4.5	2.5	125.7	75.8
6.3~11	74	4.3	9.88	0.64	65	40	21	15	5.5	3	94.2	89.3
11~19	15	2.5	16.88	0.40	100	60	50	25	6	3.5	62.6	94.1
19~25	4	1.6	26.22	0.21	130	90	58	42	17	4	19.2	82.8
					Destination pH6.0					t=a*e^(k*log[Ams])		
	# Particle	A _{MS}	Size(mm)		pHi=2.0	pHi=2.5	pHi=3.0	pHi=3.5	pHi=4.0	pHi	a	k
2~4.75	820	9.7	4.4		77	37	22	13	4	2	256.15	-0.51
4.75~6.3	270	6.7	6.4		93	55	24	15	7	2.5	178.74	-0.65
6.3~11	74	4.3	9.9		130	75	43	20	8	3	108.38	-0.72
11~19	15	2.5	16.9		175	95	54	33	10	3.5	71.11	-0.79
19~25	4	1.6	26.2		180	125	75	52	22	4	27.91	-0.83
					Destination pH=6.5							
	# Particle	A _{MS}	Size(mm)		pHi=2.0	pHi=2.5	pHi=3.0	pHi=3.5	pHi=4.0	pHi	a	k
2~4.75	820	9.7	4.4		220	90	37	24	7	2	281.12	-0.10
4.75~6.3	270	6.7	6.4		255	110	44	26	9	2.5	273.89	-0.41
6.3~11	74	4.3	9.9		255	140	58	31	12	3	142.26	-0.60
11~19	15	2.5	16.9		265	160	83	47	14	3.5	91.32	-0.64
19~25	4	1.6	26.2		270	190	105	75	24	4	29.76	-0.64
					Destination pH7.0							
	# Particle	A _{MS}	Size(mm)		pHi=2.0	pHi=2.5	pHi=3.0	pHi=3.5	pHi=4.0	pHi	a	k
2~4.75	820	9.7	4.4		400	240	75	36	11	2	443.62	-0.04
4.75~6.3	270	6.7	6.4		410	240	84	37	15	2.5	278.06	-0.07
6.3~11	74	4.3	9.9		420	250	95	45	16	3	184.21	-0.41
11~19	15	2.5	16.9		415	260	125	70	17	3.5	123.93	-0.60
19~25	4	1.6	26.2		440	270	155	100	30	4	32.57	-0.47

Appendix Figures 7.1.1~16

Appendix Figures 7.1.1 pH in proton acid solution ($pH_i=2.0$) with ellipsoid limestone particles.

Appendix Figures 7.1.2 Ca in proton acid solution ($pH_i=2.0$) with ellipsoid limestone particles.

Appendix Figures 7.1.3 pH in proton acid solution ($\text{pH}_i=2.5$) with ellipsoid limestone particles.

Appendix Figures 7.1.4 Ca in proton acid solution ($\text{pH}_i=2.5$) with ellipsoid limestone particles.

Appendix Figures 7.1.5 pH in proton acid solution ($\text{pH}_i=3.0$) with ellipsoid limestone particles.

Appendix Figures 7.1.6 Ca in proton acid solution ($\text{pH}_i=3.0$) with ellipsoid limestone particles.

Appendix Figures 7.1.7 pH in proton acid solution ($pH_i=3.5$) with ellipsoid limestone particles.

Appendix Figures 7.1.8 pH in proton acid solution ($pH_i=4.0$) with ellipsoid limestone particles.

Appendix Figures 7.1.9 Surface area vs. required reaction time at pH_f 5.5.

Appendix Figures 7.1.10 a and k vs. pH_i at pH_f 5.5.

Appendix Figures 7.1.11 Surface area vs. required reaction time at pH_f 6.0.

Appendix Figures 7.1.12 a and k vs. pH_i at pH_f 6.0.

Appendix Figures 7.1.13 Surface area vs. required reaction time at pH_f 6.5.

Appendix Figures 7.1.14 a and k vs. pH_i at pH_f 6.5.

Appendix Figures 7.1.15 Surface area vs. required reaction time at pH_f 7.0.

Appendix Figures 7.1.16 a and k vs. pH_i at pH_f 7.0.

Appendix Table 7.2.1 pH changes with the neutralization of acid solution by limestone chips.

The neutralization of acid solution by limestone chips										
	pH vs. time					Proton acid by 6.3~11mm crushed limestone chips				
Time	pH1.75	pH2.0	pH2.25	pH2.5	pH2.75	pH3.0	pH3.25	pH3.5	pH3.75	pH4.0
0	1.76	2.00	2.27	2.51	2.80	3.05	3.28	3.58	3.85	4.19
0.5	1.77	2.01	2.91	2.53	2.83	3.15	3.33	3.61	4.20	4.87
1	1.78	2.02	2.32	2.54	2.92	3.21	3.40	3.70	4.52	5.22
1.5	1.81	2.06	2.37	2.56	2.93	3.30	3.43	3.80	4.93	5.89
2	1.85	2.11	2.45	2.59	3.09	3.38	3.52	3.91	5.29	6.11
2.5	1.92	2.17	2.54	2.62	3.13	3.48	3.62	4.05	5.54	6.30
3	1.98	2.25	2.59	2.66	3.26	3.55	3.73	4.18	5.71	6.45
3.5	2.01	2.36	2.68	2.70	3.33	3.66	3.81	4.39	5.85	6.51
4	2.09	2.47	2.80	2.77	3.51	3.78	3.92	4.60	5.94	6.67
4.5	2.16	2.52	2.86	2.84	3.61	3.89	4.07	4.79	6.03	6.83
5	2.23	2.60	2.94	2.90	3.73	4.03	4.27	4.94	6.12	7.01
6	2.40	2.74	3.13	3.04	4.02	4.36	4.55	5.17	6.28	7.48
7	2.57	2.91	3.32	3.21	4.35	4.69	4.75	5.39	6.44	7.98
8	2.76	3.06	3.53	3.40	4.63	4.94	4.94	5.54	6.58	8.44
9	2.90	3.26	3.76	3.68	4.91	5.16	5.08	5.64	6.71	8.76
10	3.11	3.44	4.01	3.94	5.09	5.31	5.20	5.75	6.88	8.96
12	3.55	3.89	4.56	4.41	5.33	5.55	5.36	5.91	7.24	9.20
14	4.09	4.39	4.92	4.66	5.51	5.71	5.49	6.06	7.70	9.22
16	4.49	4.74	5.13	4.84	5.63	5.83	5.60	6.17	7.95	9.29
18	4.75	4.95	5.27	4.96	5.74	5.94	5.71	6.29	8.19	9.36
20	4.92	5.10	5.38	5.08	5.82	6.02	5.78	6.38	8.35	9.37
25	5.18	5.32	5.57	5.29	5.98	6.20	5.97	6.62	8.49	9.40
30	5.34	5.46	5.71	5.45	6.10	6.35	6.16	6.82	8.55	9.40
35	5.46	5.58	5.81	5.59	6.20	6.48	6.26	7.00	8.74	9.41
40	5.55	5.67	5.90	5.72	6.29	6.58	6.40	7.18	8.60	9.40
55	5.75	5.87	6.10	6.02	6.51	6.88	6.80	7.91	8.81	9.38
70	5.89	6.02	6.26	6.30	6.68	7.13	7.38	8.28	8.94	9.36
85	5.99	6.13	6.39	6.50	6.83	7.39	8.01	8.40	9.01	9.34
100	6.08	6.23	6.50	6.64	6.97	7.66	8.24	8.43	9.06	9.31
130	6.22	6.39	6.69	6.85	7.23	8.04	8.11	8.48	8.99	9.26
160	6.33	6.53	6.85	7.04	7.45	8.14	8.19	8.51	8.89	9.22
220	6.53	6.74	7.09	7.31	7.70	8.17	8.23	8.61	8.84	9.16
280	6.71	6.91	7.36	7.49	7.82	8.20	8.19	8.48	8.76	9.09
340	6.90	7.07	7.45	7.62	7.89	8.08	8.21	8.43	8.79	9.03

400	7.08	7.23	7.59	7.68	7.95	8.12	8.25	8.44	8.74	8.97
460	7.27	7.33	7.67	7.75	8.01	8.14	8.25	8.42	8.76	8.90
1430	7.47	7.43	7.69	7.82	7.72	8.18	8.25	8.26	8.68	8.51

Appendix Table 7.2.2 Ca changes with the neutralization of acid solution by limestone chips.

The neutralization of acid solution by limestone chips										
Ca vs. time										
						Proton acid by 6.3~11mm crushed limestone chips				
Ellips.	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)	Ca (mM/L)
Time	PH 1.75	PH 2.0	PH 2.25	PH 2.5	PH 2.75	PH 3.0	PH 3.25	PH 3.5	PH 3.75	PH 4.0
0	0.10	0.04	0.05	0.04	0.05	0.04	0.04	0.04	0.02	0.04
0.5	0.42	0.17	0.09	0.06	0.07	0.04	0.04	0.03	0.02	0.03
1	0.71	0.31	0.20	0.13	0.11	0.06	0.03	0.03	0.02	0.03
1.5	0.99	0.44	0.28	0.18	0.14	0.06	0.04	0.04	0.02	0.03
2	1.17	0.56	0.39	0.20	0.17	0.06	0.04	0.04	0.02	0.03
2.5	1.36	0.66	0.44	0.22	0.19	0.08	0.04	0.04	0.02	0.03
3	1.53	0.78	0.53	0.26	0.21	0.08	0.05	0.04	0.02	0.03
3.5	1.63	0.82	0.58	0.28	0.24	0.09	0.05	0.04	0.02	0.03
4	1.76	0.92	0.75	0.29	0.25	0.10	0.05	0.05	0.02	0.03
4.5	1.88	1.01	0.59	0.30	0.26	0.10	0.06	0.05	0.02	0.03
5	1.77	1.04	0.64	0.32	0.26	0.10	0.05	0.05	0.02	0.03
6	2.15	1.13	0.74	0.33	0.27	0.10	0.07	0.05	0.02	0.04
7	2.12	1.15	0.74	0.34	0.28	0.11	0.05	0.05	0.02	0.03
8	2.42	1.26	0.96	0.36	0.29	0.11	0.05	0.05	0.02	0.03
9	2.41	1.28	0.63	0.36	0.28	0.12	0.06	0.05	0.02	0.03
10	2.34	1.30	0.80	0.37	0.27	0.11	0.06	0.05	0.02	0.03
12	2.34	1.35	0.87	0.37	0.28	0.12	0.06	0.06	0.02	0.03
14	2.45	1.26	0.91	0.37	0.30	0.12	0.06	0.06	0.02	0.03
16	2.50	1.37	0.88	0.37	0.29	0.13	0.07	0.06	0.02	0.04
18	2.52	1.36	0.82	0.37	0.32	0.13	0.07	0.06	0.02	0.04
20	2.58	1.32	0.79	0.38	0.29	0.13	0.07	0.06	0.02	0.03
25	2.75	1.32	0.85	0.41	0.30	0.14	0.08	0.07	0.02	0.04
30	2.77	1.34	0.88	0.41	0.31	0.15	0.08	0.08	0.03	0.04
35	2.78	1.42	0.95	0.42	0.31	0.15	0.09	0.08	0.03	0.03
40	2.82	1.38	0.93	0.42	0.33	0.16	0.09	0.08	0.03	0.04
55	2.85	1.44	0.96	0.42	0.34	0.18	0.09	0.09	0.03	0.04
70	2.92	1.47	1.00	0.46	0.32	0.19	0.10	0.09	0.03	0.04
85	3.07	1.47	1.03	0.46	0.35	0.18	0.09	0.09	0.03	0.04
100	3.06	1.47	1.10	0.47	0.39	0.20	0.10	0.09	0.03	0.04
130	3.05	1.46	1.07	0.49	0.40	0.20	0.09	0.09	0.03	0.04
160	3.14	1.50	1.06	0.52	0.42	0.21	0.10	0.09	0.03	0.04
220	3.15	1.51	1.05	0.53	0.39	0.19	0.11	0.09	0.03	0.04
280	2.99	1.56	1.05	0.52	0.39	0.20	0.11	0.09	0.03	0.04
340	3.05	1.56	1.03	0.51	0.40	0.21	0.11	0.09	0.04	0.04

400	3.14	1.58	1.10	0.52	0.41	0.22	0.12	0.10	0.04	0.05
460	3.10	1.62	1.08	0.53	0.40	0.20	0.12	0.10	0.04	0.06
1430	2.89	1.52	0.89	0.46	0.41	0.20	0.15	0.12	0.05	0.15

Appendix Figure 7.2.1~4

Appendix Figure 7.2.1 pH changes as time.

Appendix Figure 7.2.2 Modeling pH changes as time.

Appendix Figure 7.2.3 Ca changes as time.

Appendix Figure 7.2.4 Modeling Ca changes as time.

Appendix Table 7.3.1 The neutralization test of proton acid solution (pHi=3) by different limestone chips.

Soln Type Heavy Coat			Soln Type Int coat			Soln Type Fresh		
2/22/99pH: 3.0 Wgt:150.506			2/22/99pH: 3.0 Wgt:148.518			2/22/99pH: 3.0 Wgt:144.002		
Time	pH	Ca(dilute)	Time	pH	Ca(dilute)	Time	pH	Ca(dilute)
0	3.00	0.07	0	3.00	0.05	0	3.00	0
0.5	3.03	0.55	0.5	3.02	0.34	0.5	3.02	0.04
1	3.04	0.55	1	3.04	0.4	1	3.04	0.06
1.5	3.06	1.02	1.5	3.05	0.57	1.5	3.07	0.08
2	3.08	1.12	2	3.06	0.61	2	3.11	0.1
2.5	3.10	1.42	2.5	3.07	0.86	2.5	3.14	0.12
3	3.11	1.62	3	3.08	1.02	3	3.16	0.15
3.5	3.13	1.75	3.5	3.09	1.36	3.5	3.19	0.16
4	3.14	1.84	4	3.10	1.19	4	3.22	0.18
4.5	3.16	1.94	4.5	3.11	1.35	4.5	3.26	0.19
5	3.18	2.16	5	3.13	1.42	5	3.28	0.23
6	3.21	2.44	6	3.15	1.77	6	3.36	0.27
7	3.24	2.59	7	3.17	2	7	3.43	0.31
8	3.29	3.03	8	3.20	2.17	8	3.50	0.34
9	3.32	3.28	9			9	3.58	0.42
10	3.35	3.48	10	3.25	2.38	10	3.65	0.47
12	3.43	3.7	12	3.30	2.9	12	3.82	0.57
14	3.51	4.24	14	3.35	3.3	14	4.02	0.61
16	3.59	4.65	16	3.41	3.74	16	4.22	0.66
18	3.67	4.77	18	3.46	3.88	18	4.45	0.69
20	3.75	5.04	20	3.52	4.1	20	4.72	0.81
25	4.00	5.65	25	3.66	4.8	25	5.58	0.87
30	4.22	6.38	30	3.82	4.98	30	5.67	0.91
35	4.54	5.66	35	3.98	5.23	35	5.78	0.96
40	4.83	6.12	40	4.16	5.72	40	5.92	1.07
55			55	4.76	5.96	55	6.23	1.05
70	5.83	6.66	70	5.33	6	70	6.45	1.08
85	6.07	6.69	85	5.65	6.58	85	6.62	1.09
100	6.23	6.86	100	5.88	6.52	100	6.78	1.25
130			130	6.21	6.77	130	6.94	1.34
160	6.77	7.44	160	6.52	7.05	160	7.10	1.42
220	7.23	8.23	220	6.93	7.8	220	7.65	1.48
320	7.84	8.7	280	7.34	7.97	280		1.55
			380	7.87	8.49			

Appendix Table 7.3.2 The neutralization of proton acid solution (pHi=2.5) by fresh limestone chips.

3/8/99 Soln Type pH: 2.5			3/12/99 Soln Type pH: 2.5		
Wgt:149.095	Coated		Wgt:143.967	Fresh	
Time	pH	Ca(dilute)	Time	pH	Ca(dilute)
0	2.50	0.01	0	2.50	-0.05
1	2.52	2.61	1	2.55	2.88
2	2.55	4.64	2	2.59	4.74
3	2.57	6.16	3	2.64	6.26
4	2.59	7.77	4	2.69	7.67
5	2.62	10.40	5		
7	2.67	12.70	7	2.88	12.05
9	2.72	11.30	9	2.98	13.72
11	2.78	15.72	11	3.09	14.71
13	2.83	18.82	13	3.22	15.52
15	2.88	20.78	15	3.35	17.83
20	3.02	18.57	20	3.70	18.94
25	3.16	24.88	25	4.10	19.81
30	3.30	27.85	30	4.63	19.51
35	3.46	30.07	35	5.06	20.28
40	3.61	29.60	40	5.19	20.83
50	3.94	28.12	50	5.48	20.84
60	4.33	31.81	60	5.67	21.87
70	4.73	32.65	70	5.82	21.81
80	5.02	30.57	80	5.93	22.16
90	5.22	31.10	90	6.03	19.98
110	5.50	33.63	110	6.21	23.2
130	5.68	34.18	130	6.35	24.44
150	5.83	33.10	150		
170	5.96	32.18	170		
190	6.09	35.04	190		
220	6.26	35.82	220	6.91	26.07
250	6.43	34.27	250	7.07	24.87
280	6.56	33.67	280	7.21	25.28
310			310	7.44	27.35
340	6.83	36.04	370	7.55	27.03
400	7.10	36.22			

Appendix Table 7.3.3 The neutralization of proton acid solution (pHi=3) by fresh limestone chips.

3/29/99 Soln Type pH: 3.0			3/29/99 Soln Type pH: 3.0		
	Coated			Fresh	
Time	pH	Ca(dilute)	Time	pH	Ca(dilute)
0	3.04	0.07	0	3.05	0.07
1	3.06	0.34	1	3.12	0.74
2	3.08	0.48	2	3.19	1.17
3	3.09	0.66	3	3.26	1.59
4	3.11	0.86	4	3.31	1.91
5	3.13	0.97	5	3.38	2.26
7	3.16	1.19	7	3.52	2.76
9	3.18	1.45	9	3.67	3.18
11	3.22	1.61	11	3.84	3.53
13	3.25	1.84	13	4.03	3.80
15	3.28	2.2	15	4.22	3.89
20	3.36	2.48	20	4.86	4.19
25	3.45	2.89	25	5.37	4.40
30	3.54	3.18	30	5.62	4.60
35	3.63	3.47	35	5.80	4.77
40	3.72	3.97	40	5.94	4.90
50	3.93	4.23	50	6.14	5.17
60	4.16	4.33	60	6.31	5.47
70	4.41	4.36	70	6.44	5.67
80	4.76	4.52	80	6.60	5.78
90	5.09	4.81	90	6.70	5.89
110	5.61	4.8	110	6.95	6.30
130	5.92	5.02	130	7.14	6.57
150	6.15	5.17	150	7.40	6.65
170	6.33	5.3	170	7.64	6.97
190	6.51	5.48	190	7.81	7.15
220	6.73	5.72	220		
250	6.98	6.12	250		
280	7.19	5.99	280		
310			310		
340			340		
400			400		
460			460		
520			520		

Appendix Table 7.3.4 The neutralization of proton acid solution (pHi=3.5) by fresh limestone chips.

3/30/99 Soln Type pH: 3.5			3/30/99 Soln Type pH: 3.5		
	Fresh			Coated	
Time	pH	Ca(dilute)	Time	pH	Ca(dilute)
0	3.55	0.02	0	3.57	0.01
1	3.70	0.38	1	3.65	0.12
2	3.86	0.49	2	3.67	0.25
3	4.01	0.60	3	3.69	0.16
4	4.25	0.48	4	3.71	0.19
5	4.38	0.78	5	3.75	0.22
7	4.72	0.86	7	3.79	0.30
9	5.17	0.93	9	3.85	0.34
11	5.48	1.02	11	3.90	0.40
13	5.70	1.10	13	3.94	0.44
15	5.87	1.11	15	3.99	0.50
20	6.14	1.17	20	4.13	0.59
25	6.36	1.34	25	4.28	0.69
30	6.54	0.14	30	4.45	0.75
35	6.71	1.50	35	4.66	0.84
40	6.86	1.66	40	4.90	0.89
50	7.95	1.72	50	5.40	0.96
60	8.17	1.82	60	5.76	1.06
70	8.37	1.89	70	5.99	1.10
80	8.50	1.91	80	6.17	1.15
90			90	6.32	1.22
110			110	6.01	1.34
130			130	6.88	1.41
150			150	7.13	1.49
170			170	7.47	1.51
190			190	7.91	1.58
220			220		
250			250		
280			280		
310			310		
340			340		
400			400		
460			460		
520			520		

Appendix Table 7.3.5 The neutralization of proton acid solution (pHi=4.0) by fresh limestone chips.

3/30/99 Soln Type pH: 4.0			3/30/99 Soln Type pH: 4.0		
	Coated			Fresh	
Time	pH	Ca(dilute)	Time	pH	Ca(dilute)
0	4.14	0.01	0	4.04	0.04
1	4.24	0.02	1	4.21	0.18
2	4.28	0.03	2	4.41	0.22
3	4.32	0.04	3	4.63	0.26
4	4.35	0.06	4	4.94	0.29
5	4.38	0.05	5	5.28	0.31
7	4.44	0.07	7	5.80	0.40
9	4.52	0.11	9	6.10	0.44
11	4.60	0.11	11	6.36	0.49
13	4.70	0.15	13	6.56	0.53
15	4.82	0.15	15	6.76	0.56
20	5.18	0.19	20	8.30	0.67
25	5.66	0.23	25	8.81	0.83
30	5.97	0.27	30	8.96	0.79
35	6.19	0.29	35	9.03	0.88
40	6.39	0.30	40		
50	6.09	0.38	50		
60	7.01	0.40	60		
70	7.52	0.48	70		
80	8.21	0.56	80		
90			90		
110			110		
130			130		
150			150		
170			170		
190			190		
220			220		
250			250		
280			280		
310			310		
340			340		
400			400		
460			460		
520			520		

Appendix Table 7.4.1 The neutralization of 0.0008M iron solutions (FeCl₃).

1.1-0.0008Fe Limestone Neutralize FeCl3 Solution

[FeCl3]=0.0008 M Limestone Size = 6.3~11mm; Initial Weight=99.697g;							
FeCl3*6H2O (Mol.Wt=270.32) Wt.=0.087g				[Fe]=42 mg/L			
The beaker filled with 400 ml water + FeCl3, The solution pH =3.10 [FeCl3]=0.0008 mol/L							
Each time pick out 0.6ml (before#15) and 1.0ml (After#16) solution and dilute with 4ml of 2% HNO3 for Fe and Ca Analysis							
				[Ca] ppm	[Fe] ppm	[Ca] ppm	[Fe] ppm
	Time	React t	pH	Diluted	Diluted	Real	Real
1	10:00	0	3.10	0.01	8.64	0.10	66.24
2	1	1	3.12	4.90	9.27	37.58	71.09
3	1'30		3.10				
4	2	2	3.09	6.01	8.27	46.05	63.42
5	2'30		3.08				
6	2'45		3.09				
7	3	3	3.10	7.08	8.00	54.28	61.30
8	4	4	3.13	8.53	8.29	65.37	63.53
9	5	5	3.17	9.50	8.26	72.83	63.32
10	6	6	3.26	10.35	8.27	79.35	63.37
11	7	7	3.34	9.76	7.49	74.81	57.43
12	8	8	3.41	10.49	7.35	80.41	56.33
13	10	10	3.55	9.01	6.02	69.10	46.13
14	12	12	3.87	12.79	7.38	98.03	56.56
15	15	15	4.32	8.67	5.01	66.45	38.43
16	19	19	4.73	8.85	4.44	67.87	34.06
17	25	25	5.16	10.67	4.55	81.78	34.88
18	33	33	5.50	10.25	3.55	78.61	27.25
19	45	45		10.15	2.98	77.79	22.81
20	11:00	60	6.06	14.63	3.75	73.15	18.73
21	11:30	90	6.39	16.28	3.17	81.40	15.87
22	12:15	135	6.77	17.18	2.42	85.89	12.08
23	13:00	180	7.04	17.36	1.81	86.78	9.03
24	50	230	7.29	17.50	1.41	87.48	7.06
25	15:35	275	7.58	18.27	1.31	91.37	6.57
26	17:12	432	7.69	19.54	4.05	97.68	20.23

Appendix Table 7.4.2 The neutralization of 0.0015M iron solutions (FeCl₃).

1.1-0.0015Fe Limestone Neutralize FeCl3 Solution								
	#3 beaker		9/23/98		[FeCl3]=0.0015 M		22.6oC	
	Limestone Size = 6.3~11mm; Initial Weight=99.819g;							
FeCl3*6H2O (Mol.Wt=270.32) Wt.=0.164g				[Fe]=92 mg/L				
The beaker filled with 400 ml water + FeCl3, The solution pH =2.86 [FeCl3]=0.0015 mol/L								
Each time pick out 0.6ml solution and dilute with 4ml of 2% HNO3 for Fe and Ca Analysis								
					[Ca] ppm	[Fe] ppm	[Ca] ppm	[Fe] ppm
Time	React t	pH	Sample #	Observe	Diluted	Diluted	Real	Real
10:05	0	2.86	0				[Ca] ppm	[Fe] ppm
6	1	2.89	1		6.03	15.42	46.3	118.2
7	2	2.86	2		7.64	13.77	58.6	105.6
8	3	2.85	3		9.61	13.65	73.7	104.6
9	4	2.86	4		10.35	13.29	79.4	101.9
10	5	2.89	5		12.09	13.13	92.7	100.6
11	6	2.93	6		12.42	12.73	95.2	97.6
12	7	2.98	7		13.12	12.90	100.6	98.9
14	9	3.08	8		14.16	12.51	108.6	95.9
16	11	3.22	9		16.85	12.68	129.1	97.2
20	15	3.49	10		17.18	12.00	131.7	92.0
24	19	3.76	11		18.06	11.15	138.5	85.4
29	24	4.09	12		18.99	9.02	145.6	69.2
35	30	4.5	13		18.37	13.51	140.9	103.6
42	37	4.74	14		20.25	6.99	155.2	53.6
52	47	5.08	15		19.40	5.66	148.8	43.4
11:05	60	5.41	16		37.53	7.90	287.7	60.6
20	75	5.7	17		22.33	4.43	171.2	34.0
40	95	5.97	18		23.35	5.22	179.0	40.0
12:03	118	6.22	19		22.72	2.97	174.2	22.7
27	142	6.39	20		25.05	3.03	192.0	23.2
59	174	6.59	21		24.06	2.13	184.4	16.3
13:53	228	6.87	22		24.46	1.64	187.5	12.6
14:55	290	7.1	23		29.24	2.65	224.1	20.3
15:56	351	7.26	24		26.65	2.79	204.3	21.4
17:13	498	7.39	25		27.58	2.62	211.4	20.1

Appendix Table 7.4.3 The neutralization of 0.003M iron solutions (FeCl₃).

1.1-0.003Fe Limestone Neutralize FeCl3 Solution								
	#5 beaker		9/23/98		[FeCl3]=0.003 M	22.6oC		
Limestone Size = 6.3~11mm; Initial Weight=99.819g; Last Weight=								
FeCl3*6H2O (Mol.Wt=270.32) Wt.=0.324g					[Fe]=168 mg/L			
The beaker filled with 400 ml water + FeCl3, The solution pH =2.313, 2.296, 2.292 [FeCl3]=0.003 mol/L								
Each time pick out 0.6ml solution and dilute with 4ml of 2% HNO3 for Fe and Ca Analysis								
					[Ca] ppm	[Fe] ppm	[Ca] ppm	[Fe] ppm
Time	React t	pH	Sample#	Observed	Diluted	Diluted	Real	Real
9:20	0	2.289	<u>1</u>		0.29	40.68	2.2	311.9
21	2	2.361	2		3.94	33.90	30.2	259.9
22		2.456	3		8.75	31.14	67.1	238.8
24		2.648	4		14.51	27.91	111.3	214.0
26		2.853	5		19.07	27.68	146.2	212.2
28		3.011	6		21.95	26.26	168.3	201.3
31		3.058	7		27.43	33.13	210.3	254.0
34		3.108	8		29.03	26.32	222.6	201.8
38		3.245	9		30.11	24.83	230.8	190.4
42		3.543	10		33.10	26.06	253.7	199.8
47		4.153	11		32.33	24.35	247.8	186.7
52		4.826	12		33.84	24.16	259.4	185.3
59		5.233	13	unclear	34.44	29.90	264.0	229.2
10:05		5.392	14		35.75	20.97	274.1	160.7
11		5.522	15		39.70	20.76	304.4	159.1
18		5.64	16		37.61	19.83	288.3	152.0
29		5.792	17		35.94	18.02	275.6	138.2
42		5.935	18		36.11	15.27	276.9	117.1
52		6.018	19		37.16	14.50	284.9	111.1
11:05		6.136	20		38.89	14.12	298.2	108.2
20		6.234	21		40.55	14.18	310.9	108.7
40		6.339	22		41.75	27.82	320.1	213.3
12:03		6.461	23		40.85	11.85	313.2	90.9
27		6.57	24		40.83	10.92	313.1	83.7
58		6.677	25		42.93	9.64	329.1	73.9
			26		41.14	8.62	315.4	66.1
			27		42.09	8.20	322.7	62.8
14:55		7.027	27		42.01	9.19	322.1	70.5
17:13		7.321	29		48.71	12.98	373.4	99.5

Appendix Table 7.4.4 The neutralization of 0.008M iron solutions (FeCl_3).

1.1-0.008Fe Limestone Neutralize FeCl3 Solution								
9/14/98				[FeCl3]=0.0085 M			20.5oC	
#4beaker Limestone Size = 6.3~11mm; Initial Weight=99.970g; Last Weight=								
FeCl3*6H2O (Mol.Wt=270.32) Wt.=0.901g				[Fe]=467 mg/L				
400 ml water + FeCl3, The solution pH =2.388, 2.390 [FeCl3]=0.00833 mol/L								
Each time pick out 0.6ml solution and dilute with 2ml of 2% HNO3 for Fe and Ca Analysis								
					[Ca] ppm	[Fe] ppm		
time	React t	pH	No.	Observed	Diluted	Diluted	[Ca] ppm	[Fe] ppm
0	9:50	2.39	0	Very light yellow	0.4	153.8	1.8	666.3
1	51	2.43	1		16.4	151.1	70.9	654.8
3	53	2.53	2		37.3	146.4	161.5	634.3
5	55	2.58	3	begin a little red	48.0	144.0	208.2	624.1
7	57	2.57	4		60.2	143.9	261.0	623.5
9	59	2.56	5	pH begin up @10:02	66.1	139.0	286.4	602.3
11	10:01	2.55	6		79.6	138.0	344.7	598.0
13	3	2.55	7		83.2	138.1	360.4	598.3
15	5	2.56	8		87.8	130.3	380.5	564.5
18	8	2.58	9	small bulbs go up	90.6	118.7	392.7	514.4
21	11	2.61	10		115.5	134.3	500.7	582.0
25	15	2.64	11		124.1	131.7	537.7	570.6
30	20	2.70	12		141.0	134.4	611.2	582.3
37	27	2.79	13		158.5	135.2	687.0	586.0
43	33	2.95	14		167.0	134.9	723.6	584.5
50	40	3.21	15	chang to red	171.7	128.2	743.8	555.5
60	50	3.70	16		170.8	123.0	740.3	533.2
66	56	3.91	17	seems a little unclear	165.4	118.2	716.6	512.3
69	59	3.96	18	precipitation produce	174.7	111.0	757.0	481.0
80	11:10	4.15	19	all unclear	175.6	104.0	760.8	450.5
90	20	4.34	20		179.6	93.5	778.4	405.2
117	37	4.62	21		180.8	88.2	783.6	382.1
130	12:00	4.95	22		192.3	83.3	833.1	360.9
151	21	5.19	23		181.0	70.7	784.3	306.4
180	50	5.47	24		194.8	122.5	844.2	530.6
213	13:23	5.68	25		206.8	88.2	896.3	382.1
257	14:07	6.00	26		192.8	94.9	835.6	411.4
370	16:00	6.25	27		187.5	108.1	812.5	468.3
585	18:15	6.63	28		202.4	64.0	876.9	277.5
					183.4	29.6	794.6	128.2

Appendix Table 7.4.5 The neutralization of 0.016M iron solutions (FeCl₃).

1.1-0.016Fe Limestone Neutralize FeCl3 Solution								
9/4/98					[FeCl3]=0.017 M		22.6oC	
Limestone Size = 6.3~11mm; Initial Weight=99.971g;								
FeCl3*6H2O (Mol.Wt=270.32) Wt.=1.802g								
400 ml water + FeCl3, The solution pH =2.255, 2.257, 2.254 [FeCl3]=0.0167 mol/L								
Each time pick out 0.6ml solution and dilute with 2ml of 2% HNO3 for Fe and Ca Analysis								
					[Ca] ppm	[Fe] ppm	[Ca] ppm	[Fe] ppm
Time	React t	pH	No.	Observed	Diluted	Diluted	[Ca] ppm	[Fe] ppm
9:50	0	2.27	0	light yellow	0	338	1	1463
51	1	2.31	1		28	373	119	1617
52	2	2.37	2		51	333	219	1443
54	4	2.47	3		69	299	299	1298
56	6	2.54	4	yellow increase	78	323	339	1402
58	8	2.55	5		98	305	425	1322
10:00	10	2.54	6	dark yellow to red	106	315	458	1364
2	12	2.53	7		136	344	588	1491
4	14	2.53	8		155	329	670	1426
6	16	2.53	9		159	325	687	1407
10	20	2.54	10	pH up, air bulbs appear	176	321	763	1393
12	22	2.54	11		169	321	731	1392
15	25	2.55	12		196	330	849	1432
19	29	2.56	13		220	295	952	1278
23	33	2.58	14		204	298	885	1291
28	38	2.61	15		237	308	1027	1336
33	43	2.64	16		292	320	1264	1389
39	49	2.71	17		299	299	1297	1296
45	55	2.82	18	become dim red	311	280	1346	1211
52	62	3.05	19		334	312	1449	1353
59	69	3.45	20		355	307	1537	1331
11:06	76	3.73	21	a little unclear arund 11:10	351	300	1522	1301
12	82	3.85	22		345	308	1494	1336
18	88	3.93	23	all unclear	309	57	1338	245
24	94	4.01	24	precipitation appears	346	365	1500	1581
43	113	4.24	26		353	388	1528	1681
12:00	130	4.46	28		359	367	1558	1592
45	175	4.92	30		377	248	1635	1074
16:00	370	5.85	31		362	0	1568	1

Appendix Table 7.4.6 The neutralization of 0.03M iron solutions (FeCl_3).

1.1-0.03Fe Limestone Neutralize FeCl3 Solution							
8/31/98				[FeCl3]=0.03 M			
Limestone Size = 6.3~11mm; Initial Weight=100.083g; Last Weight=FeCl3*6H2O (Mol.Wt=270.32) Wt.=3.604g							
The beaker filled with 400 ml water + FeCl3, The solution pH = 2.037, 2.025, 2.022 [FeCl3]=0.03333 mol/L							
Each time pick out 0.6ml solution and dilute with 2ml of 2% HNO3 for Fe and Ca Analysis							
					[Ca] ppm	[Fe]	[Ca] ppm
Time	React t	pH	Sample#	Observed Phenominon	Diluted	Diluted	[Ca] ppm
9:50	0	2.02	1		30		132
51	1	2.06	2		38		166
53	3	2.19	3		77		335
56	6	2.30	4		127		551
10:00	10	2.37	5	Color to red	156		677
5	15	2.36	6	more red	196		848
11	21	2.35	7		238		1030
17	27	2.33	8		241		1046
25	35	2.32	9		322		1394
34	44	2.33	10		359		1555
11:07	77	2.57	11		489		2119
20	90	2.87	12	Looks unclear	452		1961
40	110	3.45	13		552		2393
12:00	130	3.67	14		517		2241
12:20	150	3.89	15		548		2376
40	180	4.08	16	Precip. appears	531		2300
13:25	215	4.21	17#Sol.	Separate 2 phases	542		2349
14:25	275	4.64	19-Sol.		553		2398
15:30	340	5.00	21-Sol.		564		2445
16:40	410	5.28	23-Sol.		555		2405
17:45	475	5.40	25-Sol.		601		2604
16-Sep							
16:25		6.26	27-Sol.		572		2479
4-Sep							
10:00		7.14	28-Sol.		546		2365
9-Sep							
12:10			29-Sol.	Solution totally clear			

Appendix Table 7.4.4 The neutralization of 0.0M iron solutions (FeCl_3).

1.1-0.0 Limestone Neutralize FeCl3 Solution						
		8-28-98 [Fe3+]=0.0 M				
Limestone Size = 6.3~11mm; Initial Weight=100.083g; Last Weight=						
The beaker filled with 400 ml water + HCl solution pH = 1.480 [Fe]=0.0M						
Each time pick out 0.6ml solution and dilute with 2ml of 2% HNO3 for Fe and Ca Analysis						
				[Ca] ppm	[Fe] ppm	[Ca] ppm
Time	React t	pH	Sample#	Diluted	Diluted	[Ca] ppm
9:35	0	1.48	1	0		0
36	1	1.52	2	45		195
37	2	1.59	3	86		372
38	3	1.63	4	114		492
40	5	1.76	5	168		727
42	7	1.92	6	177		766
44	9	2.11	7	172		746
46	11	2.30	8	237		1027
49	14	2.60	9	245		1060
52	17	2.88	10	264		1145
55	20	3.22	11	255		1106
10:00	25	3.98	12	253		1094
4	29	4.56	13	253		1095
11	36	4.91	14	257		1112
17	42	5.08	15	240		1041
	48		16	276		1194
31	56	5.21	17	252		1093
37	62	5.40	18	299		1295
50	85	5.53	19	256		1110
11:30	115	5.79	20	275		1193
12:13	158	5.99	21	293		1269
12:50	195	6.10	22	298		1291
13:55	260	6.29	23	330		1430
15:00	325	6.47	24	285		1235
15:58	383	6.63	25	285		1236
17:00	455	6.81	26	294		1272
8/28/98						
9:10		7.28	27	271		1173
				583		2526

Appendix Table 7.4.8 The neutralization of 0.0005M iron solution by
saran coated limestone.

4/8/99		Fe = 0.0005M				
One available surface		DI Water =400 ml				
Time	pH	Ca (mM)	Fe(mM)	Ca(dilute)	Fe(dilute)	
Time	0.5mMFe	0.5mMFe	0.5mMFe	0.5mMFe	0.5mMFe	
0	2.97	0.02	0.55	0.17	5.4	
3	3.09	0.11	0.53	0.82	5.29	
6	3.14	0.21	0.55	1.49	5.43	
9	3.18	0.29	0.55	2.09	5.4	
12	3.20	0.36	0.53	2.58	5.23	
15	3.24	0.43	0.53	3.11	5.2	
20	3.29	0.52	0.50	3.72	4.97	
25	3.36	0.59	0.49	4.27	4.9	
30	3.44	0.67	0.50	4.82	4.93	
35	3.55	0.73	0.50	5.27	4.96	
40	3.68	0.78	0.49	5.61	4.89	
50	4.01	0.89	0.50	6.39	4.95	
60	4.52	0.93	0.49	6.66	4.83	
80	5.75	1.01	0.48	7.29	4.79	
100	6.12	1.03	0.46	7.39	4.52	
120	6.41	1.01	0	7.25	0.02	
150	6.74	0.94	0	6.76	0	
180	7.00	1.05	0	7.53	0	
210	7.22	1.05	0	7.53	0	
240	7.42	0.90	0	6.48	0	
270	7.55	0.85	0	6.15	0	
300	7.68	1.02	0	7.37	0	
330						
360						
390						
420						
450						

Appendix Table 7.4.9 The neutralization of 0.001M iron solution by saran coated limestone.

4/9/99		Fe = 0.001M				
One available surface						
DI Water =500ml FeCl3 = 0.108g						
Time	pH	Ca (mM)	Fe(mM)	Ca(dilute)	Fe(dilute)	
Time	1mMFe	1mMFe	1mMFe	1mMFe	1mMFe	
0	3.01	0.07	1.07	0.51	10.57	
3	3.14	0.11	1.05	0.79	10.41	
6	3.21	0.23	1.02	1.62	10.05	
9	3.23	0.33	0.97	2.41	9.62	
12	3.23	0.49	0.96	3.54	9.47	
15	3.24	0.55	0.96	3.98	9.5	
20	3.26	0.72	0.94	5.16	9.27	
25	3.30	0.89	0.93	6.43	9.23	
30	3.34	1.02	0.92	7.37	9.08	
35	3.41	1.14	0.89	8.23	8.85	
40	3.50	1.27	0.89	9.12	8.81	
50	3.78	1.54	0.88	11.07	8.68	
60	3.81	1.51	0.84	10.85	8.32	
80	4.73	1.75	0.85	12.58	8.42	
100	5.45	1.76	0.76	12.68	7.5	
120	5.88	1.61	0.51	11.61	5	
150	6.21	1.72	0	12.4	0	
180	6.41	1.73	0	12.42	0	
210	6.62	1.73	0	12.44	0	
240	6.83	1.88	0	13.57	0	
270	6.98	1.83	0	13.14	0	
300	7.13	1.82	0	13.09	0	
330	7.25	1.80	0	12.93	0	
360	7.39	1.82	0	13.13	0	
390	7.50	1.79	0	12.87	0	
420	7.60	1.74	0	12.54	0	

Appendix Table 7.4.10 The neutralization of 0.002M iron solution by
saran coated limestone.

4/28/99		Fe = 0.002M			
One available surface					
DI Water =400 mL			FeCl3 =		
*Note: Dilution is 4.1:0.9ml. For Fe sample 0-15 (up to 120min) diluted again at 0.75:0.75ml					
Time	pH	Ca (mM)	Fe(mM)	Ca(dilute)	Fe(dilute)
Time	2mMFe	2mMFe	2mMFe	2mMFe	2mMFe
0	2.99	0.00	2.16	0.02	10.68
3	2.97	0.30	2.16	2.13	10.68
6	3.02	0.51	2.07	3.70	10.24
9	3.02	0.73	2.08	5.22	10.29
12	3.00	0.90	2.05	6.46	10.14
15	2.98	1.08	2.00	7.80	9.89
20	2.96	1.33	1.97	9.54	9.76
25	2.96	1.61	1.96	11.59	9.69
30	2.97	1.80	1.93	12.96	9.57
35	2.99	2.09	1.98	15.02	9.81
40	3.01	2.17	1.89	15.60	9.34
50	3.09	2.62	1.98	18.88	9.81
60	3.25	2.78	1.86	20.02	9.21
80	3.72	3.12	1.85	22.45	9.16
105	4.68	2.80	1.54	20.17	7.61
120	5.21	2.50	1.41	17.99	6.97
150	5.56	2.60	1.01	18.76	5
180	5.92	2.71	0	19.52	0
210	6.14	2.77	0	19.93	0
240	6.35	3.40	0	24.51	0
270	6.54	3.19	0	23.00	0
300	6.73	3.14	0	22.61	0
330	6.87	3.09	0	22.26	0
360	7.00	3.57	0	25.70	0
390	7.12	3.32	0	23.89	0
420					

Appendix Table 7.4.11 The neutralization of 0.004M iron solution by
saran coated limestone.

4/27/99			Fe = 0.004M			
*Note: Dilution is 4.1:0.9ml. For Fe diluted again at 2.7:0.9ml						
			One available surface FeCl3 =			
DI Water =400 mL						
Time	pH	Ca (mM)	Fe(mM)	Ca(dilute)	Fe(dilute)	
Time	4.5mMFe	4.5mMFe	4.5mMFe	4.5mMFe	4.5mMFe	
0	2.70	0.02	4.46	0.17	11.04	
3	2.73	0.34	4.42	2.47	10.93	
7	2.78	0.64	4.41	4.59	10.91	
9	2.80	0.79	4.37	5.67	10.81	
11	2.82	0.98	4.55	7.06	11.27	
15	2.84	1.18	4.37	8.49	10.82	
20	2.84	1.67	4.33	12.01	10.72	
25	2.81	2.08	3.63	15.02	8.98	
30	2.79	2.36	3.09	17.10	7.66	
35	2.77	2.50	3.07	18.20	7.60	
40	2.76	2.78	3.19	20.12	7.90	
50	2.75	3.19	3.43	23.11	8.50	
60	2.75	3.47	3.30	25.00	8.16	
80	2.78	3.75	3.25	27.02	8.04	
100	2.84	3.84	3.22	27.64	7.98	
120	2.97	4.72	3.17	34.04	7.85	
150	3.26	4.74	3.05	34.10	7.54	
180	3.80	5.13	3.13	36.92	7.75	
210	4.44	5.14	3.01	37.03	7.46	
240	4.94	4.86	1.31	35.09	3.23	
270	5.21	4.72	0.21	34.01	0.72	
300	5.39	4.86	0.07	35.03	0.18	
330	5.56	5.30	0	38.16	0	
360	5.75	5.40	0	38.87	0	
390	5.94	5.33	0	38.36	0	

Appendix Table 7.4.12 The neutralization of 0.008M iron solution by
saran coated limestone.

4/23/99			Fe = 0.008M		
One available surface					
DI Water = 400ml			FeCl3 = .865g		
*Note: Dilution is 4.1:0.9ml. For Ca diluted samples 14-26 again at 0.9:0.9ml. Fe samples 0-21 diluted again at 4.5:0.75ml					
Time	pH	Ca (mM)	Fe(mM)	Ca(dilute)	Fe(dilute)
Time	10mMFe	10mMFe	10mMFe	10mMFe	10mMFe
0	2.44	0.04	9.87	0.14	13.96
3	2.51	1.33	9.76	4.79	13.80
6	2.57	2.37	9.81	8.53	13.87
9	2.62	3.15	9.79	11.34	13.84
12	2.66	3.81	9.59	13.73	13.56
15	2.70	4.34	9.34	15.62	13.21
20	2.74	4.78	9.33	17.20	13.20
25	2.74	5.59	9.35	20.14	13.22
30	2.70	6.39	8.90	23.02	12.59
35	2.67	7.19	9.09	25.87	12.86
40	2.64	8.48	9.05	30.54	12.81
50	2.60	8.60	8.41	28.64	11.92
60	2.57	9.31	8.34	33.50	11.85
80	2.56	9.30	8.41	39.21	11.91
100	2.59	10.00	7.99	28.92	11.30
120	2.65	10.10	7.85	30.54	11.19
150	2.68	10.26	7.92	36.94	11.21
180	3.20	11.46	8.07	41.26	11.42
210	3.66	11.13	7.53	40.07	10.65
240	4.12	11.40	6.98	38.87	9.87
270	4.49	11.45	6.38	37.68	9.02
300	4.78	11.80	2.69	39.17	3.81
330	5.00	10.90	0.54	35.58	0.76
360	5.14	11.39	0	41.02	0
390	5.28	12.30	0	38.04	0
420	5.36	12.03	0	43.31	0
450	5.45	13.49	0	48.57	0

Appendix Table 7.5.1 The neutralization iron solution by 0M Fe coated limestone.

Fe solution by limestone of one available surface					
		DI Water = 500ml		FeCl ₃ = 0.108g	
		4/9/99		Fe = 0.001M	
	pH	Ca(dilute)	Fe(dilute)	Ca(mmol/L)	Fe(mmol/L)
Time	0-coat	0-coat	0-coat	0-coat	0-coat
0	3.01	0.51	10.57	52	1468
3	3.14	0.79	10.41	80	1446
6	3.21	1.62	10.05	164	1396
9	3.23	2.41	9.62	243	1336
12	3.23	3.54	9.47	358	1315
15	3.24	3.98	9.50	402	1319
20	3.26	5.16	9.27	521	1288
25	3.30	6.43	9.23	649	1282
30	3.34	7.37	9.08	744	1261
35	3.41	8.23	8.85	831	1229
40	3.50	9.12	8.81	921	1224
50	3.70	11.07	8.68	1118	1206
60	4.01	10.85	8.32	1096	1156
80	4.73	12.58	8.42	1271	1169
100	5.45	12.68	0.50	1281	69
120	5.88	11.61	0	1173	0
150	6.21	12.40	0	1253	0
180	6.41	12.42	0	1255	0
210	6.62	12.44	0	1257	0
240	6.83	13.57	0	1371	0
270	6.98	13.14	0	1327	0
300	7.13	13.09	0	1322	0
330	7.25	12.93	0	1306	0
360	7.39	13.13	0	1326	0
390	7.50	12.87	0	1300	0
420	7.60	12.54	0	1267	0
450					

Appendix Table 7.5.2 The neutralization iron solution by 0.002M Fe coated limestone.

0.002M Fe coating					
	DI Water =400ml			FeCl ₃ = 0.108g	
		5/11/99		Fe = 0.001M	
	pH	Ca(dilute)	Fe(dilute)	Ca(mmol/L)	Fe(mmol/L)
Time	2mM-coat	2mM-coat	2mM-coat	2mM-coat	2mM-coat
0	3.11	0.07	9.35	7	1299
3	3.12	1.68	9.46	170	1314
6	3.13	2.09	9.29	211	1290
9	3.15	2.28	9.22	230	1281
12	3.19	2.77	9.17	280	1274
15	3.20	3.02	9.04	305	1256
20	3.18	3.45	8.99	348	1249
25	3.18	3.90	8.93	394	1240
30	3.17	4.41	8.84	445	1228
35	3.15	4.81	8.82	486	1225
40	3.20	5.23	8.65	528	1201
50	3.20	6.16	8.58	622	1192
60	3.23	7.01	8.41	708	1168
80	3.35	8.46	8.33	855	1157
100	3.60	9.12	7.53	921	1046
120	4.10	9.10	6.68	919	928
150	4.75	11.37	7.63	1148	1060
180	5.15	11.28	6.37	1139	885
210	5.42	12.14	0	1226	0
240	5.59	12.23	0	1235	0
270	5.76	13.33	0	1346	0
300	5.98	13.25	0	1338	0
330	6.13	13.47	0	1361	0
360	6.26	14.42	0	1457	0
390					
420					
450					

Appendix Table 7.5.3 The neutralization iron solution by 0.004M Fe coated limestone.

0.004M Fe coating					
	DI Water =400ml			FeCl3 = 0.108g	
5/12/99			Fe = 0.001M		
	pH	Ca(dilute)	Fe(dilute)	Ca(mmol/L)	Fe(mmol/L)
Time	4mM-coat	4mM-coat	4mM-coat	4mM-coat	4mM-coat
0	3.11	0.09	10.43	9	1449
3	3.13	7.51	10.25	759	1424
6	3.14	7.84	10.09	792	1402
9	3.15	8.29	9.99	837	1387
12	3.15	8.30	9.84	838	1367
15	3.15	8.93	9.72	902	1350
20	3.14	9.54	9.56	964	1328
25	3.13	10.16	9.41	1026	1307
30	3.12	10.68	9.42	1079	1309
35	3.11	11.25	9.25	1136	1285
40	3.11	11.74	9.14	1186	1270
50	3.12	12.63	8.82	1276	1225
60	3.14	13.90	8.92	1404	1238
80	3.15	15.62	8.31	1578	1154
100	3.19	17.06	8.79	1723	1221
120	3.25	18.16	8.26	1834	1147
150	3.60	18.95	7.94	1914	1102
180	4.10	19.75	7.69	1995	1069
210	4.45	20.14	6.95	2034	966
240	4.70	20.52	6.95	2073	966
270	4.90	20.76	0.00	2097	0
300	5.10				
330	5.30				
360	5.40				
390					
420					
450					

Appendix Table 7.5.4 The neutralization iron solution by 0.006M Fe coated limestone.

0.006M Fe coating					
	DI Water =200ml			FeCl3 = 0.054g	
5/6/99			Fe = 0.001M		
	pH	Ca(dilute)	Fe(dilute)	Ca(mmol/L)	Fe(mmol/L)
Time	6mM-coat	6mM-coat	6mM-coat	6mM-coat	6mM-coat
0	3.00	0.18	10.62	18	1475
3	3.00	5.66	10.52	572	1461
6	3.01	5.91	10.78	597	1497
9	3.01	6.22	10.68	628	1483
12	3.01	6.52	10.71	659	1488
15	3.01	6.65	10.65	672	1479
20	3.01	7.00	10.65	707	1479
25	3.01	7.49	10.85	757	1507
30	3.01	7.64	10.68	772	1483
35	3.01	7.90	10.62	798	1475
40	3.00	8.16	10.37	824	1440
50	3.00	8.95	10.49	904	1457
60	2.99	9.51	10.34	961	1436
80	2.98	11.63	10.26	1175	1425
100	3.02	11.17	9.15	1128	1271
120	3.05	12.15	8.99	1227	1249
150	3.14	14.83	9.55	1498	1326
180	3.27	15.65	9.37	1581	1301
210	3.45	17.38	9.49	1756	1318
240	3.64	17.42	9.12	1760	1267
270	3.92	17.99	8.85	1817	1229
300	4.12	16.58	7.24	1675	1006
330	4.23	19.95	0	2015	0
360	4.36	20.29	0	2049	0
390					
420					
450					

Appendix Table 7.5.5 pH changing rate.

pH changes as the reaction time (dpH/dt)				
Time	0Coat	2coat	4coat	6coat
0	0.0460	0.0030	0.0062	0.0003
3	0.0210	0.0033	0.0042	0.0023
6	0.0077	0.0067	0.0020	0.0010
9	0.0003	0.0133	0.0000	0.0003
12	0.0017	0.0033	-0.0011	-0.0003
15	0.0040	-0.0042	-0.0017	-0.0006
20	0.0080	-0.0008	-0.0023	0.0004
25	0.0090	-0.0010	-0.0016	-0.0008
30	0.0132	-0.0040	-0.0007	-0.0002
35	0.0182		0.0000	-0.0010
40	0.0203	0.0007	0.0007	-0.0004
50	0.0310	0.0024	0.0017	-0.0004
60	0.0362	0.0062	0.0006	-0.0008
80	0.0359	0.0125	0.0020	0.0021
100	0.0215	0.0250	0.0030	0.0017
120	0.0108	0.0217	0.0117	0.0031
150	0.0070	0.0133	0.0167	0.0041
180	0.0070	0.0091	0.0117	0.0060
210	0.0069	0.0056	0.0083	0.0064
240	0.0049	0.0057	0.0067	0.0093
270	0.0052	0.0074	0.0067	0.0068
300	0.0039	0.0048	0.0067	0.0037
330	0.0047	0.0044	0.0033	0.0042

Appendix Table 7.5.6 Coating thickness vs. iron concentration.

Coating Thickness vs. Fe Concentration				
Coating Solution Fe mmol/L	Coating Thickness (um)	Time of Fe removal (min)	Final pH	
	0	0	120	6.98
	2	12.5	210	5.76
	4	20	270	4.90
	6	30	300	3.92

VITA

Name Qingyun Sun

Birth Date May 22, 1962

Birth Place Xuzhou, China

Education

Xuzhou 10 th High School	1975-1980
China University of Mining & Technology, Xuzhou	1980-1984
China University of Mining & Technology, Beijing	1987-1990

Degree Received

Bachelor of Chemical Engineering	
China University of Mining & Technology	1984
Master of Science of Environmental Engineering	
China University of Mining & Technology	1990