PROCESSES OF ZINC AND NICKEL REMOVAL IN OXIC LIMESTONE SYSTEMS AND THE APPLICATION TO METAL MINE DRAINAGES

by

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ABSTRACT

Acid mine drainage (AMD) is a persistent problem in the US and abroad. Generally AMD is characterized by low pH and high dissolved metal concentrations. When this water is discharged into a watershed, the direct negative effects on stream biota and potential indirect effects on human drinking water supplies can be severe. Thus in treatment of AMD the goals are pH neutralization and metals removal. Limestone is an inexpensive and effective treatment option to achieve these goals. Primary metal removals in limestone treatment systems are well documented, but secondary metal removals are not. The quantification and processes of these metal removals can lead to better design of subsequent treatment systems, and also more effective limestone systems.

The quantification and processes of the secondary metals zinc and nickel were examined in batch reactor simulations of oxic limestone treatment of a synthetic AMD. Variables effecting removal include influent iron concentrations, secondary metal concentrations, effluent pH, and alkalinity. The solid phase that is produced in this treatment was subjected to a sequential extraction procedure to help elucidate the processes of zinc and nickel removal. PHREEQC, a computer modeling program, was used to describe the reactions taking place in the batch reactors to better understand the processess of removal. The results of these batch reactor experiments were compared to a passive bench scale limestone treatment system, and also to an active pilot scale system.

The major processes of removal for both zinc and nickel were surface interactions with the precipitated iron from solution, including sorption and co-precipitation. Surface interactions between the secondary metals and the $CaCO_3$ were found to be negligible. Although the direct interaction between the secondary metals and the $CaCO_3$ were

negligible, the amount of inorganic carbon in solution did affect the surface chemistry of the precipitated iron, which had an indirect effect on secondary metal removal.

Relationships between influent secondary metal and iron concentrations allowed for the creation of a predictive tool to describe the amount of secondary metal removal that can be expected from a limestone system. This tool was compared to the secondary metal removals in two types of limestone treatment systems, and was found to be a relatively good indicator of secondary metal removal.

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Nothing in the cry
of cicadas suggests they
are about to die.
-Basho

This one goes out to all the cicadas.

CHAPTER 1

ACID MINE DRAINAGE: CAUSES AND TREATMENTS

1.1 Acid Mine Drainage

In order to extract metal or coal ore out of the ground, it is self-evident that a large amount of rock that was not previously exposed to atmospheric conditions now will be. The exposure of these once buried rock types are the major cause of acid mine drainage (AMD). The holes that are dug to extract the ore open a pathway for the downward flux of atmospheric gasses, as well as giving a path of least resistance for sub-surface water (either ground water from below or infiltration waters from above) to become a surface water. The mixture of the gasses, water flow and often microbial inputs, can create a water with low pH and high dissolved metal concentrations (Benner et al. 1999). The major pathway of water contamination is through the oxidation of the metal-sulfide complexes, which are predominated by pyrite (FeS). As the pyrite is exposed to atmospheric oxygen both the iron(II) and sulfide can oxidize to iron(III) and sulfate, respectively. Iron(III) will precipitate as a metal-hydroxide complex at pH values higher than approximately 3.5. This precipitation causes a drop in pH. Thus AMD is created (Benner et al. 1999, Ziemkiewicz et al. 1997, Kairies et al. 2005). These reactions are represented by equations 1-3 below (Cravotta and Trahan 1999).

$$FeS_{2(s)} + H_2O + 3.5\ O_2 = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \tag{1}$$

$$Fe^{2+} + 0.25\ O_2 + H^+ = Fe^{3+} + 0.5\ H_2O \tag{2}$$

$$Fe^{3+} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ \tag{3}$$

As the pH of the water in the mine is lowered, more metal species will dissolve into the water as the water flows to the surface.

The main characteristics of AMD, and the reason for it being such an environmental concern, are the low pH, and high concentrations of dissolved metals (Kairies et al. 2005, Ziemkiewicz et al. 1997). As the AMD flows to a receiving water the low pH of the AMD will generally lead to a lower pH in the receiving water. This lower pH can then have a negative affect on biota living in the watershed. The other major concern is the elevated dissolved metal concentrations. Although many of the metals present in AMD are required for life, they are often present in extremely elevated concentrations in AMD (Cravotta 2006, Lee et al. 2002). At these concentrations the metals can become toxic. Also, depending on local geologic formations, there can be metals that are toxic to humans, like lead, cadmium, and chromium (Ziemkiewicz et al. 1997, Whiting 2004). Therefore the major goals in AMD treatment are acid neutralization and metal removal.

1.2 AMD Treatment Methods

Many of the mines that are producing AMD are historical mine sites, in that they were mined sometime in the past, and the company or individual who had the mining claim either cannot be found, or no longer exists. Thus often it falls to the EPA to remediate the water and the mining site. As there are hundreds of abandoned mines in Colorado alone, and EPA funds are generally limited, the most preferred treatment alternatives are generally passive in nature (Al et al. 2000, Skousen 1991, Cravotta and Trahan 1999, Watzlaf 2004). These passive treatment systems (PTS) are characterized by placing a treatment material such that the AMD can flow through it by gravity. As the water flows through the treatment material, the pH is neutralized and the metals are removed. The goal with PTS is to use enough treatment material so that the reactor will last for many years. The mechanisms of metal removal are generally an application of a small part of a more global metal cycling pathway, which is already known to occur in the environment. There are two major divisions of passive AMD treatment. The line that creates these two divisions is whether the system is biotic or abiotic.

Biotic treatment systems generally exploit a naturally occurring microbial process to treat the water. These biotic systems are generally permeable reactive barriers, anaerobic wetlands, or sulfate reducing bio-reactors (SRB)(Benner et al. 1999). Although different in design, the treatment of the water occurs in similar fashion between these systems. The high levels of dissolved sulfate in AMD allow for the introduction of a class of anaerobic microbes called sulfate reducers. These microbes are capable of using the sulfate as an electron acceptor. When this is coupled with an electron donor, typically organic material, the resulting products are sulfide and bicarbonate (Chang et al. 2000). The produced sulfide reacts with available metals to form insoluble metal sulfide complexes, and the bicarbonate adds alkalinity to the water that can lead to a subsequent increase in pH. Although all the processes are not fully understood, and there are still design issues in building SRB's and anaerobic wetlands, both have potential as long-term treatment alternatives (Kalin 2004).

The other major division of treatment systems is abiotic in nature. These types of systems can be either passive or active, but generally use a compound with an excess of alkalinity to consume the acidity of the incoming water. Common materials include NaOH, quick lime, steel slag material, or limestone (Cravotta and Trahan 1999, Watzlaf et al. 2004, Wu et al. 2003, Komnitsas et al. 2004). These materials raise the pH of the water to precipitate the metals. Depending on the system and the mine water, it is possible that the pH needs to be raised to a pH of 10 to precipitate the metals present. This limits the choices from the above list of possible chemicals and can also limit the choice between active and passive systems. However in passive abiotic systems limestone is often the treatment material of choice due to its low cost, ease to procure, and chemical characteristics (Wu et al. 2003, Cravotta and Trahan 1999, Watzlaf et al. 2004, Skousen 1991, Ziemkiewicz et al. 1997).

1.3 Limestone Use in AMD Treatment

Limestone can be used in many ways depending on the mine site, chemical characteristics of the mine water, and treatment goals. The traditional use of limestone has been to achieve the stated goal of pH neutralization.

The chemical reactions of limestone dissolution which lead to pH neutralization, as well as produce an effluent with net alkalinity, can proceed by any of the reactions 4-6 (Cravotta and Trahan 1999).

$$CaCO_{3(s)} + 2\ H^+ = Ca^{2+} + H_2O + CO_{2(g)} \tag{4}$$

$$CaCO_{3(s)} + H_2O + CO_{2(g)} = Ca^{2+} + 2\ HCO_3^- \tag{5}$$

$$CaCO_{3(s)} + H_2O = Ca^{2+} + HCO_3^- + OH^- \tag{6}$$

These reactions are shown for a general idea of the processes responsible for the pH change and alkalinity addition. Which of these reactions dominates as well as the speciation of the carbonates are dependant on the type of limestone system, as well as water quality characteristics in the system (Letterman 1995, Sherman and Barak 2000, Lowenthal and Marais 1976). In general the rate and extent of limestone dissolution are determined by the pH, partial pressure of CO_2, and activities of Ca^{2+} and bicarbonate near the surface of the limestone (Cravotta and Trahan 1999).

1.3.1 Limestone in Passive Treatment

There are two major types of limestone treatment systems that are passive in nature. Deciding which one to construct for a specific mine site is dependant on the influent water chemistry. If the water has a high ratio of iron(II):total iron, and a low dissolved oxygen content, an anoxic limestone system can be used (Skousen 1991, Watzlaf et al. 2004). However, if much of the total iron is present as iron(III), or there is a large amount of dissolved oxygen, an oxic limestone system would need to be built

(Ziemkiewicz 1997, Ziemkiewicz et al. 1994, Sibrell et al. 2000). Although they may seem minor, these small differences in water quality and subsequent design of limestone systems leads to major differences in the chemistry of water treatment, and also the fate of the metals in these systems.

1.3.1.1 Anoxic Limestone Systems

In an anoxic limestone system, the general requirement is that the influent water has a low dissolved oxygen content (<2mg/L), and also the dissolved iron must be predominantly present in its reduced form, iron(II) (Skousen 1991). Another option is to intercept the water in the sub-surface where it is more likely that these conditions exist (Watzlaf 2004). The reason for these constraints is the pH neutralization that occurs in a limestone system. If properly designed and operating correctly, a passive limestone system can raise the pH of an influent mine water from <2, to an effluent pH that is circum-neutral (~6.5-7) (Cravotta and Trahan 1999, Robbins et al. 1999). Over this pH range, iron(III) will precipitate as a metal hydroxide, whereas iron(II) does not. Therefore, if the iron present is mostly iron(II), and there is insufficient oxygen to oxidize it to iron(III), the iron will pass through the drain. If not, the precipitation of iron(III), and to a lesser extent aluminum(III), causes two major problems: armoring, and clogging (Skousen 1991, Watzlaf et al. 2004).

When iron(III) precipitates in a limestone system, it will often precipitate directly onto the limestone surface itself. This forms an armored crust on the limestone that drastically slows the limestone dissolution (Ziemkiewicz 1997). If a prolonged retention time is not used in a limestone system to account for this reduced rate of limestone dissolution, the limestone system will most likely fail for the reason that there is not enough contact time between the AMD and the limestone to allow for neutralization. This same process occurs with aluminum(III) in AMD, and cannot be controlled by redox conditions. However, because the aluminum hydroxides that form are less compact than the iron hydroxides, the aluminum precipitates are often flushed out of the drain as particulate matter (Skousen 1991).

The other major concern with having large amounts of iron(III) in the water, is that the precipitates can clog or partially clog a limestone system. As the iron(III) hydroxides precipitate in the system, they can also fill available pore spaces leading to clogging and short-circuiting (Ziemkiewicz et al. 1994, Cravotta and Trahan 1999).

The basic design of a passive, anoxic limestone system is such that the limestone is buried to stop oxygen infiltration from the surface while maintaining water flow through the system (Watzlaf et al. 2004). Besides the lack of the armoring and clogging that can occur, there is an added incentive to an anoxic limestone system. Namely, if the system is built so that oxygen cannot infiltrate, carbon dioxide cannot leave the treatment system. Therefore there is an increased level of dissolved carbon dioxide in these systems, which forces Equation 5, from above, to proceed more vigorously. The net result is an elevated concentration of carbon dioxide in the limestone system effluent, as well as elevated alkalinity (Cravotta and Trahan 1999). Generally, after an anoxic limestone drain, there is an oxidation pond where the excess carbon dioxide is released to the atmosphere, with a subsequent increase in pH, while atmospheric oxygen oxidizes the iron(II) to iron(III) which will then precipitate (Skousen 1991). There should be enough alkalinity produced in the limestone system that the overall acidity produced from the hydrolysis and precipitation of the iron(III), will not negatively affect the pH.

1.3.1.2 Oxic Limestone Systems

In contrast to anoxic limestone systems are oxic limestone systems. For waters with high amounts of dissolved oxygen (>2mg/L) or large amounts of oxidized soluble iron, an oxic limestone system can be the treatment option of choice (Ziemkiewicz et al.

1997, Ziemkiewicz et al. 1994, Cravotta and Trahan 1999). These types of systems are generally open to the atmosphere, and are generally site limited due to the recurring problems of armoring and clogging. The iron in these types of systems is either predominantly in the form of iron(III) or there is sufficient oxygen to cause the oxidation to iron(III), thereby causing the issues, previously discussed, of armoring and clogging. In order to counteract these concerns, it is recommended to build these types of limestone treatment systems on steep slopes to increase water velocity to a point where the iron precipitates are flushed from the drain, and the limestone is at least partially scoured by these precipitates to maintain un-armored limestone surfaces (Ziemkiewicz et al. 1994). Both the iron(III) and aluminum(III) will precipitate within these systems, as opposed to the iron(II) in anoxic systems which precipitates in a subsequent oxidation pond after exiting the limestone system.

Occasionally water flow, high acidity loads, or limited area at a mine site dictate the use of an active treatment system. One example of an active treatment system is the pulsed limestone bed system (Sibrell et al. 2000, Sibrell et al. 2003a, Sibrell et al. 2004). In this system, through the active pumping that occurs during water treatment, the limestone surface is scoured to the point that armoring is not an issue. Also, the metal precipitates that form are flushed from the system by the active pumping of the water.

Due to the water chemistry common in metal mine drainages, anoxic limestone systems are not always going to be an option. In many metal mine drainages, there are already significant amounts of oxidized iron and dissolved oxygen. Thus limestone systems for metal mine drainages will favor the use of oxic treatment conditions.

1.3.2 Secondary Metals

Current use of limestone as an AMD treatment material has led to documentation of both the pH neutralization capacities as well as primary metal removals. Primary metals include iron, aluminum, and manganese. To use limestone as a treatment material for metal mine drainages the fate of the secondary metals also needs to be known. From a treatment perspective the secondary metals include all the metals except iron, aluminum, and manganese, which need to be removed prior to discharge. Common examples include zinc, nickel, copper, lead, and cadmium. The removal of these secondary metals in limestone systems has been documented (Cravotta and Trahan 1999, Watzlaf et al. 2004, Lee et al. 2002), but their fate, and method of removal remains an unexplored topic.

1.4 Secondary Metal Removal in Limestone Systems

The fate of the primary metals in limestone drains has been well documented. Iron, and aluminum can either precipitate in the treatment system, or in a post-limestone step. It is generally believed that under the conditions in a limestone system, they precipitate as metal hydroxides as already discussed. Manganese is largely unaffected by the general limestone design (Skousen 1991). Both the potential quantities of removal and the processes of removal of the secondary metals remains unknown. This is mainly due to the fact that much of the research done with limestone treatment systems has focused on coal mine drainages. There are significant water chemistry differences between coal mine and metal mine drainages. Generally speaking, coal mine drainages are relatively high in primary metal concentrations, and relatively low in secondary metal concentrations, whereas metal mine drainages can be high in both primary and secondary metals concentrations (Wildeman and Schmiermund 2004, Cravotta 2006). Metal mine drainages also generally have a wider array of metal species than coal mine drainages.

Due to the elevated metal concentrations and the problems caused by metals in limestone systems discussed earlier, metal mine drainages have not generally been treated using limestone systems. This does not mean, however, that limestone systems cannot be used, it just means that the design of metal mine drainage limestone treatment systems needs to be different than a similar system designed for a coal mine drainage. Also the fates and potential quantities of secondary metals removal can be different due to the differences in water chemistry. The major potential processes for metal removal can include discrete precipitation, sorption to either the limestone surface or the primary metal precipitates, and also co-precipitation reactions.

Discrete precipitation includes the precipitation of the metals as a metal-hydroxide, or metal-carbonate complex. There are other possible species for discrete precipitation within a limestone system; however, due to the water chemistry in a limestone system, it is assumed that the hydroxides and carbonates would dominate.

Sorption reactions include metal accumulations on any available surface (Van Cappellen et al. 1993, Dzombak and Morel 1990, Zachara 1991, Stumm 1992). For the purpose of the experiments completed here, sorption can be thought of as the lowest degree of interaction between a secondary metal ion and an available surface. This is true in the sense that many sorption type reactions are reversible by making minor changes to solution chemistry and not necessarily altering the sorbent surface.

Co-precipitation is often the endpoint of a reaction that starts with sorption. Many mechanisms for co-precipitation start with a sorption step, and then through many different potential pathways, the sorbed ion becomes a part of the chemical lattice of the surface to which it had sorbed (Wersin et al. 1989, Karthikeyan et al. 1997, Bertsch et al. 1989, Okumura and Kitano 1986, Stumm 1992). For the purposes of these experiments, co-precipitation is the highest degree of interaction between a secondary metal ion and a surface, and thus the least easily reversible.

1.5 Retention Times in Limestone Systems

Another major design consideration that needs to be addressed when designing a limestone system for metals removal is the retention time. Retention time is important for several reasons.

The first reason retention time is important is to counteract armoring. Within metal mine drainages, there can be significant amounts of oxidized iron. This large amount of oxidized iron will armor the limestone surface (Ziemkiewicz et al. 1994). In the design of a limestone system, the retention time should be long enough to allow for treatment even though the limestone surface is armored. Previously, armoring has been purposefully avoided and retention times were based on a non-armored dissolution rate (Cravotta 2003). In a limestone system designed for metal removal this problem cannot be avoided, so it is better to focus on what the limestone system is capable of using an armored dissolution rate, as opposed to an un-armored dissolution rate (Ziemkiewicz et al. 1997).

The second reason retention time is important, is to offset the effect of the metals precipitating in the drain. As these metals precipitate, the pore spaces will fill. As these pore spaces fill, the retention time will become shorter. At some point, the retention time will drop below what is required to allow for armored limestone dissolution. At that point, the system will no longer successfully treat the AMD. In the original design of the limestone system, there needs to be an oversizing of the system to allow for the filling of much of the void spaces while maintaining the requisite retention time for treating the AMD. It may also be that the current design goal of building a passive limestone system to last for thirty years without manual inputs is not appropriate for drainages with high metal concentrations. A more realistic goal for these new types of limestone systems will be to design for a much smaller span of time, and then perform some manual maintenance in some way (flushing precipitates out, dig limestone and precipitates out of system then refill, etc.) to ensure system permeability and treatment efficacy.

A final reason for the importance of retention time is the processes of metal removal. Some of these reactions are relatively slow, requiring several hours to days before maximization (Trivedi and Axe 2001). In order to design a limestone treatment system with the expressed goal of metal removal, these reactions need to be allowed to proceed toward completion. The only way to do this in a passive system is to increase the retention time. The longer the water is in contact with the limestone and primary metal precipitates, the higher the percentage of filled sorption sites will be, and thus higher metal removals will be seen.

1.6 Motivation/Justification of Research

One of the major goals in AMD treatment is metal removal. In the field, limestone systems have been shown to remove metals, both primary and secondary, to varying degrees. What is not known about these metal removals are the processes involved, and thus the major variables that can affect removal.

Figure 1.1 shows a small section of a solubility diagram for zinc hydroxide and carbonate. The range shown is within the pH and dissolved carbon dioxide range typical of AMD (Cravotta 2006). On the graph, the area above the line represents the pH and zinc concentrations where each phase is supersaturated. It can be seen that of the two most probable phases, zinc hydroxide or zinc carbonate, that zinc carbonate is the phase controlling zinc precipitation. In other words, if discrete zinc precipitation were occurring, the zinc would be precipitating as zinc carbonate. However, it should be noted that both zinc carbonate and zinc hydroxide still have relatively high solubilities in this range. Most AMD does not have zinc concentrations that would allow for zinc carbonate precipitation within the water quality parameters of limestone treatment system effluents (Cravotta 2006). Figure 1.2 shows the same relationships for nickel hydroxide and

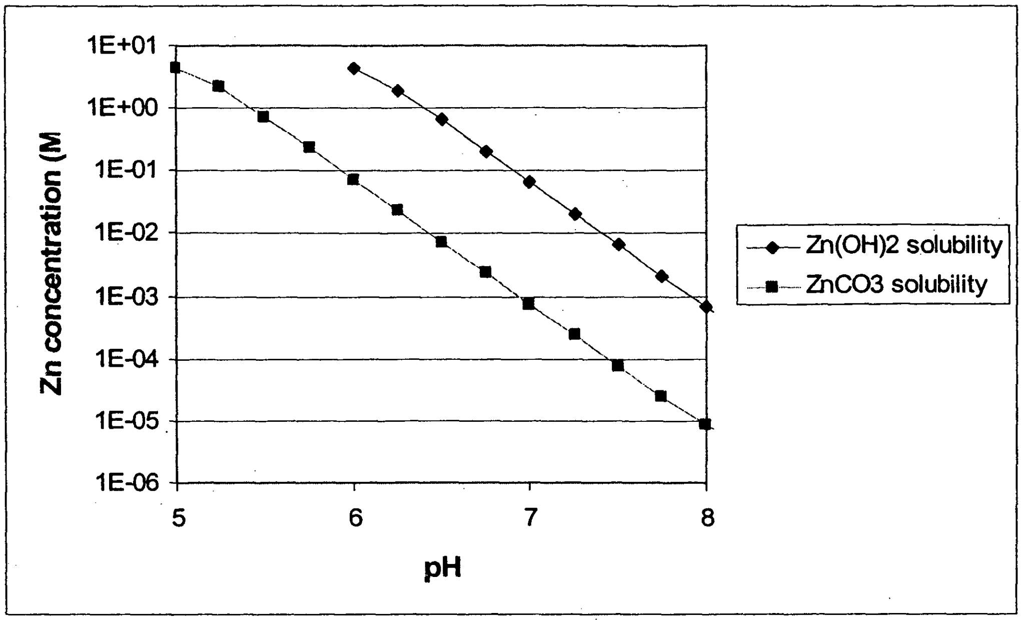

Figure 1.1- Zinc hydroxide and carbonate solubility at a $pCO_2 = -1.5$ and $pSO_4^{2-} = 0.4$

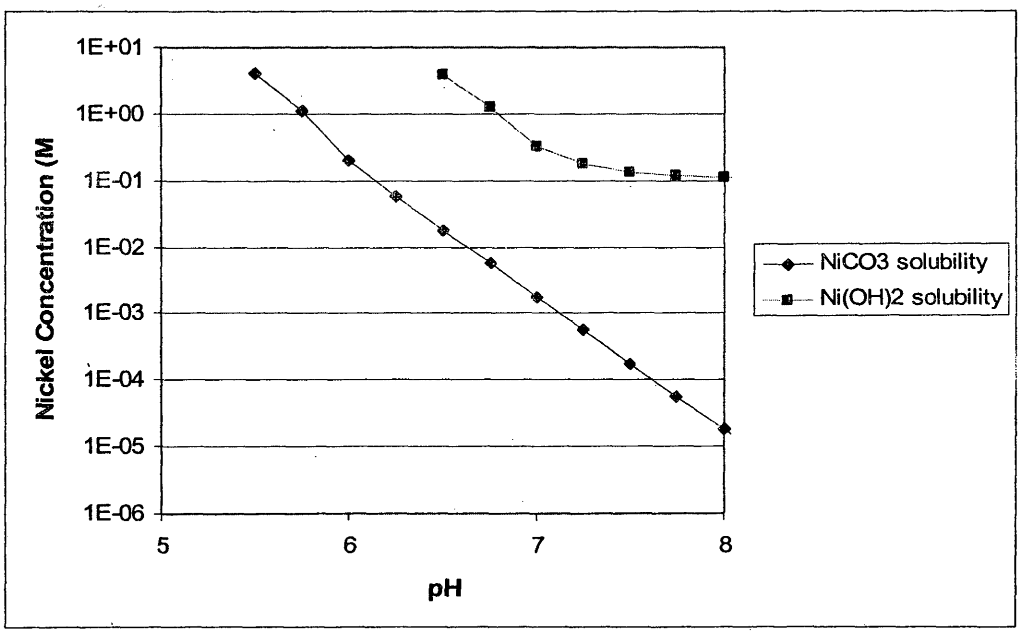

Figure 1.2- Nickel hydroxide and carbonate solubility at a $pCO_2 = -1.5$ and $pSO_4^{2-} = 0.4$

carbonate precipitates. Nickel solubility in the range of interest would be controlled by nickel carbonate. Again though, the nickel concentrations required for this precipitation are rare in AMD.

Despite the fact that the secondary metals are undersaturated with respect to their respective hydroxide and carbonate species, there is still evidence of their removal (Cravotta and Trahan 1999, Cravotta 2006, Watzlaf et al. 2004, Wu et al. 2003, Lee et al. 2002, Komnitsas et al. 2004). In cases where undersaturation of zinc and nickel precipitates are indicated but the zinc and nickel are still removed, surface related reactions such as sorption and co-precipitation are postulated (Okumura and Kitano 1986, Cravotta and Trahan 1999, Lee et al. 2002). However, there are multiple surfaces and varying conditions in limestone systems that can affect these surface interactions.

The two major surfaces available in limestone systems are the limestone surface itself, or discretely precipitated primary metal surfaces, such as hydrous ferric oxide (HFO). Both of these surfaces have been shown to sorb and/or co-precipitate zinc and nickel to varying degrees under specific conditions (Zachara et al. 1991, Zachara et al. 1989, Trivedi and Axe 2001, Dzombak and Morel 1990). Significant zinc and nickel associations to calcite have been shown to occur only at conditions that are not typically found in limestone system effluents, specifically at pH values of ~6-7 (Zachara 1989, Zachara 1991). Sorption to HFO, however, has been shown to occur over a much broader range of conditions (Dzombak and Morel 1990). However no one has examined these metal sorption and co-precipitation reactions in limestone systems. This leads to three hypotheses:

Hypotheses #1: Secondary metal solubility will be controlled by surface interactions.

Hypothesis #2: HFO will act as a surface for zinc and nickel removal under conditions found in an oxic limestone system.

Hypothesis #3: $CaCO_3$ will not act as a surface for zinc and nickel removal under conditions found in an oxic limestone system.

To test these hypotheses two types of experiments need to be conducted. The first type is to vary the amount of iron and secondary metal concentrations to determine if there is a relationship between the iron and secondary metal removal. This will directly test hypothesis #2. In these experiments $CaCO_3$ will act as the alkalinity producing mechanism. The amount of $CaCO_3$ added in these experiments will be constant regardless of iron or secondary metal concentrations. The more iron present leads to more available sorption sites, which should lead to higher removals of the secondary ions from solution. In order to validate hypothesis #1, the data from this experiment would show an increasing trend in secondary metal removal for an increasing amount of added iron.

The second type of experiment will test hypothesis #3. In this type of experiment, the amount of secondary metal added will be constant, and the alkalinity source will be variable. In one set of experiments the alkalinity producing mechanism will be the $CaCO_3$, and in the other set a liquid NaOH solution will be used. The addition of the NaOH will allow for pH change similar to that seen with the $CaCO_3$, but because it is added as a solution there are no available surfaces to which the secondary metals can sorb. The expected outcome of these experiments is that there will be no difference regardless of alkalinity source. This would test hypothesis #3.

1.6.1 Extraction Procedure

In order to test all three hypotheses, a selective extraction procedure will be used. A selective extraction procedure uses multiple solutions with varying chemical characteristics to selectively extract chemical components from a solid phase and into a solution phase (Tessier et al. 1979). Depending into which extraction fluid a chemical component solubilizes, certain information can be gained based on the chemical properties of the extractant and extraction fluid. The idea in a selective extraction procedure is to use increasingly stringent solutions to chemically alter the solid and effect continued release of chemical components into the varied solutions. In these experiments using a selective extraction procedure will help to determine the level of association between the secondary metal ions with both the $CaCO_3$ and the HFO.

There are many posssible extraction procedures that can be used to help fractionate metals in a solid phase (Quevauviller 1998, Quevauviller 1998a, Tessier et al. 1979). Many of these tests use a single extraction fluid as opposed to sequential extractions, which use more than one. The amount of information that could be obtained through a single solution extraction procedure would be minimal in the context of separating secondary metals that had interacted with two possible surfaces. Thus a sequential extraction is more appropriate in the experiments described herein. The two possible interaction surfaces for the secondary metals are calcium carbonate, and precipitated iron. Thus the extraction procedure needs to separate between these two types of surfaces. Sequential extractions with a metal complexing agent, like EDTA, are more readily applicable to studies examining metal bioavailability (Quevauviller 1998, Quevauviller 1998a). Because this study does not focus on bioavailability, procedures with metal complexing agents were not used. The procedure described by Tessier et al. 1979 is specifically designed to fractionate the metals in present in sediments, without the use of metal complexing agents, and has specific extraction solutions to differentiate between carbonate association and iron association.

The extraction procedure used leads to a total of five potential fractions. Each of these fractions and what they could represent are presented below. It is important to note that the name of each fraction was operationally defined, and the name does not necessarily represent the mechanism of the secondary metal removal.

1.6.1.1 Solution/Dissolved

Any metal that is present in this fraction represents metals that were not removed from solution to the solid phase based on the available surfaces, and chemistry of the solution. In the context of a limestone based treatment system the metals in this fraction represent what would be present in the limestone system effluent. Depending on the treatment goals, these metals would have to be removed from solution by a subsequent treatment process.

1.6.1.2 Easily Exchangeable

This fraction represents, but is not necessarily limited to, metals that are easily desorbed from the solid phase. It is assumed that these metals are sorbed and, mechanistically speaking, have not begun to co-precipitate. The sorption processes possible include loose coordination with any available surface (either $CaCO_3$ or the iron precipitates) such as a cation sorbing to hydrated surface layer.

1.6.1.3 Carbonate Associated

For the secondary metals present in this fraction, the processes and fates can include metals that discretely precipitated as hydroxides or carbonates, and metals that had sorbed to or co-precipitated with the $CaCO_3$. For this last group, the metals that would dissolve in this phase obviously did not dissolve in the preceding, easily exchangeable, phase. Thus, it is assumed that the sorption process for the metals that solubilized in this fraction is different from the sorption process for the metals that solubilized in the easily exchangeable fraction.

For the iron that solubilizes in this fraction, the mechanism is much simpler. It is assumed that under the conditions studied, the iron was precipitating as a hydrous ferric oxide (HFO). The generally used chemical formula for this species is $Fe(OH)_3$. This species should not, in general, be soluble at a pH of 5. Thus, any of the iron that is present in this phase is associated with the $CaCO_3$ in some way or the HFO being produced is not as stable as assumed. The possibilities for the interaction between iron and $CaCO_3$ can include, but are not limited to, sorption, cationic substitution into the $CaCO_3$ structure, or a surface interaction that led to iron co-precipitating with $CaCO_3$.

1.6.1.4 Iron Associated

The secondary metals in this phase represent metals that had co-precipitated with the HFO. The exact mechanism of this co-precipitation cannot be determined through the use of extraction solutions. One possible mechanism includes sorption of the secondary metal, which is then incorporated into the HFO structure by subsequent hydrolysis of the secondary metal leading to a new surface and continued sorption of new ions.

1.6.1.5 Residual

This is a complete dissolution of any remaining solid in a strong acid solution. Iron that would be present in this phase would most likely be a more mineralized form than the simple HFO precipitate. Secondary metals would be ions that had co-precipitated with the iron and became part of the mineralized iron surface.

1.6.2 Use of Batch Reactors

As an actual method of water treatment, limestone systems are flow through systems. Because the overall goal of these experiments is to in fact simulate AMD treatment in an oxic limestone system, the most preferred way to study the chemical interactions would be in flow through devices, such as a packed column. This approach was not used in these studies predominantly due to the issues surrounding water flow in a flow through system. If a column had been used, the iron precipitation in the column itself could have led to the same preferential flow paths that plague field systems. It would be difficult to determine whether the removals being seen were a function of water chemistry, or in fact were somehow related to the flow in the system. Batch reactors do not share this problem and the amount of reaction time between the AMD and the $CaCO_3$ can be carefully controlled.

1.6.3 Computer Modeling

Computer modeling is a convenient tool to help describe chemical reactions in solution. In these experiments the program PHREEQC is used as a technique to help describe the interactions between the available surfaces and solution.

PHREEQC is an equilibrium chemistry model that determines chemical species and describes reactions in solution. In the case of the experiments described herein, the solution chemistry in the reactors can be described by this program by controlling the extent of $CaCO_3$ dissolution as well as the effective amount of carbon dioxide in the headspace. Using these two variables, the pH, alkalinity, and dissolved calcium concentration in the output of the model will be compared to the experimental values to determine whether the model is accurately describing solution conditions. However, as it has been hypothesized that the secondary metal solubility will be controlled by surface interactions, a surface complexation model is also needed.

The surface model used in the PHREEQC program is the double layer model described in Dzombak and Morel, 1990. Conceptually the model is made up of a surface layer and the diffuse layer, which is a thin section of the bulk solution that is in direct contact with the surface. In this model the diffuse layer is the component that actually interacts with the surface, and the bulk solution is simply a source and sink for the ions present in the diffuse layer. The major variables under control in the surface modeling portion are: the sorption site densities, the surface area of the available surfaces, and the thickness of the diffusion layer. The thermodynamic values describing the interactions between the secondary metals and the available surfaces were assumed to be constant and were found in Zachara et al. 1988, Zachara et al. 1991, Zhu 2002, Benjamin 2002, and Dzombak and Morel 1990.

1.6.4 Summary

In the experiments to follow the removal of the secondary metals zinc and nickel are examined by simulating limestone treatment in batch reactor systems. Their removals as a function of pH, alkalinity, and primary metal concentrations are delineated. Also, the potential processes for removal, sorption, precipitation, or co-precipitation, are explored through the use of a selective extraction procedure. Through the combination of these techniques with computer modeling, factors controlling zinc and nickel solubility in limestone systems are examined.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Synthetic Mine Water

All chemicals used throughout the experimental process were reagent grade.

Synthetic mine water was used to give more control over the variables of interest. For each metal (Fe, Zn, and Ni), a parent solution was made from metal sulfate salts, in a dilute (0.02N) sulfuric acid solution. The pH in all of these solutions was 2.1 ±0.1. The calculated metal concentrations in these parent solutions were: Fe = 700 mg/L , Ni = 450 mg/L, Zn = 450 mg/L. The iron solution was made by using ferrous sulfate, then adding a small amount of 30% hydrogen peroxide to oxidize the iron from iron(II) to iron(III). It is assumed that all the dissolved iron was present in the ferric, iron(III), oxidation state. This was done to minimize the redox chemistry that otherwise could have occurred in the reactor vessels. From these more concentrated parent solutions, volumes were taken to get the desired concentrations in the reactor vessels.

For each experiment, the mine water consisted of a mixture between the iron solution, and a secondary metal solution. The reactor vessel was a 50mL centrifuge tube. The metal concentrations used are summarized in Table 2.1. These values are measured values in the batch reactors. In order to get the desired concentration, and to ensure that each reactor vessel had the same amount of mine water, the solutions were brought up to 45mL with the 0.02N sulfuric acid solution. Using this solution maintained the low pH to mimic actual AMD.

	Iron Concentrations (mg/L)				
	0	54	540	62	620
Zinc Conc. (mg/L)	5.3	5.3	5.3		
	10.7	10.7	10.7		
	16.0	16.0	16.0		
	21.3	21.3	21.3		
	26.7	26.7	26.7		
Nickel Conc. (mg/L)	5.8			5.8	5.8
	11.6			11.6	11.6
	17.3			17.3	17.3
	23.1			23.1	23.1
	28.9			28.9	28.9

Table 2.1- Summary of metal concentrations used

2.2 Mine Water Treatment with $CaCO_3$

Once the mine water solutions were in the reactor vessels, 0.10g of powdered, reagent grade $CaCO_3$ were added. The main reason $CaCO_3$ was chosen over actual limestone is the fact that limestone generally has detectable concentrations of trace metals in the mineral matrix. As the limestone would dissolve, this would add un-constrained variables into solution and cause error in calculating the mass balance in data interpretation steps.

Upon the addition of the $CaCO_3$, carbon dioxide bubbles started to form almost immediately. These solutions were capped, and vigorously shaken by hand for approximately 30 seconds to suspend the $CaCO_3$, and then vented to the atmosphere. It was desired for the headspace to approximate atmospheric conditions. To this end, the reactor vessels were vented twice daily (approximately every 12 ± 3 hours) during the reaction time.

The mine water and $CaCO_3$ were allowed to react for four days. This was accomplished by placing the vials on a shaker table set at ~150 rpm. For the first 12 hours when the carbon dioxide liberation was at its highest, the vials were mixed in an upright position to minimize leakage. As the pressure increased in the reactor vial, it would cause separation between the lid and the vial, which led to leaking. For the balance of the reaction time, the vials were mixed in the horizontal position to maximize the surface area between the liquid and gas phases.

The four-day reaction time was used for three main reasons. The first of which is due to the potential mechanisms of metal removal, and to allow for relatively slow reactions to proceed toward completion, as already discussed. The second major reason is that after four days the pH change started to stabilize (data not shown). Between day three and four there was only a modest change in pH, and that difference got even smaller between days four and five. The final reason for the four-day reaction time is the measured water quality characteristics at the end of that time. Effluent pH of properly designed and operating limestone systems in the field is generally between six and seven. After four days of reacting, the pH in the reactor vessels was typically in or near this range.

2.3 Mine Water Treatment with NaOH

The dissolution of $CaCO_3$ causes a pH gradient over the four-day reaction time in the reactor vessels. It was attempted to mimic this same gradient with the NaOH. To that end, once the primary metal and secondary metal solutions were combined and brought up to 45 mL, the pH was adjusted by adding the NaOH (~1% w/v) dropwise, until a pH of approximately 4.5 was attained. The vials were then allowed to react for 24 hours. On day two of the reaction time, the vials were vented as usual, and the pH was raised to approximately 5.5. This same procedure was repeated over days three and four raising the pH to 6.5 and 7.0, respectively. For these experiments the only carbonate input was from atmospheric carbon dioxide dissolving into solution.

In order to determine if the atmospheric inputs of carbon dioxide had any effect on the metals in solution, the same procedure was repeated for both nickel and zinc at the lower iron concentration, with one minor change. Instead of these solutions being open to the atmosphere, they were purged with argon gas. Once the mine waters had been made, argon was bubbled through solution for ten minutes. The pH was adjusted as previously described, and the vials were re-purged for another ten minutes. It is assumed that this purging process not only forced all the dissolved carbon dioxide out of solution, but that it also filled the headspace with argon as opposed to being open to atmospheric conditions. On each day when the pH in the reactor vessel was changed, the vials were re-purged before being replaced on the shaker table.

2.4 Selective Extraction Procedure

In order to differentiate between the different potential fates of the metals in the solid phase, a selective extraction procedure was performed on the solid phase after the four-day reaction time. To separate the solid from the liquid between each step, the vials were centrifuged at 10,000g for thirty minutes. The supernatant was sampled for characteristics of concern, and the next extraction was performed on what remained of the solid phase without removing it from the centrifuge tube, thus minimizing mass loss. The method used is a modification of Tessier et al. 1979. This modified extraction procedure led to five total fractions that include: solution, easily exchangeable, carbonate associated, iron associated, and residual. It is important to note that the names of these fractions stem from operational definitions, and do not necessarily reflect the fate of the metal. Following is the procedure for and explanation of what each fraction can represent.

2.4.1 Solution

Once the reaction time was complete, the pH of each vial was measured. The vial was then centrifuged, and the supernatant was sampled for an alkalinity titration, as well as soluble metals. Alkalinity titrations were performed colorimetrically using a Hach digital titrator.

2.4.2 Easily Exchangeable

To the solid phase from the previous step was added 10mL of a 1M $MgCl_2$ solution. The vial was vigorously shaken by hand to re-suspend the solids. It was then placed on a shaker table and allowed to react for one hour. At which time it was again centrifuged and a sample was taken for soluble metal analysis.

2.4.3 Carbonate Associated

For this fraction, an acetate buffer was used. To make this solution a 1M sodium acetate solution was prepared. To this solution the pH was adjusted down to 5.0 with acetic acid. Ten milliliters of buffer were added to the solid phase of the preceding extraction. This solution was shaken vigorously by hand to re-suspend the solids, and then placed on the shaker table for 30 minutes. In the experiments that had only the $CaCO_3$ and mine water (i.e. no iron), the $CaCO_3$ had completely dissolved by the 30 minute mark, which is the justification for the time requirement in this extraction. It is important to use just enough time to dissolve the $CaCO_3$ and not more, as the extraction fluid could potentially start to dissolve the iron phase, which would not be desirable.

Once the extraction was complete and centrifuged, a sample was taken for soluble metals analysis.

2.4.4 Iron Associated

The extraction fluid in this phase was a 0.04M hydroxylamine hydrochloride solution prepared in 25%(v/v) acetic acid. Fifteen milliliters were added to the remaining solid phase. The solution was then placed in a hot water bath at 93 ± 3°C for 2.5 hours with hand agitation approximately every thirty minutes. Two and a half hours was all that was required to dissolve the remaining precipitate, except in a limited number of cases. Once cooled, the extraction was centrifuged and a sample was taken for metals analysis.

2.4.5 Residual

This fraction led to a complete dissolution of any solid that was left after the subsequent extractions. It was accomplished through a 30%(v/v) nitric acid solution, with gentle agitation.

2.5 Metals Analysis

When each sample for metals analysis was taken, it was acidified with nitric acid to a pH<2. For all of the extractions except the carbonate extraction a few drops were sufficient. Due to the buffering capacity of the carbonate extraction fluid, 0.5mL of nitric acid was required for a 7mL sample. Concentration values from analysis were corrected for this dilution.

Samples were analyzed using an inductively coupled plasma optical emission spectrophotometer (ICP-OES). A series of dilutions ranging from 1:5 to 1:80 were prepared to check for potential interferences from the extraction fluids. A 1:10 dilution showed no significant concentration differences from a 1:20 or 1:40 dilution, whereas there was small deviation with the 1:5 dilution. The samples at 1:80 dilution factors were often approaching detection limits. All extracted samples (not the solution phase samples) were analyzed at 1:10 dilution.

2.6 Modeling Approach

The first step in the modeling process was to achieve an accurate description of the solution chemistry. To this end, the amount of $CaCO_3$ dissolution was controlled by varying the saturation index. This allowed for an accurate description of the dissolved calcium concentration, as well as contributing to alkalinity and pH. Furthermore, the effective partial pressure of carbon dioxide in the headspace was varied, and contributed both to alkalinity and pH of the solution. Because these two variables are inter-related, an iterative process was used until the modeled dissolved calcium concentration, pH, and alkalinity were consistent with the experimental data.

The second step in the modeling process was to fit the data related to the surface chemistry involved in the reactor vessels. Chemical reactions describing the interactions between the secondary metals and the $CaCO_3$ and between the secondary metals and the precipitated iron were entered into the model. Once the thermodynamic descriptors were entered, the model was fit to the data by varying the thickness of the diffuse layer, the surface area of the available surfaces, and the sorption site density.

The chemical equations used with their respective thermodynamic values as well as their referenced sources, and copies of the PHREEQC input files can be found in the appendix.

CHAPTER 3

RESULTS FROM THE BATCH REACTORS

3.1 Statistical Significance of Results

For each set of experiments, an increasing amount of secondary metal was used relative to the iron. However, actual duplicates of a single secondary metal concentration and a single iron concentration were only performed on a small subset of all the experimental conditions. Thus a form of linear regression was used to test the statistical significance of the extraction procedure and the results. The method and equations used are described in Dowdy and Wearden, 1991.

With an increasing influent mass of secondary metal, there was a corresponding increase in the output for all of the extraction procedures. Thus a linear trend line was created from the data points and the intercept was forced through zero. An example of these relationships is shown in Figure 3.1. By comparing each of the data points to the trend line independently, a standard deviation of the trend line was obtained. Using this standard deviation, a t-test was performed to determine the statistical significance of the line. In all experimental cases, the t-value was significantly higher than the required t-value (2.353 for three degrees of freedom) for statistical significance. Data shown without error bars was subjected to the t-test and was found to be statistically significant (see Tables 3.1 and 3.2).

Data presented with error bars represent replicates that were performed on the boundary conditions with respect to the metal concentrations for experiments with calcium carbonate treatment. Error bars represent ± 1 standard deviation. In general the smaller the metal mass in a designated fraction, the larger the standard deviation was

Table 3.1- Summary of experimental trend lines and r^2 values for each fraction.

		Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Secondary Metal	Mass Fe	Slope of Trend line	r^2 value	Slope of Trend line	r^2 value	Slope of Trend line	r^2 value	Slope of Trend line	r^2 value
Nickel	0	1.031	0.999	NA	NA	NA	NA	NA	NA
	2.8	0.788	0.989	0.053	0.808	0.125	0.753	0.043	0.850
	28	0.291	0.949	0.152	0.977	0.328	0.979	0.247	0.934
Zinc	0	1.043	0.998	NA	NA	NA	NA	NA	NA
	2.4	0.552	0.975	0.042	0.98	0.408	0.977	0.009	0.901
	24	0.198	0.864	0.079	0.911	0.62	0.971	0.167	0.863

NA = Insignificant amounts of mass were present in these fractions. Therefore no trendline could be produced.

Table 3.2- Summary of the standard deviations of the trendlines produced, and calculated t-values. Student's t-value for three degrees of freedom = 2.353.

		Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Secondary Metal	Mass Fe	Standard Deviation	Calculated t-value	Standard Deviation	Calculated t-value	Standard Deviation	Calculated t-value	Standard Deviation	Calculated t-value
Nickel	0	0.01	97.06	NA	NA	NA	NA	NA	NA
	2.8	0.04	25.44	0.01	134.34	0.02	51.91	0.05	22.43
	28	0.04	29.85	0.01	102.99	0.02	22.43	0.02	45.20
Zinc	0	0.02	45.28	NA	NA	NA	NA	NA	NA
	2.4	0.04	22.55	0.003	350.04	0.02	40.8	0.004	258.85
	24	0.04	22.97	0.01	77.44	0.05	22.3	0.02	43.14

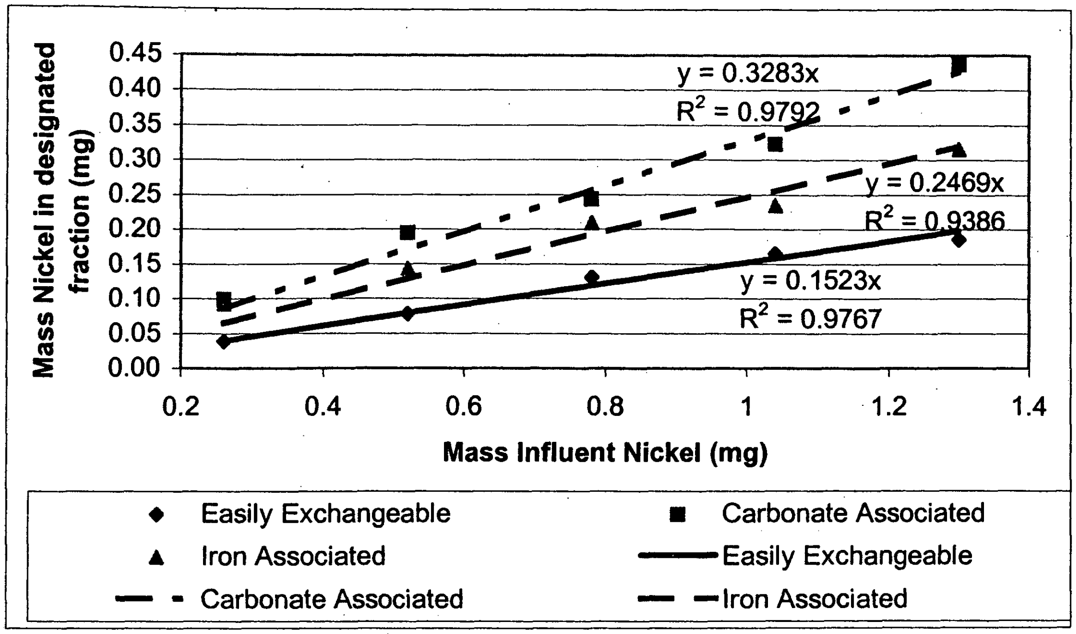

Figure 3.1- Mass nickel in each phase vs. mass nickel in the influent. Experimental conditions: TOTFe = 28mg, $CaCO_3$ treatment, open to the atmosphere

between the replicates. Raw data for the replicates with their average values and standard deviations, as well as data on the mass balances for non-replicated experiments, are all located in the appendices.

3.2 Iron Distributions in the Sequential Extraction

As can be seen in Figures 3.2 and 3.3, the distribution of iron in the extraction procedure did not follow what was expected. Significant amounts of iron re-dissolved in the carbonate associated fraction, despite the assumed precipitation of $Fe(OH)_{3(s)}$ and the chemical conditions in the carbonate associated extraction solution. A discussion of the iron distributions and their meanings is left to subsequent chapters.

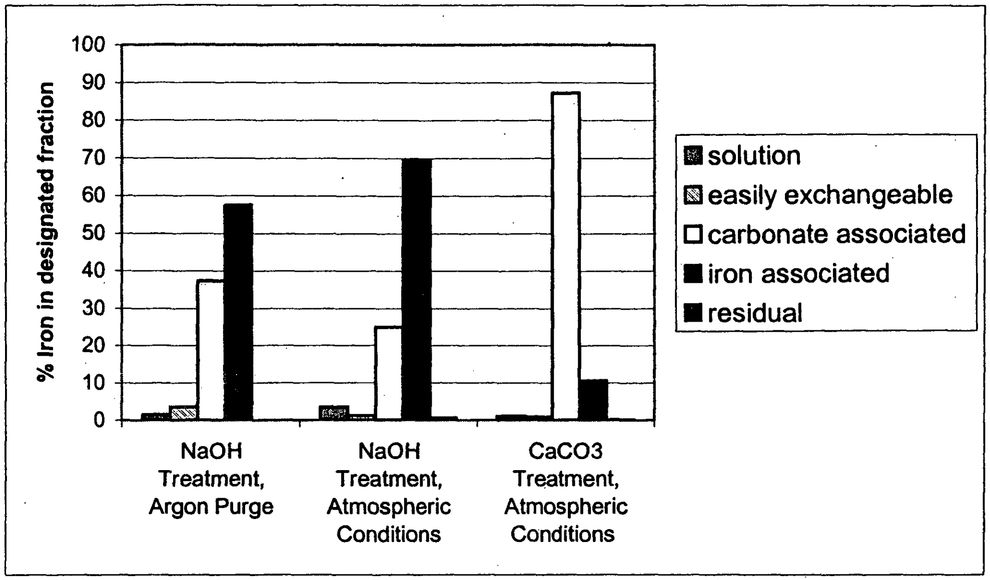

Figure 3.2- Iron distributions in the extraction procedure based on experimental conditions, TOT Fe = 2.8mg, TOT Zn = 0.96mg

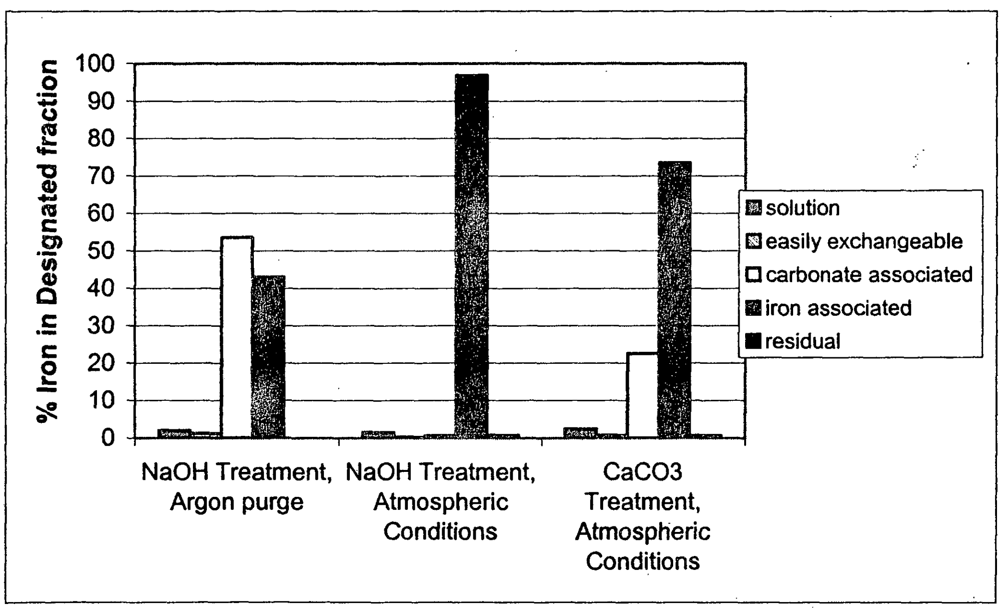

Figure 3.3- Iron distributions in the extraction procedure based on experimental conditions, TOT Fe = 2.8mg, TOT Ni = 1.0mg

3.3 Calcium Distributions

In the sequential extraction procedure, the calcium acted as expected. The most influential determining factor as to which fraction the calcium was dissolved in was the influent iron concentration. As can be seen in Figure 3.4, increasing iron concentrations led to increasing amounts of calcium in the solution phase. In the high iron experiments (Fe = 540 or 620mg/L) the $CaCO_3$ was almost completely dissolved (~90% in solution), whereas in the experiments with lower iron concentrations (Fe = 54 or 62mg/L) and no iron added the dissolution was not as extensive (~60%). The increasing amount of calcium in solution is consistent with the neutralization of the increased mineral acidity caused by the presence of the iron.

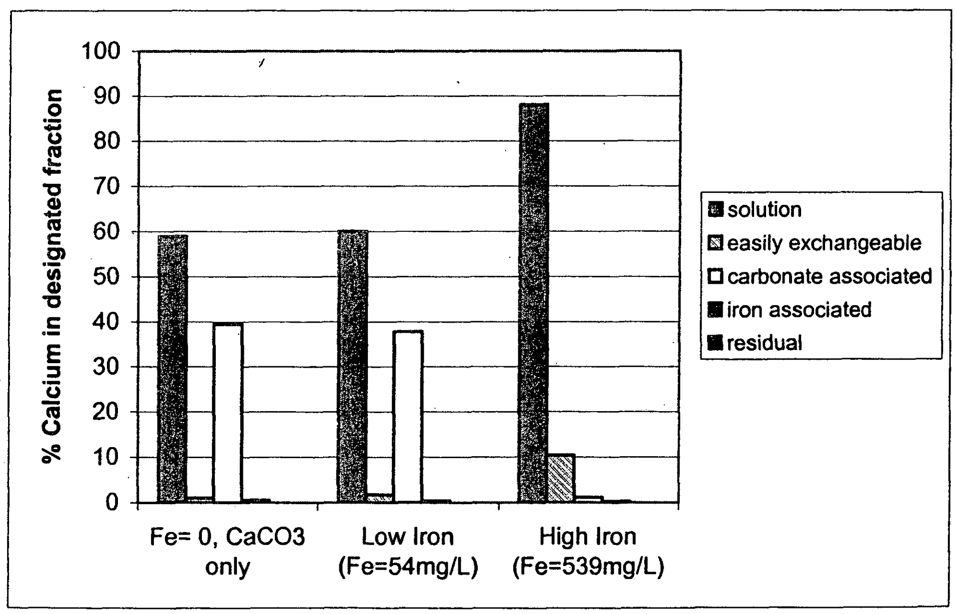

Figure 3.4- Calcium distributions as a function of increasing iron concentrations. Data taken from an experiment where TOT Zn= 0.96mg, but is representative for all variations of secondary metal concentrations.

3.4 Effect of Iron Concentration

It is expected that increasing iron concentrations relative to the secondary metal concentrations would lead to an increasing amount of secondary metal removal. This was indeed the case.

3.4.1 Zinc Removals

Due to the dependence of zinc removal on iron concentration that can be seen in Figure 3.5, the removal of zinc can be normalized as a function of the iron:zinc ratio. Thus, combining the results from all of the $CaCO_3$ experiments, determining the ratio between the iron and zinc, and comparing them to the zinc removal will create Figure 3.6. The equation for the line of best fit is a modified version of the Langmuir isotherm. Through minimizing the squared differences values can be found to fit the equation to the data. The equation is:

$$\% \text{ removal} = \% \text{ removal}_{max} * \text{Fe:Zn ratio}/(\text{Fe:Zn ratio} + C). \qquad (1)$$

For zinc, % removal_{max} is equal to 90.5, and C is a constant equal to 3.0. Although this graph fits a Langmuir type relationship, it is only an empirical tool that could be used to predict the amount of zinc removal from AMD that is to be treated with a limestone system and does not necessarily give any insight to the removal mechanisms.

Comparing and contrasting the results between the experiments that used NaOH for treatment to those that used $CaCO_3$ for treatment, begins to reveal actual processes of removal as opposed to only quantification discussed above. Although there is no solid carbonate added to the system in Figure 3.7, there is still zinc being solubilized in the carbonate associated extraction. This was originally an unexpected result as there can be

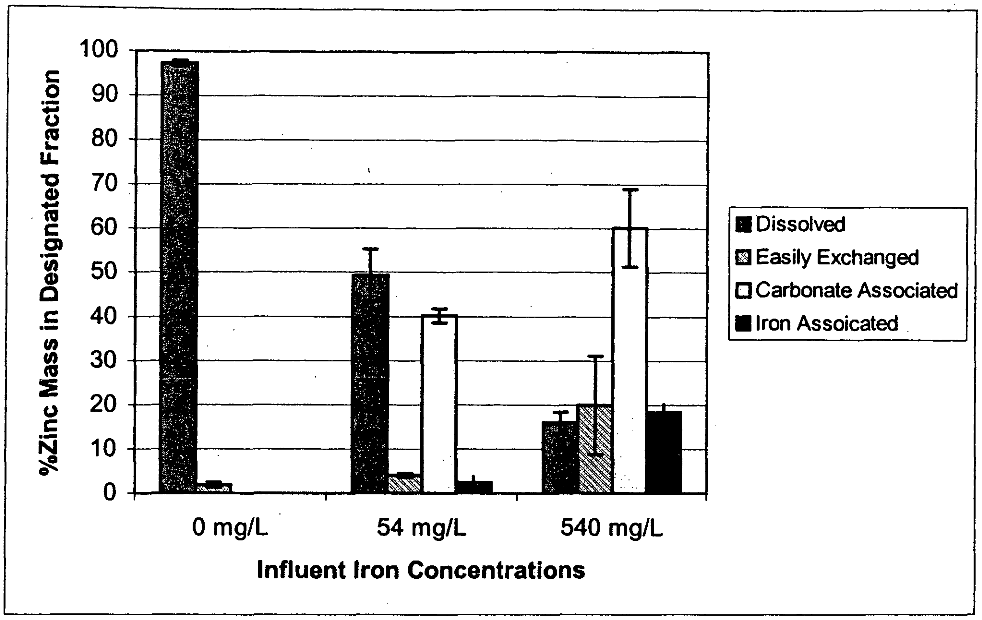

Figure 3.5- Zinc distributions as a function of influent iron concentration TOTZn = 0.72mg, Experimental pH range: 6.2-7.1

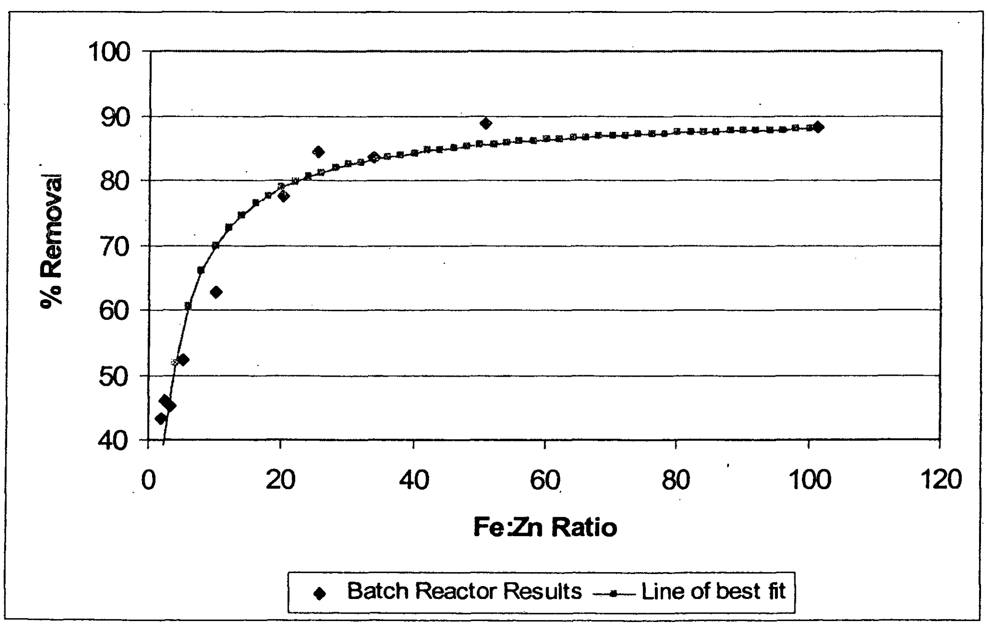

Figure 3.6- Zinc percent removal versus Fe:Zn Ratio, pH range:6.4-7.0

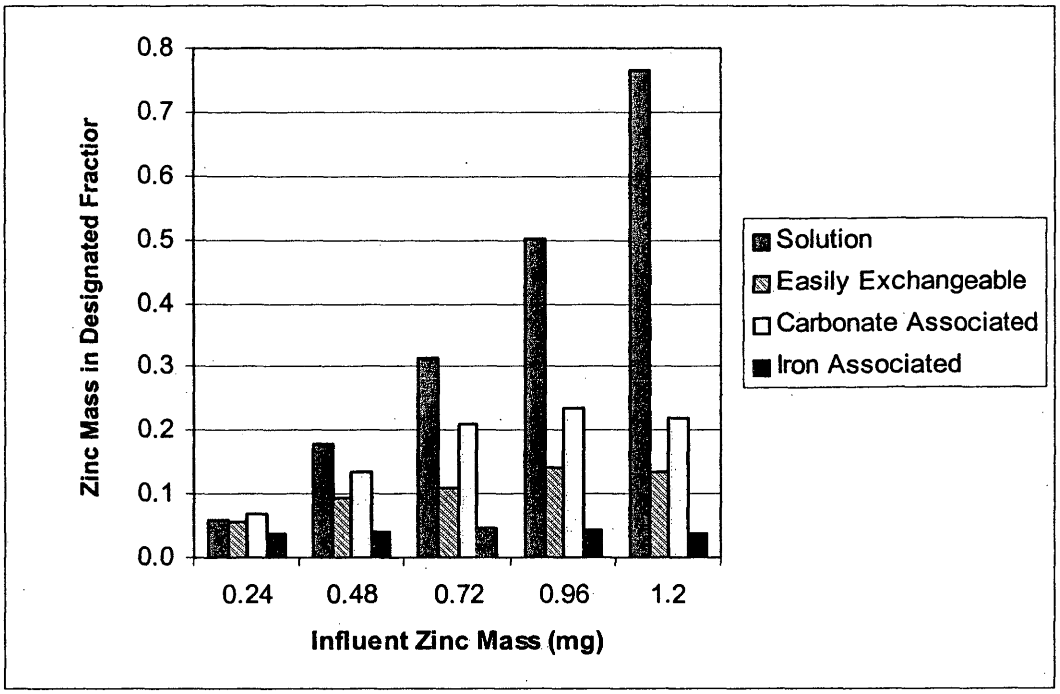

Figure 3.7- Zinc distributions as a function of influent zinc concentrations: NaOH treatment, open to the atmosphere, TOTFe= 2.8mg

no discrete zinc hydroxide or zinc carbonate precipitation, and there is no solid carbonate phase. Thus the experiments were designed with the argon purge to determine whether or not carbon dioxide from the atmosphere was enough to create some sort of carbonate phase in solution. As can be seen from Figure 3.8, there is an increasing trend with increasing inorganic carbon inputs of zinc in the carbonate phase. However, even with the highest amount of inorganic carbon additions (using $CaCO_3$ and open to the atmosphere), there is still not a high enough pH or high enough alkalinity for the discrete precipitation of the zinc hydroxides or carbonates. A further discussion of the implications of this finding is left to subsequent chapters.

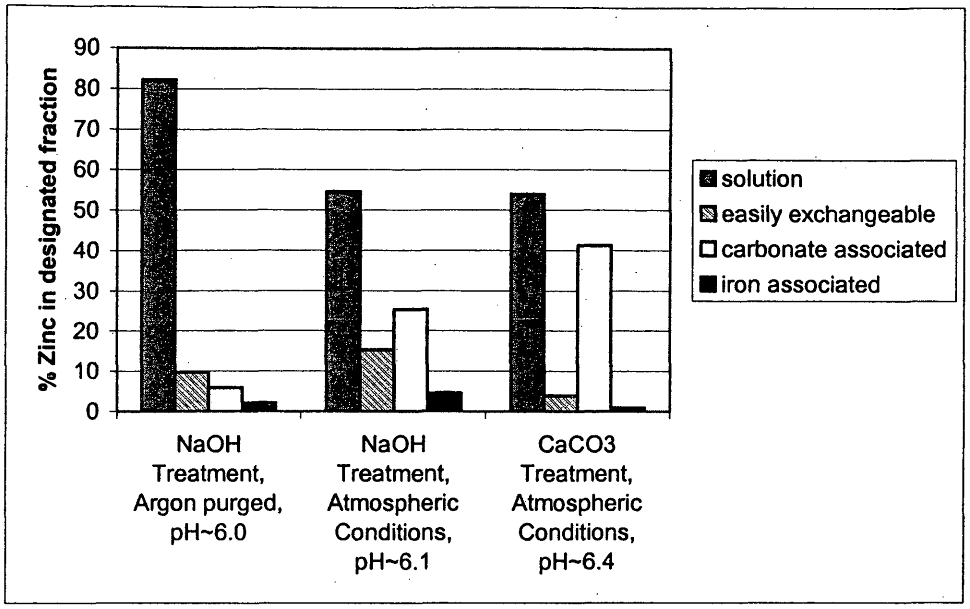

Figure 3.8- Zinc distributions as a function of inorganic carbon inputs: TOTFe= 2.8mg, TOTZn= 0.92mg

3.4.2 Nickel Removals

The nickel removals follow the same general trends as zinc with respect to influent iron concentration. Figures 3.9 and 3.10 show the distributions of nickel as a function of iron concentration and the normalization of nickel removal to the iron:nickel ratio, respectively. It can be seen from Figure 3.10 that for the same increase in iron concentration, the amount of nickel removal was higher than for the zinc. In other words nickel is more affected by iron concentrations than was zinc. The equation for the line of best fit in Figure 3.10 is identical to Equation (1), except that instead of the iron:zinc ratio, the iron:nickel ratio should be used. The % $removal_{max}$ for nickel is 94.6, and the constant is equal to 10.7.

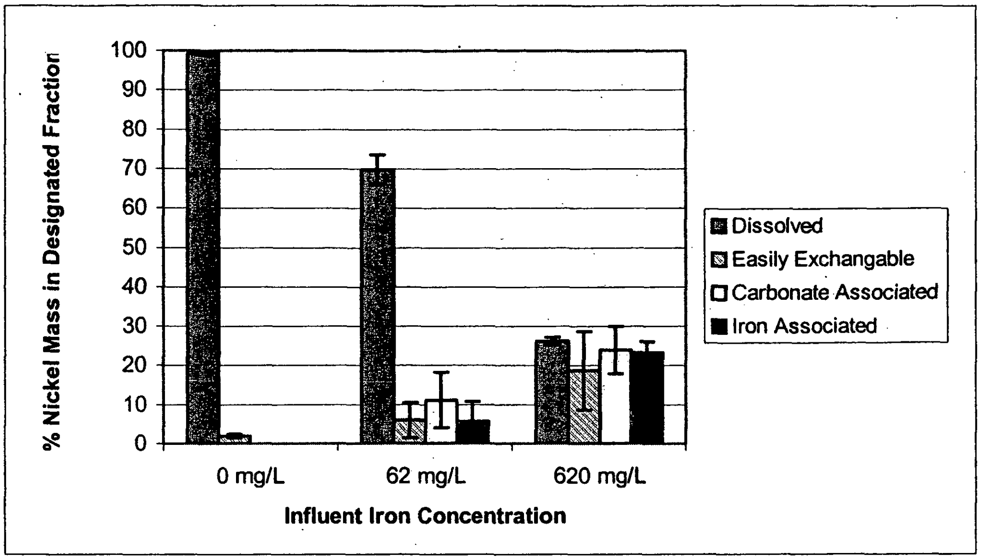

Figure 3.9- Nickel distributions as a function of increasing iron concentration; TOTNi = 0.78 mg, Experimental pH range: 6.6-7.0

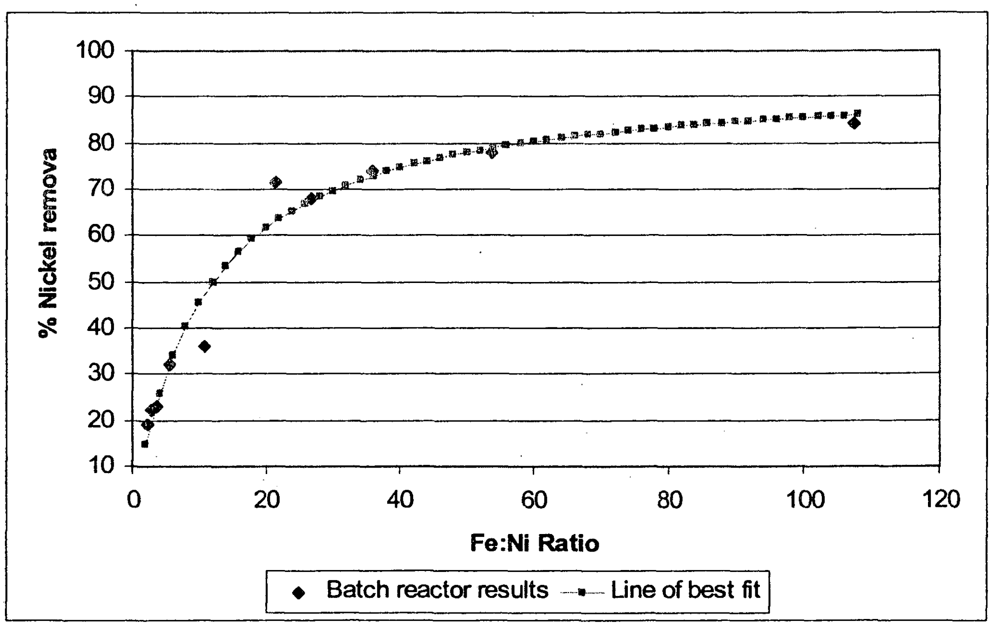

Figure 3.10- Nickel removals as a function of Fe:Ni ratio, pH range: 6.6-7.1

There were also differences between zinc and nickel removals with regard to inorganic carbon inputs. Figure 3.11 shows how the distribution of nickel changes with changing inorganic carbon inputs. When pH change is affected by NaOH treatment, it can be seen that there is no significant difference between the argon purged experiments and the experiments that were open to the atmosphere. However, there is a small difference when $CaCO_3$ is used, and the system is open to the atmosphere. This is far less drastic than the results for this same experiment were for zinc.

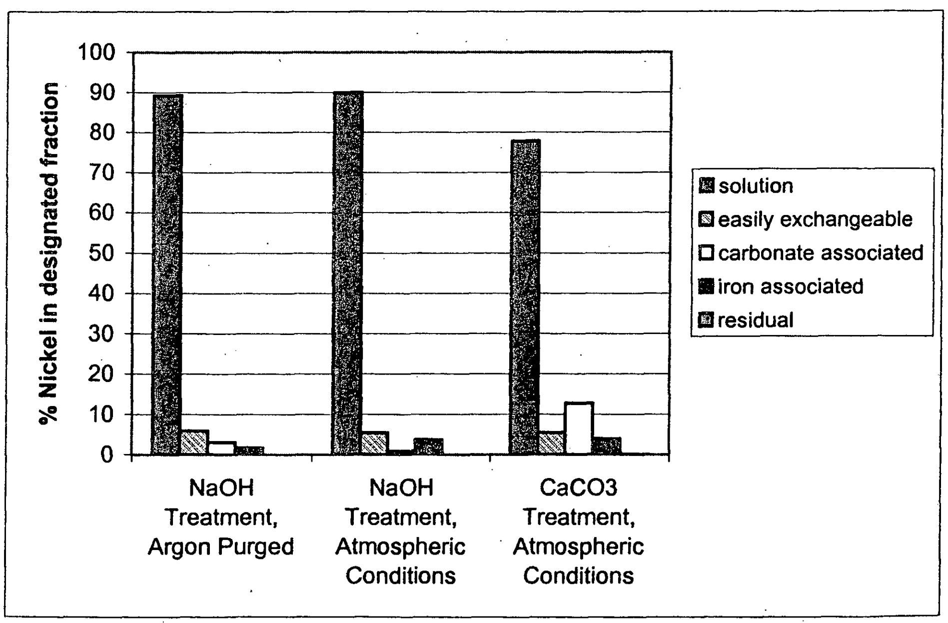

Figure 3.11- Nickel distributions based on varying inorganic carbon inputs

TOTNi = 0.96mg, TOTFe = 2.8mg

Table 3.3- Alkalinity and pH ranges for the given experimental conditions

Experimental Conditions	Metals Present	pH range	pH average	Alkalinity range	Alkalinity average
CaCO3 treatment	Fe and Zn	6.4-7.0	6.7	100-205	178
Open to the atmosphere	Fe and Ni	6.6-7.1	6.8	90-180	150
NaOH treatment	Fe and Zn	5.7-7.0	6.2	3-8	6
Open to the atmosphere	Fe and Ni	6.0-6.4	6.2	3-6	5
NaOH treatment	Fe and Zn	5.9-6.1	6.0	3-7	4
Argon purged	Fe and Ni	6.0-6.2	6.1	3-7	5

Alkalinities in mg/L as $CaCO_3$

3.5 pH and Alkalinity

The ranges and averages of pH and alkalinity can be seen in Table 3.3. The biggest differences are the differences between the reactors that used $CaCO_3$ and those that did not. The reactors that used $CaCO_3$ have much higher alkalinities and slightly higher pH, than those that did not. In the vials that were treated with NaOH, the pH was raised to 7 for the reaction time between day three and four. However, on day four when pH was measured, the pH had dropped.

3.6 Results of the PHREEQC Modeling Program

The fitting parameters of pH, alkalinity, and dissolved calcium concentration were satisfied when the calcite saturation index was equal to -0.2, and the pCO_2 in the headspace was $10^{-1.5}$. Thus, although the batch reactors were assumed to be "open", the modeling suggests that this was not the case. Although, elevated carbon dioxide concentrations relative to atmospheric conditions are common in AMD (Cravotta 2006).

The only fitting parameter that seemed to be important in the PHREEQC modeling was the density of sorption sites on the HFO. The data could not be successfully fit by changing the surface area of the iron precipitates, or by changing the thickness of the diffusion layer. For both of these parameters the default values of 600 m^2/g and 10^{-8} m, respectively, were used. The modeled surface interactions between $CaCO_3$ and both zinc and nickel using the available thermodynamic data was found to be negligible. By varying the density of sorption surface sites on the HFO, the experimental data was successfully modeled. Table 3.4 shows the values used for sorption site density for each experimental condition, as well as average values from Dzombak and Morel 1990. Type 1 sites are sorption sites that preferentially bind cations from solution. Type 2 sites represent sites that can bind anions or cations (Dzombak and Morel, 1990). It can be seen that the values needed to fit the data were, much higher than average values.

Figures 3.12 through 3.15 show isotherm relationships of the removal data for both zinc and nickel at the higher and lower iron concentrations. Both experimental data and modeled data are on each graph. Comparing the experimental data to the modeled data one can create a correlation value, which gives an idea for how well the model fits the data.

Table 3.4- Surface site densities used in modeling the data

		Modeled Sorption Site Density (mol sites/mol Fe)				
	Sorption site type	TOTFe= 2.4mg	TOTFe= 24mg	TOTFe= 2.8mg	TOTFe = 28mg	Dzombak and Morel
Zinc	Type 1	1.1	0.36			0.005
	Type 2	44.7	14.5			0.2
Nickel	Type 1			5.3	0.035	0.005

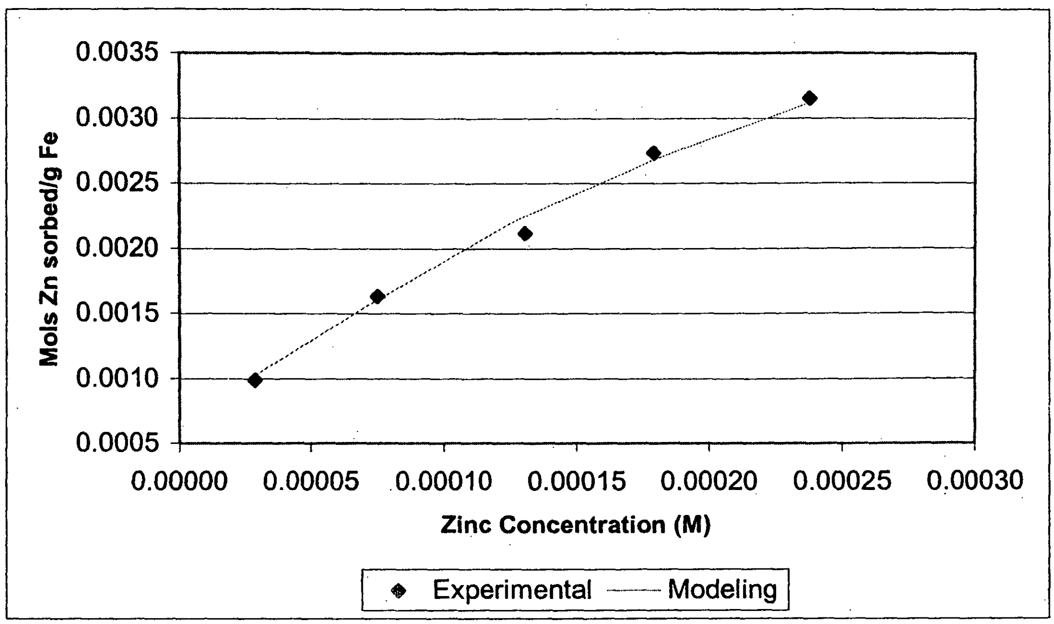

Figure 3.12- Experimental and modeled data for zinc, TOTFe = 2.4mg, correlation value between data and model = 0.997

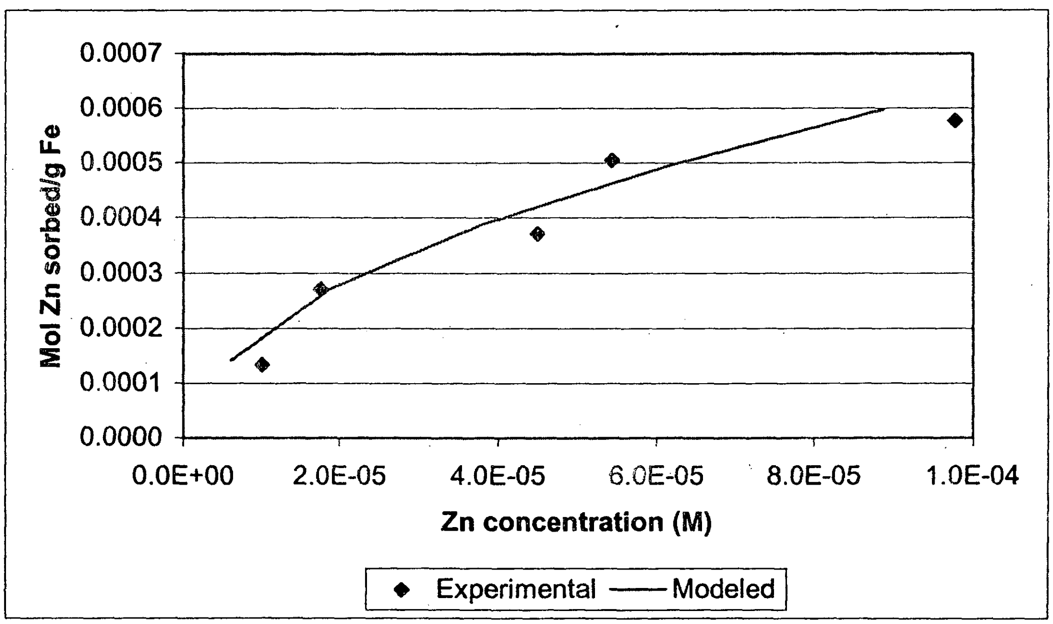

Figure 3.13- Experimental and modeled data for zinc, TOTFe = 24mg, correlation value between data and model = 0.995

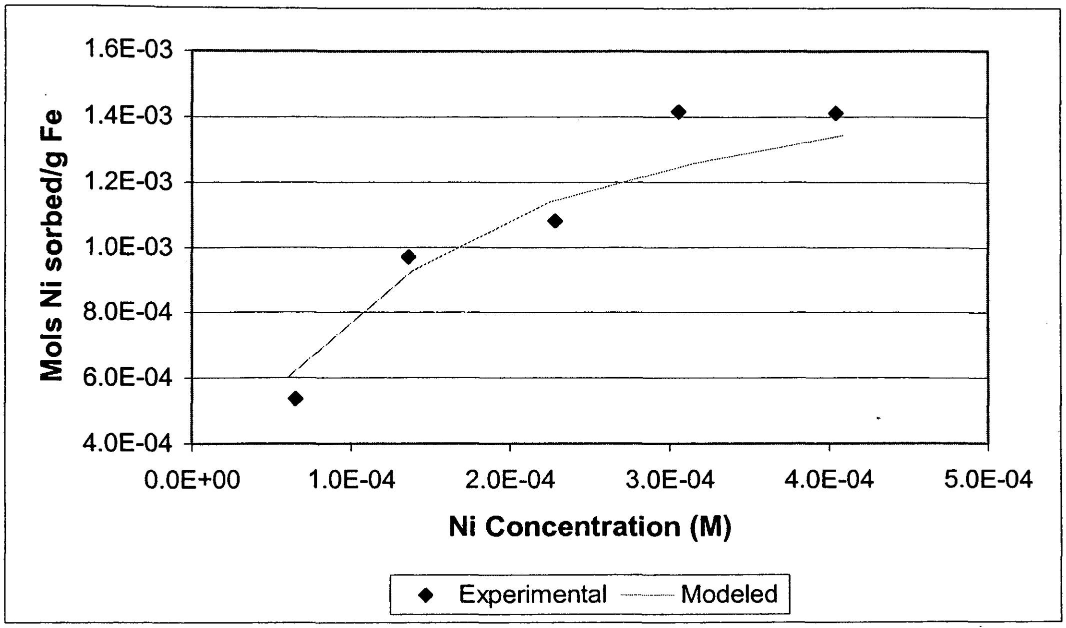

Figure 3.14- Experimental and modeled data for nickel, TOTFe = 2.8mg, correlation value between model and data = 0.962

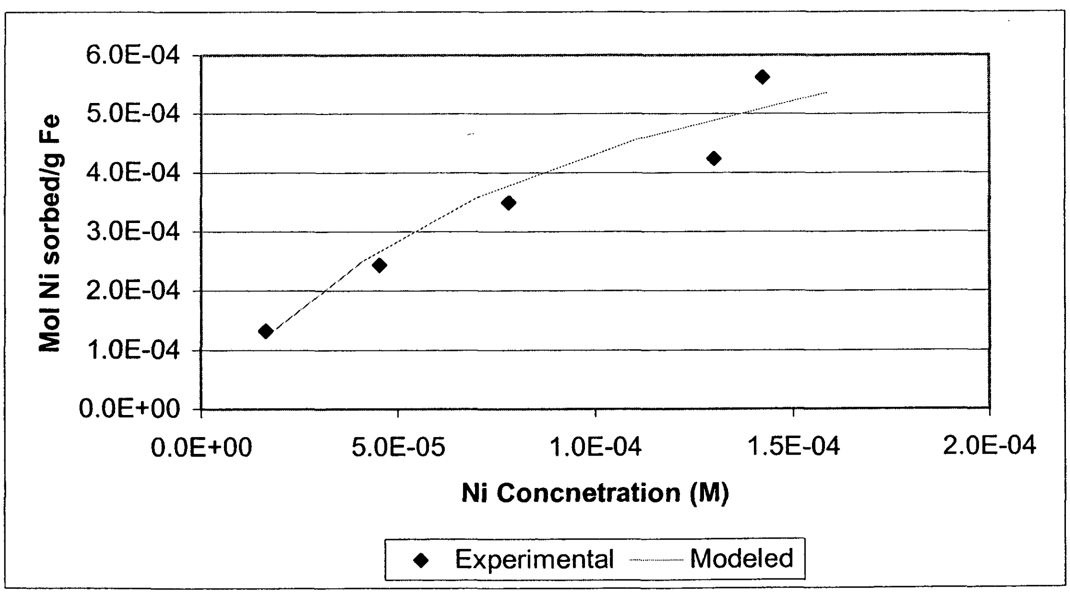

Figure 3.15- Experimental and modeled data for nickel TOTFe = 28mg, correlation value between model and data = 0.962

CHAPTER 4

DISCUSSION OF BATCH REACTOR RESULTS

4.1 Solubility Controls on Zinc and Nickel

There are three major possible controls on zinc and nickel solubility in limestone systems. The first is discrete precipitation as a hydroxide or carbonate complex. As discussed in Chapter One, this is a thermodynamic impossibility given influent concentrations of zinc and nickel, and effluent water quality with respect to pH and alkalinity. This removes discrete precipitation as a potential solubility control. If the solubility is not dictated by conditions in solution, the other potential processes are surface motivated. These surface processes include sorption and co-precipitation to the $CaCO_3$, sorption to the HFO, and co-precipitation with the HFO. These will each be discussed in more detail.

4.1.1 Sorption and Co-precipitation to $CaCO_3$

In the experiments where there was no iron present, there were no significant removals of either zinc or nickel (See Figures 3.5 and 3.9). This suggests that the interaction between the $CaCO_3$ and either of the secondary metals is minimal under the conditions studied. This is consistent with other studies that have examined zinc and nickel sorption to actual calcite (Zachara et al. 1991, Zachara et al. 1988). In those studies, significant nickel sorption to the calcite did not occur until a pH of ~8 or higher. This is significantly higher than any pH in this study, as well as any documented effluent pH from a limestone treatment system in the field. For nickel then, it can be concluded that sorption to or co-precipitation with the $CaCO_3$ is negligible, and does not control nickel solubility.

Zinc is slightly different in the sense that it started to interact with the calcite at a lower pH. On the sorption edges presented by Zachara et al. 1988 for zinc sorption to calcite, about 10% of the zinc had sorbed to the calcite surface at a pH of 7, depending on experimental conditions. Although rare, a pH of 7 in a limestone system is conceivable depending on the design. Thus, it is possible that there is some zinc removal in limestone systems due to interactions with the limestone itself. However, as with nickel, the batch reactors in this study had negligible zinc removal when iron was not present (see Figure 3.5). If there are surface interactions between the zinc and the $CaCO_3$, they are negligible in this study.

4.1.2 Zinc and Nickel Sorption to the HFO

One of the pitfalls of the experimental design used in this study was that there is not a good method of separating the easily exchangeable fraction into amounts of the secondary metal that were associated with the $CaCO_3$, and amounts associated with the iron. Initially, this separation was conceivably possible by comparing results between experiments that only had the $CaCO_3$ with the experiments that only had iron, and seeing what the difference was between them. However, because there is no significant interaction between the secondary metals and the $CaCO_3$, it can be assumed that all the secondary metals that were re-dissolved in the easily exchangeable extraction fluid had reversibly interacted with the precipitated iron.

Despite the operational definition of "carbonate associated" put forth by Tessier et al. 1979, it is entirely possible that some of the secondary metal that dissolves in the carbonate associated fraction is not actually carbonate associated. It is probable that much of what is re-dissolved in this fraction is a more complex sorption reaction between the secondary metal and the iron surface. With the increasing degree of stringency in the extraction solutions, closer associations between the secondary metals and the iron could be removed as the sequential extraction proceeded. Thus, despite the name, the secondary metal that dissolves in the carbonate associated phase is actually associated with the precipitated iron, but in a far less reversible way than the secondary metals that re-dissolve in the easily exchangeable fraction.

4.1.3 Zinc and Nickel Co-precipitation with HFO

Moving from sorption to co-precipitation an entire new realm of removal has been entered. Once the secondary metal has co-precipitated with the HFO, only significant changes to the properties of HFO or to its structure will re-liberate the secondary metal ion. At this point the metal would be considered an impurity in the slowly forming iron mineral phase. In these experiments complete dissolution of the HFO was the method of liberation of the secondary ions. Unlike the other phases, the ions that dissolved into the iron associated phase were indeed associated with the iron. Not only were they undoubtedly associated with the iron it is unlikely that they were near the surface of the HFO. Instead the secondary metals had migrated into the HFO structure or had many other layers sorb and precipitate in between the secondary ion and the solution, effectively hiding them from the previous extraction fluids. This process is by far the least reversible of any of the removal processes.

4.2 Comparison of Metals in the Carbonate Associated Extraction

For the pH and alkalinity range involved in this study, it is not surprising that the iron precipitates control zinc and nickel solubility. However, the iron itself did not always act as expected. It was assumed in the beginning, and by many in the literature, that the precipitated form of iron in limestone treatment systems is HFO, or any one of its closely related species (Watzlaf 2004, Cravotta and Trahan 1999, Kairies et al. 2005). However, this species should not be soluble in the carbonate associated fraction. And yet, depending on experimental conditions, there were often significant iron concentrations in that extraction. There are two possible explanations for this. One is that the HFO, due to experimental conditions, does not have the assumed $Fe(OH)_3$ chemical formula and structure, and thus does not have the assumed chemical properties. This would allow for partial solubilization in the carbonate associated phase. The other possibility is that the iron is in some way associated with the $CaCO_3$.

Figures 4.1 and 4.2 show the amount of the secondary metal extracted into the carbonate associated fraction against the amount of iron and calcium, respectively. Figure 4.1 shows a strong linear relationship between nickel and iron. This further shows the association and solubility control that iron has on nickel. Figure 4.2 shows no clear relationship between the nickel and the calcium. This lack of relationship further shows that the $CaCO_3$ is not controlling nickel solubility. Figures 4.3 and 4.4 show these same relationships but for experiments with higher iron additions. The linear relationship between nickel and iron, Figure 4.3, is weak at best. The complete lack of relationship between the nickel and calcium, Figure 4.4, is still apparent. The main difference between these two experimental conditions is the amount of $CaCO_3$ that dissolved.
In comparing and contrasting the relationships between the experiments with high and low iron additions (Figure 4.1-4.4), it starts to become apparent that the iron is controlling the nickel solubility, and the $CaCO_3$ is interacting in some way with the iron. When the $CaCO_3$ is almost completely dissolved due to the elevated iron, the relationship between nickel and iron in the carbonate phase breaks down. This would suggest a more complicated mechanism than nickel removal based on sorption and co-precipitation with the HFO.

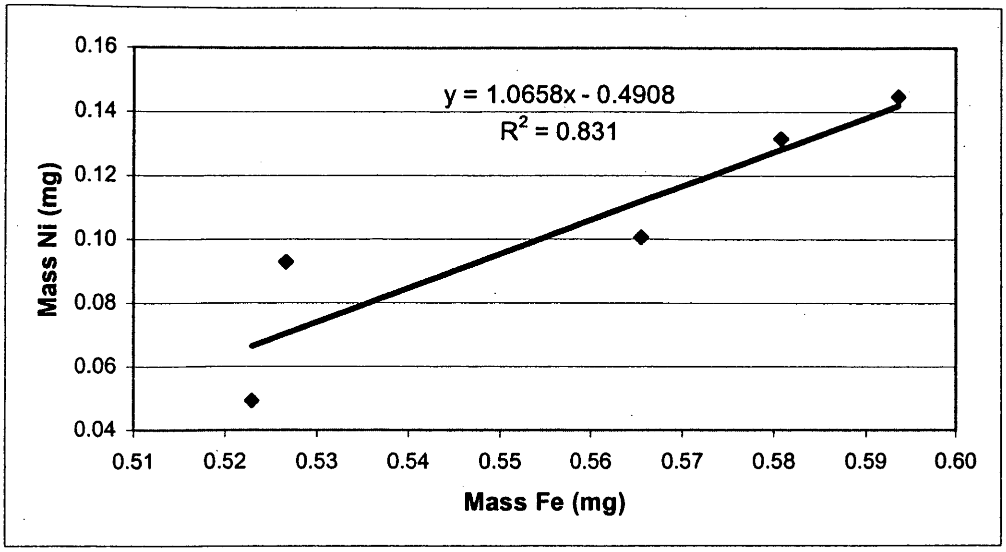

Figure 4.1- Nickel mass in the carbonate associated extraction vs. iron mass in the carbonate associated extraction, TOTFe= 2.8 mg, Nickel variable

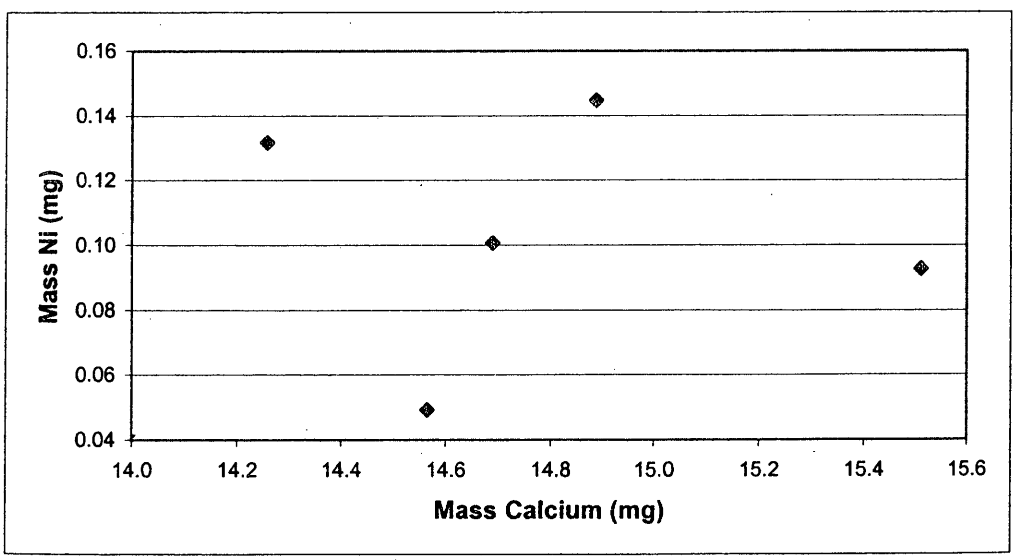

Figure 4.2- Nickel mass in the carbonate associated extraction vs. calcium mass in the carbonate associated fraction, same experimental conditions as Figure 4.1

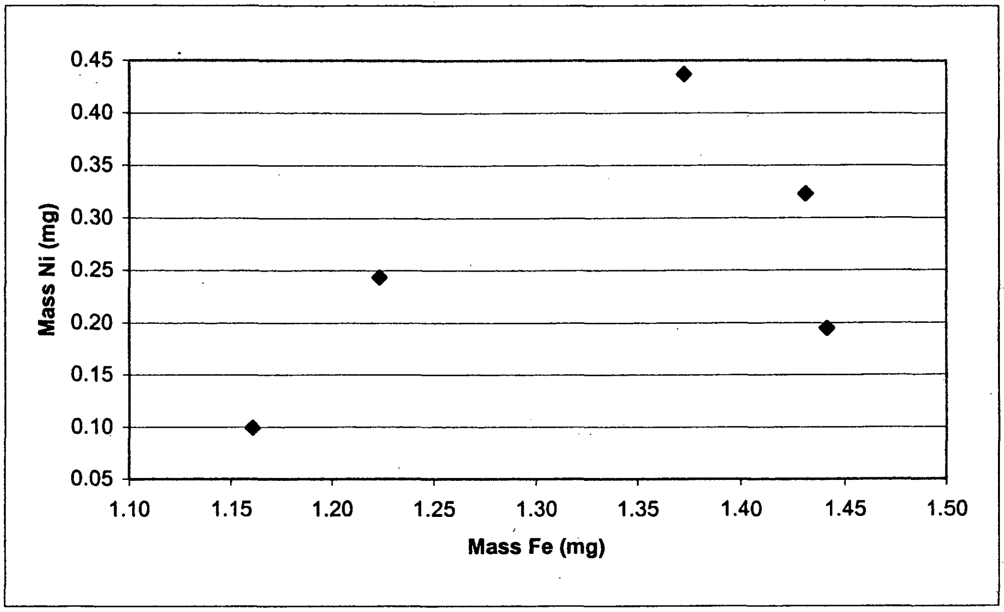

Figure 4.3-'Mass nickel in carbonate associated fraction vs. mass iron in carbonate associated fraction: TOTFe= 28mg, Nickel variable

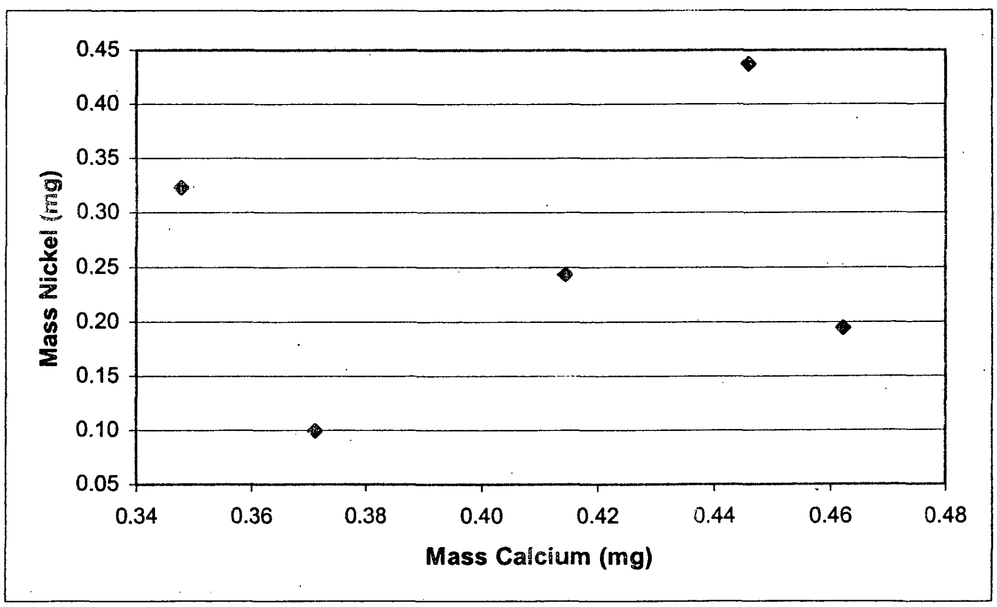

Figure 4. 4- Mass Nickel in carbonate associated fraction vs. mass calcium in carbonate associated fraction: TOTFe= 28mg, Nickel variable

The same types of figures just discussed for nickel, can also be created for zinc in the carbonate phase (Figures 4.5-4.8). However, the zinc relationships are slightly different than the nickel relationships. Namely, the zinc shows a weak but potentially significant relationship to the calcium. This is consistent with previous studies, as well as other observations in this study. However, in the experiments with high iron additions, there is the same breakdown in linear relationships that was seen with the nickel.

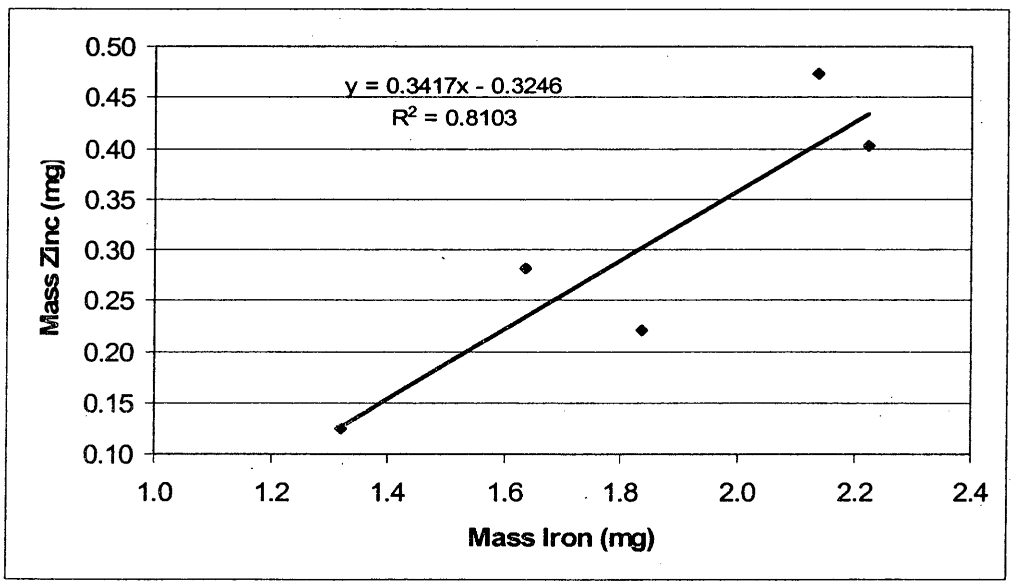

Figure 4.5- Mass zinc vs. mass iron in the carbonate associated extraction. TOTFe= 2.8mg, Zinc variable

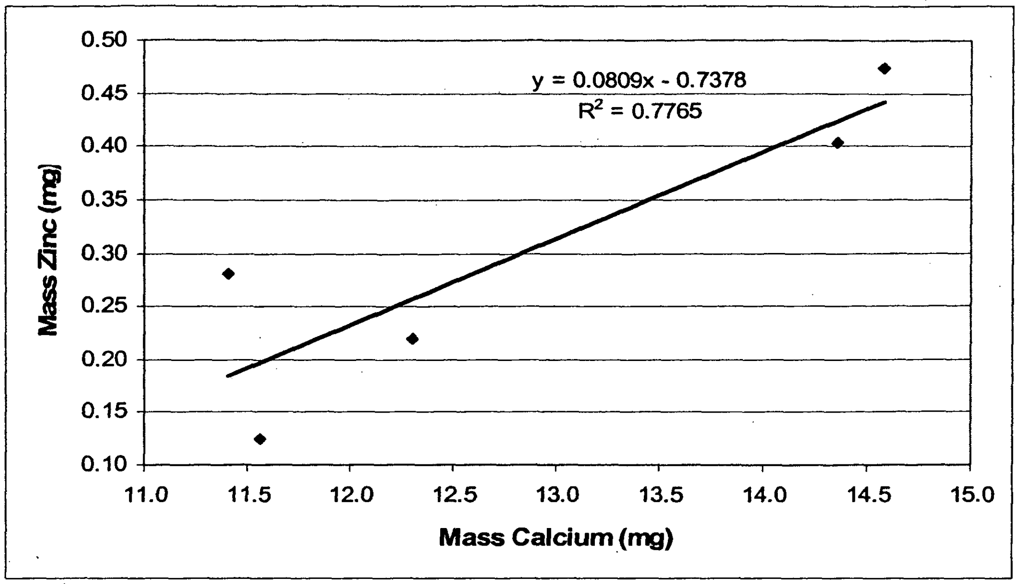

Figure 4.6- Mass zinc vs. mass calcium in the carbonate associated extraction, same experimental conditions as Figure 4.5

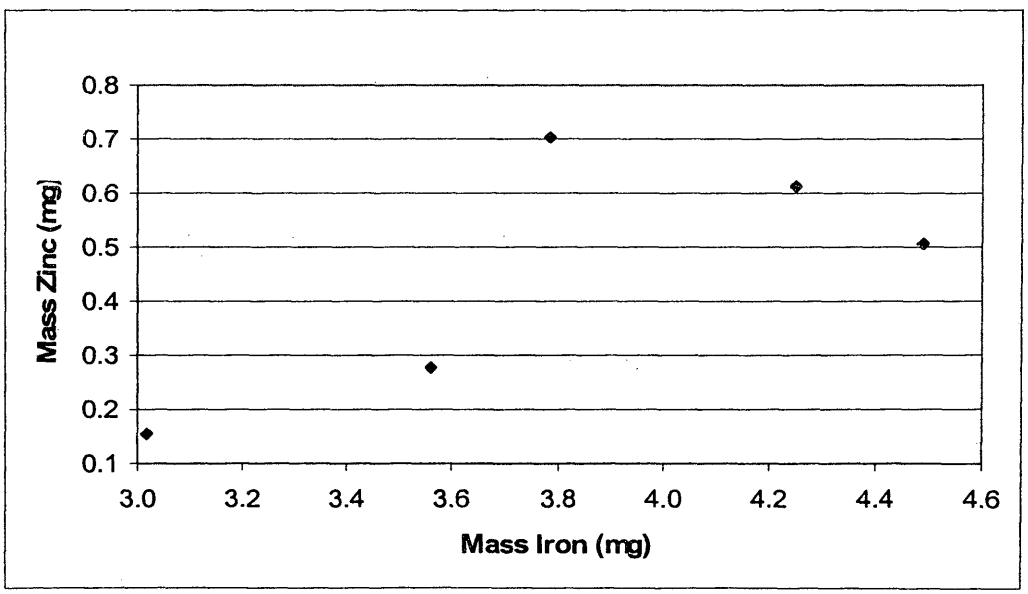

Figure 4.7- Mass zinc vs. mass iron in the carbonate associated extraction. TOTFe= 28mg, Zinc variable

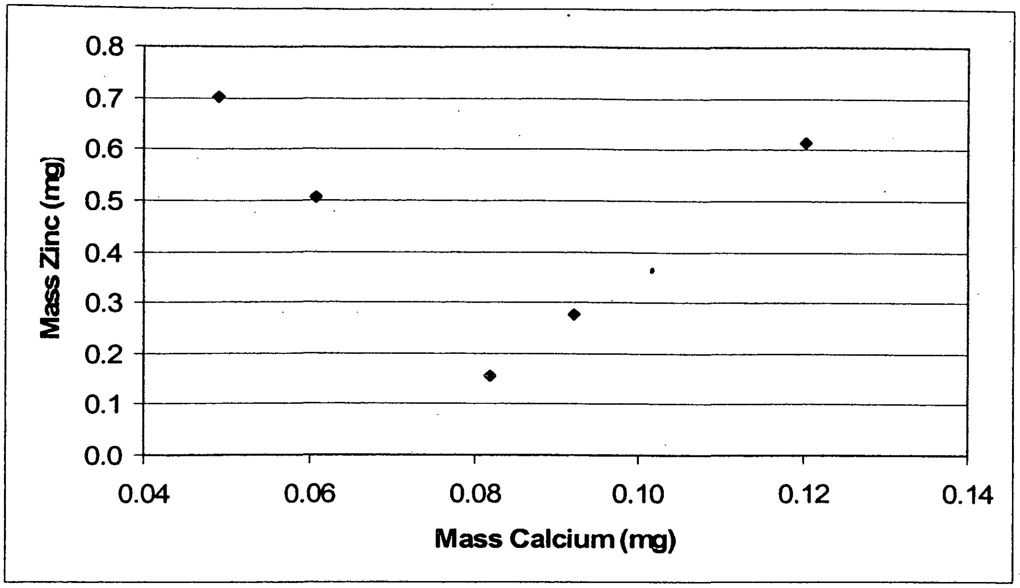

Figure 4.8- Mass zinc vs. mass calcium in the carbonate associated extraction, same experimental conditions as Figure 4.7

If in fact the iron and calcium were somehow associated, the carbonate associated fraction would show that relationship. In the experimental process, iron and $CaCO_3$ were added at constant ratios while the secondary metal concentrations were variable. Therefore, instead of iron and calcium having some sort of linear relationship, it would instead be a constant ratio between iron and calcium in the carbonate associated fraction. As can be seen in Table 4.1, the Fe:Ca ratios under the variable metal additions were in fact fairly constant. Also, the same relationship holds whether the secondary metal is nickel or zinc. Furthermore, the experiments with higher iron led to much higher Fe:Ca ratios. In the experimental process, the experiments with higher iron led to more $CaCO_3$ dissolution. Thus, there was more calcium in solution and less in the solid phase. This smaller mass in the solid phase led to smaller amounts to be extracted, which in turn led to higher Fe:Ca ratios.

Table 4.1- Fe:Ca ratios in the carbonate associated fraction for variable metal concentrations. In all the experiments 100mg of $CaCO_3$ was used.

	TOTFe = 2.8mg	TOTFe = 28mg	TOTFe = 2.8mg	TOTFe = 28mg
Experimental Conditions:	Zinc Variable	Zinc Variable	Nickel Variable	Nickel Variable
Fe:Ca Ratio	0.11	11	0.036	3.1
	0.15	8	0.034	3.1
	0.14	14	0.038	3.0
	0.15	10	0.041	4.1
	0.15	13	0.040	3.1
Average:	0.14	11	0.038	3.3
Standard deviation:	0.02	2	0.003	0.5

4.3 Effects of Carbonate Inputs on Secondary Metal Removal

In the experiments completed that varied the amount of inorganic carbon input, certain patterns emerge. One of those is the effect that the inorganic carbon has on the iron, and the other is the effect that the inorganic carbon has on the secondary metals.

4.3.1 Inorganic Carbon Inputs Effect on Iron

It was expected that the iron precipitates would not dissolve in the carbonate associated extraction. This was not in fact the case (see Figures 3.2 and 3.3). It was also unexpected that the inorganic carbon inputs would have any effect. There are several possible reasons for the iron being present this extraction solution. The first of which being acetate complexation of iron(III). The extraction procedure proposed by Tessier et al. 1979 uses acetate in the carbonate associated fraction. Acetate is known to complex iron(III). Thus at least part of the reason for the iron in the carbonate associated fraction could be acetate complexation and not at all related to metal removal in limestone treatment systems. Another possibility is the degree of crystallinity that the HFO was able to achieve. HFO is thermodynamically unstable and will eventually dehydrate and condense into the mineralized forms of iron oxide/hydroxide of goethite and hematite (Dzombak and Morel 1990). It is possible that the iron that is dissolving in the carbonate associated fraction is less mineralized than the iron that dissolves in the iron associated fraction. The method put forth by Tessier et al. 1979 is designed specifically for sediments where it is a relatively good assumption that most of the iron would be present as the more mineralized forms and not as a fresh precipitate. One should be mindful of these potential limitations when using the procedure to examine freshly precipitated iron species.

4.3.2 Inorganic Carbon Inputs Effect on the Secondary Metals

The relationship between inorganic carbon inputs and the secondary metals is more straight forward. For both zinc and nickel the increasing inorganic carbon inputs led to increasing amounts of the secondary metal in the carbonate associated extraction. With nickel this increase in the carbonate associated fraction led to a higher percent removal. For zinc the amount in solution stayed the same and the amount in the easily exchangeable fraction declined, thus suggesting different removal processes depending on conditions (see Figures 3.8 and 3.12). However, it is difficult to reconcile these results with the unexpected effects that inorganic carbon had on iron. It is clear that the inorganic carbon has an effect on the iron precipitates. Whether this effect forces a different form of iron precipitate chemical structure, or the inorganic carbon solely effects the exposed surfaces of the precipitated iron is still unknown.

4.4 Importance of pH and Alkalinity

All of these results and discussions are based on results in a certain pH and alkalinity range. They are only valid in the range reported in Chapter 3. This is most important when considering the use of Figures 3.6 and 3.10 for the forward prediction of secondary metal in limestone systems. Sorption and thus co-precipitation are pH dependant reactions. Also, in these types of systems, as the alkalinity increases so does the calcium ion concentration. The calcium does compete for surface sorption sites to a certain extent, thus displacing the ability of the secondary metals to be removed. Therefore extrapolation of the data and relationships outside of this range is not recommended.

4.5 Implications of the Modeling

The data was successfully modeled using higher than average estimates for the density of the sorption sites on the HFO. There are two possible explanations for this.

The first is related to how the iron precipitates were created. It is known that the density of sorption sites is dependant on how the HFO is created (Dzombak and Morel 1990). In these experiments to simulate AMD treatment the HFO was created by mixing several elements in one vial, including the iron, secondary metals and limestone surrogate. The methods discussed in Dzombak and Morel 1990 are more stepwise in nature. There, the HFO is created and aged without other ions in solution, and then the sorbate is added. Due to the unique method of creating the HFO used in these experiments, it appears that a mineral form was created that has a much higher apparent site density than HFO. In other words, the iron precipitates in these experiments are not a pure form of HFO, but instead a different mineral containing a mixture of all the elements that were present in the reactor vials. The apparent elevated site density that this mineral possesses has positive implications when considering secondary metal removals. The higher the site density, the more secondary metal removal can occur.

Second, this unique method of creating the iron precipitates could have led to reactions beyond surface chemistry. As the iron precipitated into this new mineral form, it is possible that the secondary metal ions were removed by entrapment in the mineral matrix. The elevated apparent site density could be indicative of these reactions that are currently unaccounted for. The only pathway that the modeling program had to control secondary metal concentrations is through the site density estimates and the thermodynamic data entered describing the possible reactions between the secondary metal ions and the available surfaces. There are no reactions or other descriptors for physically motivated removal of the secondary metal ions. Thus if the physical removal of secondary ions was occurring, the surface site density would have to be elevated for the model to fit the data.

4.6 Summary of Solubility Controls on Zinc and Nickel

These results allow for conclusions on the three hypotheses formulated in Chapter One. The first was that secondary metal solubility would be controlled by surface interactions. This hypothesis proved to be true. For effluent water chemistry without any available surfaces, there was no secondary metal removal. But with the addition of sorption and co-precipitation surfaces and reactions, there was significant secondary metal removal. The second hypothesis, that the HFO would act as a surface for secondary metal removal, also proved to be true. In fact, the iron in the reactor vessels had the greatest control of secondary metal solubility. The third hypothesis was that the $CaCO_3$ would not act as a surface of removal. This hypothesis also proved true, however, the $CaCO_3$ does play a role in secondary metal removal. It is simply not a direct role. As previously discussed the inorganic carbon from the $CaCO_3$ can significantly alter the

HFO surface, thus effecting the secondary metal removal. Although $CaCO_3$ does not act as a surface for removal, it does contribute in an indirect way.

CHAPTER 5

PERFORMANCE OF LIMESTONE TREATMENT SYSTEMS FOR METAL MINE DRAINAGES

5.1 System Descriptions

Two different limestone treatment systems were analyzed for performance based on pH neutralization capacity, as well as metal removals. One was a passive bench-scale reactor, and the other was an active pilot scale system (Sibrell 2000). Both systems were tested using water from the Argo Tunnel in Idaho Springs, Colorado. Currently, there is a full scale water treatment plant at this site that treats the mine water using lime precipitation, and filtering of the precipitates.

5.1.1 Passive Bench Scale Reactor

The passive bench scale reactors were conceptually similar to the cubitainers used by Cravotta 2003. They were designed to mimic gravity fed oxic limestone treatment systems. Basically they were made from four liter jugs with a drain hole drilled at the two liter water level. The reactors were filled by volume up to the point of the drain hole with two different sizes of limestone. One reactor had 0.75" limestone and the other had 1.5" limestone. Unlike Cravotta, these reactors were lightly capped to allow for atmospheric gasses to fill the headspace, but to minimize evaporation. Also, these bench scale reactors were flow through systems. The influent tube was placed down through the limestone so that the general flow regime was up through the limestone, and out through the drain hole. Although the water was pumped into the reactor, the outflow was regulated by gravity. The flow through the system averaged around 150mL/day. Using a porosity estimation of 50%, the calculated retention time at start up is approximately seven days.

The mine water was pumped through this system with periodic samplings (at least once a week) for pH, alkalinity, flow rate, total and dissolved metals concentrations. pH was measured using a pH probe calibrated with pH 4 and pH 7 buffers. Alkalinity was measured colorimetrically using a Hach digital titrator. Flow rate was monitored using a graduated cylinder and clock. Total metal concentrations were measured in samples that were unfiltered and acidified with HNO_3 to a pH <2. Dissolved metals were passed through a 0.45 micron filter, then acidified. Metal concentrations were determined using an ICP-OES.

5.1.2 Active Pilot Scale Treatment

This system is well described in literature as it has been used to treat mine drainages at various locations (Sibrell and Watten 2003, Sibrell et al. 2003a, Sibrell et al. 2000, Sibrell et al. 2005). The reactor system uses sand-size limestone as the major treatment material. The mine water is pumped through vertical columns where it mixes and scours the limestone surface while dissolving the limestone. Because this occurs in a closed system, the produced carbon dioxide from this dissolution remains dissolved in the water. Precipitates that may form are flushed out of the system by the active pumping. As part of the treatment regime, the water also passes through a packed bed reactor where an optional addition of carbon dioxide can be made to the mine water. The added carbon dioxide leads to more limestone dissolution, and thus higher alkalinity and pH in the effluent. There is also a stripping device that allows for recycle of the carbon dioxide from the effluent to the influent. Upon elution from the treatment system, there is a large amount of dissolved carbon dioxide. This is removed from solution by pumping atmospheric air through the water. Upon removal of the carbon dioxide, the pH increases further.

Experiments were conducted with this system varying flow rates, and carbon dioxide inputs to maximize treatment efficiency. The flow rates tested were 30, 45, and 60 gallons per minute (gpm), and the CO_2 inputs were 0, 10, and 25 standard liters per minute (SLPM). Treatment efficiency was measured as a function of neutralization capacity, alkalinity production, and metal removals.

Metal samples were taken and filtered through a 0.45 micron filter before being acidified with HNO_3 to a pH<2. Alkalinities were determined by titrating an effluent sample to a pH of 4.3 with 0.02N H_2SO_4. Hot acidity determinations were completed on a sample of the influent by adding about seven drops of 30% hydrogen peroxide to 100 mL of sample and heating to boiling for 10 minutes. Once cooled a titration of the solution was completed with 0.02N NaOH to a pH of 8.3.

5.2 Argo Tunnel Water

The pertinent water quality data for the water used in these systems is summarized in Table 5.1. The high variability is due to two reasons depending on the system. For the bench scale system, a large amount of mine water was gathered, and then stored on the bench as it was pumped into the reactor. As the water aged metal concentrations varied. At the pilot scale level, the variation in the water quality was due to the operations in the currently active treatment plant. The plant uses sand and mechanical filters to remove precipitates from the water. As need arises, these filters are backwashed into the influent holding tank. The precipitates that are backwashed have un-dissolved lime as well as metal precipitates that can potentially dissolve when mixed with the acidic mine water. This leads to a partial neutralization of the mine water in the holding tank, which causes the metal and pH variability.

Table 5. 1- Water quality data for Argo Tunnel

		Range	
	Average	Low	High
Aluminum	11.5	9.30	20.8
Copper	4.19	3.40	5.20
Cadmium	0.115	0.099	0.139
Iron	35.2	0.021	95.6
Manganese	62.8	50.3	77.6
Nickel	0.179	0.15	0.228
Zinc	37.5	28.6	45.9
pH	3.2	2.9	4.6
Metal concentrations in mg/L			

5.3 Treatment Goals of the Passive System

The treatment goals of the passive system were as a pre-treatment unit for a passive bio-reactor. This separation of function is advantageous for multiple reasons. The first is pH neutralization. The target microbes in SRB systems are not acidophilic. They tend to be neutrophiles, which have the highest activity levels at more neutral pH levels. Thus, if the pH of an AMD source is below a pH of ~5.0, the microbes' activity is hampered at best, which is un-desirable in the construction of small, highly efficient reactors. If the water is neutralized before entering the bio-reactor, this decline in microbial activity will not be present, and thus the bio-reactor can be physically smaller in design.

The next argument in favor of pre-treating AMD is the metal removal that occurs. Iron(III) and aluminum tend to precipitate as hydroxides as the pH increases through the reactor. These precipitates have a tendency to clog or partially clog bio-reactors leading to a decrease in efficiency and possible failure of the reactor. Removing these metals before they arrive in a bio-reactor would reduce clogging of the bio-reactor. Furthermore, the secondary metals that are present in AMD can be toxic to the microbes. So, if the secondary metal concentrations are lowered, the microbes will again be less inhibited leading to smaller reactor design.

The final reason for pre-treating a water is the ability to more easily handle the precipitates. Limestone systems for metal mine drainages may require periodic maintenance due to sludge accumulation in the limestone system itself. However, it is preferential to perform this maintenance on a limestone system versus a bio-reactor. If the bio-reactor is clogged by precipitates and must be drained to remove solids, much of the microbial activities of interest will stop due to the fact that the anaerobic microbes are being exposed to oxygen. When the bio-reactor is put back on line, there is a high possibility of reduced microbial activity for potentially long periods of time, thus leading to reduced treatment. However, limestone based treatment does not rely on finicky microbes, but instead chemical processes. A limestone system can be started and stopped at will with minimal reduction in treatment efficiency. Therefore it is easier to handle solids in limestone systems than in microbial systems without affecting treatment efficiency.

For all of these reasons, the treatment goals of the passive limestone systems were pH neutralization and metals removal.

5.4 Results from the Passive System

The treatment goals for the passive treatment system were achieved. The system was operational for about nine months before treatment efficiency declined. The proposed reason for this failure is a shortened retention time and increased dispersion due to the metal precipitates conglomerating in the drain.

5.4.1 pH Neutralization

The average influent pH to the system was 2.7. The average effluent pH values before treatment failure began were 6.2 for the 0.75" limestone reactor, and 5.4 for the 1.5" limestone reactor. Figure 5.1 shows the pH values for the influent and effluents over the entire time the reactors were online. Treatment failure began at approximately day 200 for the 1.5" limestone, and at day 220 for the 0.75" limestone. Inability to maintain effluent pH and metal removals were the determining factors in failure. Specifically, when the pH was below ~6.0, the percent metal removals severely declined. However, both sizes of limestone effectively neutralized the water to a point that microbial activity in a subsequent bio-reactor would not be hampered.

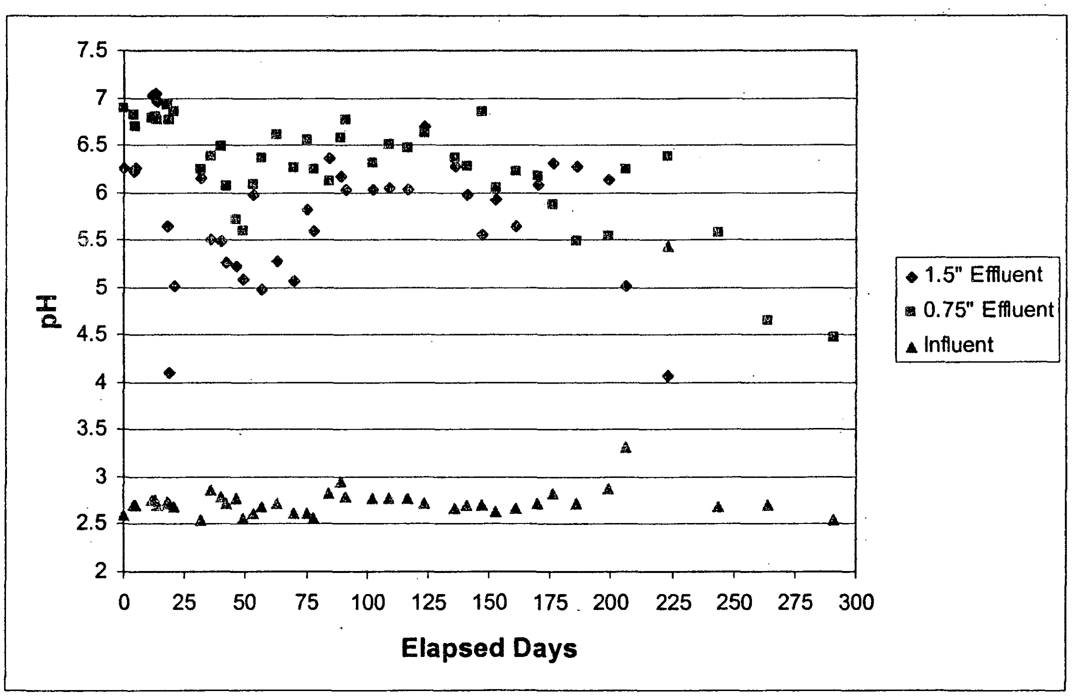

Figure 5.1- pH versus time for the passive reactors with 0.75" or 1.5" sized limestone

5.4.2 Metals Removal

Table 5.2 shows the average effluent metal concentrations as well as the concentration ranges before failure. Table 5.3 shows the percent metal removals. Iron and aluminum were essentially completely removed from solution. Copper was removed as long as the pH was greater than 6. As the pH was generally higher in the 0.75" reactor, copper removals were also better. Zinc had variable removals that were also pH dependant, but also dependant on the iron concentrations. Manganese was generally conserved.

Table 5.2- Averages and ranges of metal concentrations in the limestone system effluent

	Average Effluent Concentrations:		Concentration Ranges (mg/L): 0.75" Limestone		1.5" Limestone	
Metal	0.75"Limestone	1.5" Limestone	Maximum	Minimum	Maximum	Minimum
Iron	0.010	0.116	0.015	BDL	0.230	0.017
Aluminum	0.346	1.16	0.941	0.030	1.97	0.140
Copper	0.323	0.901	0.533	0.055	1.58	0.143
Zinc	22.4	26.7	28.8	10.6	32.5	15.6
Manganese	66.0	62.6	75.8	45.3	72.8	42.5

Table 5.3- Average percent metal removals from the passive limestone systems

Metal	0.75" Limestone	1.5" Limestone
Iron	99.97%	99.6%
Aluminum	97.8%	92.3%
Copper	91.1%	73.6%
Zinc	32.7%	24.9%
Manganese	7.30%	11.9%

5.4.3 Tracer Tests

Once the limestone systems had failed, an ionic strength based tracer test was performed on both of the reactors. A potassium chloride solution (~1M) was made and the conductance was measured. The influent to the limestone systems was moved to this solution. The effluent of the limestone was directed to a flow through cell where the probe to a conductance meter was placed. Thus the amount of tracer input, the amount of elapsed time, and the amount of tracer output from the system were measured. The data was analyzed to determine the retention time of both systems. The data is summarized in Table 5.4. The 1.5" reactor had a longer time until breakthrough, and a higher percent mass recovery suggesting less dead spots. Also, the difference between performance of the respective reactors and their retention times, could be explained by surface area differences between the two systems.

5.4.4 Comparison to the Batch Reactor Experiments

From Figures 3.5 and 3.10, equations were produced that allow for the forward

Table 5. 4- Summary of the tracer test data

	0.75" Reactor	1.5" Reactor
Retention time:	2.7 days	4.3 days
Elapsed time at breakthrough:	12 Hours	38 hours
Void space volume at failure:	621 mL	705 mL
Mass recovery of the tracer:	80%	91%

prediction of zinc and nickel removal based on the primary:secondary metal ratio. Picking discrete points from the data collection in these passive limestone systems will give an idea of how reliable and useful these equations are. Table 5.5 shows data from three points in time of the 0.75" passive limestone system. It can be seen that the zinc is generally better predicted than the nickel. Also the predicted removals for zinc tend to under predict actual zinc removal while the predicted removals for nickel tend to over predict actual nickel removal. These two different phenomena have separate explanations.

For the under prediction of zinc removal it is hypothesized that the aluminum that is also present in this mine water was also affecting zinc solubility. As the aluminum flows through the treatment system it precipitates as hydrous aluminum oxide (HAO). Much like HFO, HAO is an effective metal sorbent. This control on secondary metal solubility was not accounted for in the batch reactors. Thus the under prediction can be explained by surface interactions with the precipitated aluminum.

The over prediction of nickel removal can be related to the fact that the nickel concentrations were exceedingly low in this water relative to the other metals present. It is possible that the other metals are out competing nickel for binding sites on the available iron and aluminum precipitates. In the case of the batch reactors there was only nickel, iron, and calcium present. The competition between the ions would have been much lower in the batch reactors where the overall amount of dissolved cations was lower. Thus leading to the over prediction when examining a more complex water than was found in the batch reactors.

5.5 Treatment Goals/Results of the Active System

The low cost and ease of procurement are two of the main driving forces behind the use of limestone in AMD treatment. The goal of the active system is to pre-treat the

Table 5.5- Predicted and actual metal removals in the passive limestone system

	Iron:Secondary Ratio	%Removals	
		Actual	Predicted
Nickel	213	26.6	90.1
	272	23.7	91.0
	91	29.4	84.7
Zinc	0.98	29.5	22.2
	1.42	29.5	29.1
	0.52	31.2	13.3

water for subsequent chemical treatment with a lime slurry. The goal would be a less expensive overall treatment system by combing partial treatment with the limestone and completing the treatment with a lime slurry. The immediate treatment goals were neutralized pH and metals removal.

5.5.1 pH Neutralization

The effluent pH ranged from 5.2-7.4 depending on water flow rates and carbon dioxide inputs and the average was 6.3. However, there was no clear connection between effluent pH and experimental conditions. There is a possibility that the lack of connection was caused from the variable input into the system. This pH average and range are only slightly higher than what was seen in the passive system. The major difference in water quality between the two systems was the produced alkalinity. The alkalinity in the passive system was always below 60 mg/L as $CaCO_3$, and averaged 30mg/L as $CaCO_3$. In the pilot system, the alkalinity ranged from 19-213 mg/L as $CaCO_3$ depending on flow conditions.

5.5.2 Metals Removal

The metals removal mirrored that seen in the passive system. Iron and aluminum had removals >98%. Copper removal ranged from 50-95%, and was heavily pH dependent. Zinc removals range from 5-65%, and showed a general increasing removal trend with increasing pH. The batch reactor experiments also show that iron plays a large role in the solubility control of zinc. Nickel and manganese were generally conserved through the entire system.

5.5.3 Comparison to the Batch Reactor Experiments

Despite the differences in design and application between this system, the passive system and the batch reactors, the chemistry between the three is fairly similar. Thus the same predictions that were calculated for the passive system, can be calculated for the active system as well. These results are summarized in Table 5.6. It can be seen that the variability of these predictions compared to the actual removals is much higher than was seen in the passive system. The explanations for these discrepancies are also slightly

Table 5.6- Predicted and actual removals in the active treatment system

	Iron:Secondary Ratio	% Removals	
		Actual	Predicted
Nickel	420	7.1	92.2
	23.9	16.5	65.3
	59.2	46.0	80.1
Zinc	0.11	38.0	3.4
	0.48	58.4	12.4
	1.67	56.4	32.4

different.

First of all, only soluble metal concentrations were measured in the active treatment system. Many times there were visual particulates in the mine water with the characteristic orange color of iron(III) precipitates. Thus it can be assumed that the total iron concentration was higher than the dissolved iron concentration. Particulate iron can also participate in surface chemistry reactions. So for zinc, where removal was under predicted, it is possible that if total influent iron had been measured the predicted value would have been closer to the actual removal value. For nickel the same arguments apply as were hypothesized in the passive bench scale reactor.

For both metals, another major difference between the active treatment system and both the batch reactors and the passive bench scale systems, is the respective retention times. The estimated retention time for the active system is ~30 minutes. The retention time in the passive system was 3-8 days, and the retention time in the batch reactors was 4 days. The extent that the surface interactions can proceed are time dependent. Thus it stands to reason that the predictions for the active system may be further from the actual removals than in the passive system.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The major control on zinc and nickel solubility under the conditions found in an oxic limestone treatment system is the amount of iron present. As the pH changes from acidic to circum-neutral iron precipitation occurs. This precipitation of iron is as an impure HFO species that can potentially contain any of the chemical species present, including bicarbonate, carbonate, sulfate, calcium, zinc or nickel. This as yet unidentified iron precipitate has a high apparent site density which leads to more secondary metal removal than would be expected if a more pure form of HFO were created.

The precipitated iron species formed on the $CaCO_3$ surface, leading to partial armoring in the batch reactors. This armoring was not so extensive as to noticeably affect the $CaCO_3$ dissolution, but was indicated in the sequential extraction procedure. It is suspected that this iron forming on the $CaCO_3$ surface is the impure form of the HFO and that these iron precipitates are the iron species that are controlling the secondary metal solubility.

pH and alkalinity also exhibit some control on the secondary metal solubility as would be expected for cation sorption to an available surface. But this control on solubility was significantly less pronounced than the control exhibited by the precipitated iron.

Comparing the results from the batch reactors to both bench scale and pilot scale limestone treatment systems gave relatively good estimations of secondary metal removals. Complicating factors in attempting to apply the batch reactor results were:

metal competition between the ions present in an actual mine water that were not present in the batch reactors, the presence of dissolved aluminum in the mine water, and the varied retention times of the different systems.

6.2 Future Work

Although these experiments have shed light on the solubility controls of zinc and nickel in limestone based treatment systems, there is still much more to know. First of which, is the interaction between the precipitated iron and the calcium carbonate. It is unclear from these experiments just what the interaction is between these two species. It appears that the elevated levels of dissolved inorganic carbon in limestone treatment systems have an effect on the iron precipitates. Whether the inorganic carbon is only affecting the surface chemistry of the iron, or if the inorganic carbon is somehow becoming part of the precipitated iron mineral structure is still unknown. In order to help determine the effect of the inorganic carbon, a move toward surface chemistry based experiments and away from extraction solutions would be warranted.

A second area for future study would be to examine how iron(II) reacts in limestone systems. Due to the design and water chemistry differences between anoxic and oxic limestone systems, the fate of iron(II) is different than that of iron(III). There is generally a mixture of iron(II) and iron(III) in AMD. Thus only knowing how iron(III) behaves with respect to both the limestone and controlling secondary metal solubility gives only a partial view as to what the metal removal processes are in a limestone treatment system.

A third area would be to examine the extent that aluminum can also control secondary metal solubility. Precipitated aluminum species can scavenge metal ions from solution in the same manner as the precipitated iron species. However, to what extent these reactions would occur, and whether there are complicating issues with respect to aluminum precipitation as was seen with the iron precipitation is still unknown. This interaction would be difficult to examine through the use of the experimental procedures described herein due to the comparable solubility of $CaCO_3$ and aluminum hydroxides.

Another issue that was raised in these experiments that remains unresolved is how competition for binding sites can affect secondary metal removal. The different secondary metals that can be present in AMD have different affinities for iron precipitates. In theory the amount of removal of the secondary metal ions through interactions at the precipitated iron surface would follow the same trends as those binding affinities. However, it may be possible that relative concentrations between the metal ions in AMD may be a larger driving force in competition than the inherent attractions between the secondary metal ions and available surfaces.

A final area that was not addressed in these experiments, but is important in understanding metal removal processes, is kinetics. All of the results/discussions present here are based on the four day reaction time that was allowed in the experimental design. The rate at which these secondary metal reactions with the iron precipitates occur is still unknown. This would be an important issue when designing limestone based treatment systems with varying retention times. Furthermore, kinetic experiments would help to determine some of the actual mechanisms of secondary metal removal.

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APPENDIX A

This appendix contains the mass balances for experiments completed. For each experiment the experimental conditions are given. These conditions include the type of treatment, amount of iron present, and which of the secondary metals is variable. The fractions of the extraction procedure are given lower case roman numerals as identifiers. The code for these numerals is as follows:

Solution = Dissolved Metals
Fraction i = Easily Exchangeable
Fraction ii = Carbonate Associated
Fraction iii = Iron Associated
Fraction iv = Residual

The percent error in the mass balance was calculated through comparing the total mass measured to the total mass added for each element. Positive values indicate more was measured than was added, while negative values indicate that more was added than was measured.

The letters ND stand for "not determined". For the mass balance calculations these values were assumed to be zero.

Experimental Conditions: $CaCO_3$ Treatment, No Added Iron, Nickel Variable

Nickel Mass Balances

	Initial Conc (mg/L) Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni Fraction (i)	Mass Ni Fraction (ii)	Mass Ni Fraction (iii)	Mass Ni Fraction (iv)	Total Mass Ni Measured	%error
B-1	5.8	0.26	0.28	0.00	0.00	0.00	0.00	0.285	9.6
B-2	11.6	0.52	0.54	0.00	0.00	0.00	0.00	0.549	5.6
B-3	17.3	0.78	0.81	0.01	0.00	0.00	0.00	0.815	4.5
B-4	23.1	1.04	1.08	0.01	0.00	0.00	0.00	1.082	4.0
B-5	28.9	1.3	1.33	0.01	0.00	0.00	0.00	1.336	2.8

Percent Measured Ni in each fraction

	solution	i	ii	iii	iv
B-1	98.6	1.4	0.0	0.0	0.0
B-2	99.2	1.6	0.0	0.0	0.0
B-3	99.3	1.9	0.0	0.0	0.0
B-4	99.4	2.4	0.0	0.0	0.0
B-5	99.5	2.4	0.0	0.0	0.0

Calcium Mass Balances

	(mg) Mass Ca Added	Mass Ca in Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
B-1	40	22.48	0.544	17.03	0.126	0.003	40.177	0.4
B-2	40	22.52	0.600	16.69	0.068	0.001	39.882	-0.3
B-3	40	21.98	0.617	16.81	0.177	0.003	39.593	-1.0
B-4	40	21.87	0.582	17.31	0.091	0.002	39.863	-0.3
B-5	40	21.92	0.619	16.96	0.063	0.004	39.561	-1.1

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
B-1	55.9	1.4	42.4	0.3	0.0
B-2	56.5	1.5	41.9	0.2	0.0
B-3	55.5	1.6	42.5	0.4	0.0
B-4	54.9	1.5	43.4	0.2	0.0
B-5	55.4	1.6	42.9	0.2	0.0

Experimental Conditions: CaCO3 Treatment, TOTFe = 2.8mg, Nickel Variable

Nickel Mass Balances

	(mg/L) Concentration Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni Fraction (i)	Mass Ni Fraction (ii)	Mass Ni Fraction (iii)	Mass Ni Fraction (iv)	Total Mass Ni Measured	%error
2B-1	5.8	0.26	0.17	0.02	0.05	0.03	0.00	0.268	3.3
2B-2	11.6	0.52	0.36	0.04	0.09	0.04	0.00	0.530	1.9
2B-3	17.3	0.78	0.60	0.04	0.10	0.04	0.00	0.783	0.4
2B-4	23.1	1.04	0.81	0.06	0.13	0.04	0.00	1.037	-0.3
2B-5	28.9	1.3	1.07	0.06	0.14	0.05	0.00	1.321	1.6

Percent Measured Ni in each fraction

	solution	i	ii	iii	iv
2B-1	64.0	7.7	18.3	9.9	0.1
2B-2	68.0	7.1	17.5	7.4	0.0
2B-3	76.9	5.5	12.9	4.7	0.1
2B-4	77.9	5.5	12.7	3.9	0.0
2B-5	80.8	4.7	11.0	3.5	0.0

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
2B-1	62	2.8	0.08	0.01	0.52	2.17	0.02	2.8	0.1
2B-2	62	2.8	0.07	0.02	0.53	2.16	0.01	2.8	-0.5
2B-3	62	2.8	0.07	0.02	0.57	2.00	0.04	2.7	-4.0
2B-4	62	2.8	0.06	0.02	0.58	1.90	0.02	2.6	-7.9
2B-5	62	2.8	0.06	0.02	0.59	1.97	0.02	2.7	-5.2

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
2B-1	2.7	0.4	18.7	77.6	0.7
2B-2	2.5	0.6	18.9	77.6	0.5
2B-3	2.5	0.7	21.0	74.4	1.3
2B-4	2.5	0.8	22.5	73.6	0.7
2B-5	2.2	0.6	22.4	74.1	0.7

Calcium Mass Balances

	(mg) Mass Ca Added	Mass Ca in Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
2B-1	40	23.69	0.851	14.56	0.375	0.002	39.480	-1.3
2B-2	40	23.98	0.784	15.51	0.463	0.003	40.745	1.9
2B-3	40	23.66	0.772	14.69	0.204	0.003	39.331	-1.7
2B-4	40	23.82	0.794	14.26	0.219	0.003	39.098	-2.3
2B-5	40	24.10	0.847	14.89	0.393	0.004	40.235	0.6

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
2B-1	60.0	2.2	36.9	1.0	0.0
2B-2	58.9	1.9	38.1	1.1	0.0
2B-3	60.2	2.0	37.3	0.5	0.0
2B-4	60.9	2.0	36.5	0.6	0.0
2B-5	59.9	2.1	37.0	1.0	0.0

Experimental Conditions: $CaCO_3$ Treatment, TOTFe = 28mg, Nickel Variable

Nickel Mass Balances

	(mg/L) Concentration Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni Fraction (i)	Mass Ni Fraction (ii)	Mass Ni Fraction (iii)	Mass Ni Fraction (iv)	Total Mass Ni Measured	%error
1B-1	5.8	0.26	0.04	0.04	0.10	0.09	0.00	0.276	6.2
1B-2	11.6	0.52	0.12	0.08	0.19	0.14	0.00	0.539	3.7
1B-3	17.3	0.78	0.21	0.13	0.24	0.21	0.00	0.795	2.0
1B-4	23.1	1.04	0.34	0.17	0.32	0.24	0.00	1.073	3.1
1B-5	28.9	1.3	0.38	0.19	0.44	0.32	0.01	1.320	1.6

Percent Measured Ni in each fraction

	solution	i	ii	iii	iv
1B-1	15.6	13.8	35.9	33.6	1.0
1B-2	22.2	14.5	36.1	26.6	0.6
1B-3	26.0	16.5	30.6	26.4	0.6
1B-4	32.0	15.4	30.1	22.0	0.5
1B-5	28.5	14.1	33.1	23.9	0.4

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
1B-1	622	28	0.05	0.06	1.16	20.99	5.44	27.7	-1.1
1B-2	622	28	0.10	0.09	1.44	22.74	2.46	26.8	-4.2
1B-3	622	28	0.31	0.04	1.22	20.73	4.67	27.0	-3.7
1B-4	622	28	0.22	0.03	1.43	22.13	4.22	28.0	0.1
1B-5	622	28	0.13	0.03	1.37	20.58	5.58	27.7	-1.1

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
1B-1	0.2	0.2	4.2	75.8	19.6
1B-2	0.4	0.3	5.4	84.8	9.2
1B-3	1.1	0.1	4.5	76.8	17.3
1B-4	0.8	0.1	5.1	78.9	15.1
1B-5	0.5	0.1	5.0	74.3	20.2

Calcium Mass Balances

	(mg) Mass Ca Added	Mass Ca in Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
1B-1	40	36.3	4.2	0.4	0.1	0.0	40.866	2.2
1B-2	40	37.1	4.4	0.5	0.1	0.0	42.053	5.1
1B-3	40	35.7	4.4	0.4	0.1	0.0	40.542	1.4
1B-4	40	35.8	4.4	0.3	0.0	0.0	40.553	1.4
1B-5	40	36.0	4.5	0.4	0.1	0.0	40.989	2.5

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
1B-1	88.7	10.2	0.9	0.2	0.0
1B-2	88.3	10.5	1.1	0.1	0.0
1B-3	88.0	10.9	1.0	0.2	0.0
1B-4	88.2	10.8	0.9	0.1	0.0
1B-5	87.7	11.0	1.1	0.2	0.0

Experimental Conditions: NaOH Treatment, No Added Iron, Nickel Variable

Nickel Mass Balances

NOC Blank	Initial Conc (mg/L) Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni Fraction (i)	Mass Ni Fraction (ii)	Mass Ni Fraction (iii)	Mass Ni Fraction (iv)	Total Mass Ni Measured	%error
B-1	5.8	0.26	0.241	0.002	0.001	0.001	0.000	0.245	-5.9
B-2	11.6	0.52	0.504	0.002	0.002	0.001	0.000	0.509	-2.1
B-3	17.3	0.78	0.746	0.004	0.001	0.000	0.000	0.751	-3.8
B-4	23.1	1.04	0.974	0.002	0.001	0.002	0.000	0.979	-5.9
B-5	28.9	1.3	1.236	0.002	0.001	0.001	0.000	1.240	-4.6

Percent Measured Ni in each fraction

	solution	i	ii	iii	iv
B-1	98.6	0.6	0.4	0.4	0.0
B-2	98.9	0.5	0.4	0.2	0.0
B-3	99.4	0.5	0.1	0.0	0.0
B-4	99.5	0.2	0.1	0.2	0.0
B-5	99.6	0.2	0.1	0.1	0.0

Experimental Conditions: NaOH Treatment, TOTFe = 2.8 mg, Nickel Variable

Nickel Mass Balances

NOC	Initial Conc (mg/L) Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni Fraction (i)	Mass Ni Fraction (ii)	Mass Ni Fraction (iii)	Mass Ni Fraction (iv)	Total Mass Ni Measured	%error
2B-1	5.8	0.26	0.17	0.04	0.01	0.04	0.00	0.25	-4.4
2B-2	11.6	0.52	0.37	0.06	0.01	0.06	0.00	0.50	-3.7
2B-3	17.3	0.78	0.54	0.09	0.02	0.09	0.00	0.74	-4.5
2B-4	23.1	1.04	0.90	0.05	0.01	0.04	0.00	1.00	-4.0
2B-5	28.9	1.3	1.06	0.05	0.01	0.05	0.00	1.18	-9.1

Percent Measured
Ni in each fraction

NOC	solution	i	ii	iii	iv
2B-1	67.9	14.5	3.0	14.3	0.3
2B-2	72.9	12.4	2.7	11.9	0.1
2B-3	73.0	11.5	3.2	12.0	0.3
2B-4	89.9	5.5	0.9	3.7	0.0
2B-5	90.0	4.3	1.1	4.5	0.1

Iron Mass Balances

NOC	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
2B-1	62	2.8	0.04	0.01	0.02	2.54	0.03	2.64	-5.8
2B-2	62	2.8	0.05	0.00	0.03	2.58	0.02	2.67	-4.5
2B-3	62	2.8	0.03	0.01	0.02	2.48	0.04	2.58	-7.8
2B-4	62	2.8	0.04	0.01	0.02	2.54	0.02	2.62	-6.4
2B-5	62	2.8	0.05	0.00	0.02	2.50	0.02	2.59	-7.4

Percent Measured
Fe in each fraction

NOC	solution	i	ii	iii	iv
2B-1	1.3	0.4	0.8	96.2	1.2
2B-2	1.7	0.0	1.0	96.6	0.7
2B-3	1.1	0.4	0.7	96.2	1.6
2B-4	1.5	0.3	0.6	96.8	0.8
2B-5	1.8	0.2	0.7	96.4	0.8

Experimental Conditions: NaOH Treamtent, TOTFe = 28mg, Nickel Variable

Nickel Mass Balances

	(mg/L) Concentration Ni in soln	mg Mass Ni Added	Mass Ni in Solution	Mass Ni in Fraction (i)	Mass Ni in Fraction (ii)	Mass Ni in Fraction (iii)	Mass Ni in Fraction (iv)	Total Mass Ni Measured	%error
1A-1	5.8	0.26	0.022	0.0908	0.042	0.067		0.223	-14.4
1A-2	11.6	0.52	0.075	0.1728	0.101	0.117		0.466	-10.4
1A-3	17.3	0.78	0.168	0.2365	0.133	0.157		0.694	-11.0
1A-4	23.1	1.04	0.208	0.2900	0.208	0.214		0.920	-11.5
1A-5	28.9	1.3	0.387	0.331	0.225	0.227		1.170	-10.0

Percent Measured Ni in each fraction

	solution	i	ii	iii	iv
1A-1	10.0	40.8	19.0	30.3	0.0
1A-2	16.1	37.1	21.7	25.1	0.0
1A-3	24.2	34.1	19.2	22.5	0.0
1A-4	22.6	31.5	22.6	23.3	0.0
1A-5	33.1	28.2	19.2	19.4	0.0

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
1A-1	620	28	0.120	0.0366	1.550	21.011		22.7	-18.9
1A-2	620	28	0.156	0.0292	1.970	22.012		24.2	-13.7
1A-3	620	28	0.081	0.0193	2.064	22.185		24.3	-13.0
1A-4	620	28	0.101	0.0336	2.083	22.385		24.6	-12.1
1A-5	620	28	0.068	0.028	2.351	22.241		24.7	-11.8

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
1A-1	0.5	0.2	6.8	92.5	0.0
1A-2	0.6	0.1	8.2	91.1	0.0
1A-3	0.3	0.1	8.5	91.1	0.0
1A-4	0.4	0.1	8.5	91.0	0.0
1A-5	0.3	0.1	9.5	90.1	0.0

Experimental Conditions: $CaCO_3$ Treatment, No Iron Added, Zinc Variable

Zinc Mass Balance

	Initial Conc (mg/L) Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
A-1	5.3	0.24	0.26	0.01	0.00	0.00	0.0	0.267	11.1
A-2	10.7	0.48	0.52	0.01	0.00	0.00	0.0	0.527	9.8
A-3	16.0	0.72	0.77	0.02	0.01	0.00	0.0	0.792	10.0
A-4	21.3	0.96	1.01	0.02	0.01	0.00	0.0	1.036	7.9
A-5	26.7	1.2	1.23	0.02	0.01	0.00	0.0	1.262	5.2

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
A-1	96.7	2.9	0.3	0.1	0.0
A-2	98.4	1.3	0.3	0.1	0.0
A-3	97.3	1.9	0.7	0.1	0.0
A-4	97.3	1.7	0.9	0.1	0.0
A-5	97.1	1.7	1.1	0.1	0.0

Calcium Mass Balances

	mg Mass Ca Added	Mass Ca Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
2A-1	40	21.6	0.43	14.8	0.12	0.00	36.9	-7.6
2A-2	40	22.0	0.44	13.4	0.23	0.00	36.1	-9.8
2A-3	40	21.3	0.43	14.6	0.22	0.00	36.5	-8.7
2A-4	40	21.5	0.39	14.4	0.19	0.00	36.5	-8.8
2A-5	40	20.6	0.40	15.7	0.16	0.00	36.9	-7.7

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
A-1	58.6	1.2	39.9	0.3	0.0
A-2	61.0	1.2	37.1	0.6	0.0
A-3	58.4	1.2	39.9	0.6	0.0
A-4	58.9	1.1	39.5	0.5	0.0
A-5	55.9	1.1	42.6	0.4	0.0

Experimental Conditions: CaCO3 Treatment, TOTFe = 2.4mg, Zinc Variable

Zinc Mass Balances

	Initial Conc (mg/L) Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
2A-1	5.3	0.24	0.084	0.01	0.12	0.01	0.00	0.224	-6.7
2A-2	10.7	0.48	0.221	0.02	0.22	0.01	0.00	0.464	-3.2
2A-3	16.0	0.72	0.384	0.03	0.28	0.01	0.00	0.701	-2.7
2A-4	21.3	0.96	0.527	0.04	0.40	0.01	0.00	0.977	1.8
2A-5	26.7	1.2	0.701	0.05	0.47	0.01	0.00	1.236	3.0

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
A-1	37.3	3.6	55.4	3.7	0.0
A-2	47.6	3.8	47.4	1.1	0.0
A-3	54.8	4.0	40.1	1.0	0.0
A-4	53.9	3.9	41.2	0.9	0.0
A-5	56.7	4.3	38.3	0.7	0.0

Iron Mass Balances

	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
2A-1	2.424	0.073	0.031	1.32	0.752	0.003	2.180	-10.1
2A-2	2.424	0.085	0.017	1.84	0.274	0.002	2.214	-8.7
2A-3	2.424	0.049	0.028	1.63	0.395	0.002	2.108	-13.0
2A-4	2.424	0.029	0.022	2.22	0.271	0.002	2.546	5.1
2A-5	2.424	0.025	0.022	2.13	0.280	0.002	2.462	1.6

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
A-1	3.4	1.4	60.5	34.5	0.13
A-2	3.8	0.8	82.9	12.4	0.08
A-3	2.3	1.3	77.5	18.7	0.10
A-4	1.1	0.9	87.2	10.6	0.09
A-5	1.0	0.9	86.6	11.4	0.08

Calcium Mass Balances

	mg Mass Ca Added	Mass Ca Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
2A-1	40	22.9	0.70	11.6	0.07	0.00	35.3	-11.8
2A-2	40	23.0	0.66	12.3	0.09	0.00	36.0	-9.9
2A-3	40	23.6	0.56	11.4	0.08	0.00	35.6	-11.0
2A-4	40	22.8	0.66	14.4	0.15	0.00	38.0	-5.0
2A-5	40	23.2	0.61	14.6	0.08	0.00	38.4	-3.9

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
A-1	65.0	2.0	32.8	0.2	0.0
A-2	63.8	1.8	34.1	0.3	0.0
A-3	66.2	1.6	32.0	0.2	0.0
A-4	60.1	1.7	37.8	0.4	0.0
A-5	60.3	1.6	37.9	0.2	0.0

Experimental Conditions: CaCO3 Treatment, TOTFe = 24.2 mg, Zinc Variable

Zinc Mass Balances

	(mg/L) Concentration Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
1A-1	5.3	0.24	0.029	0.02	0.15	0.050	ND	0.249	3.6
1A-2	10.7	0.48	0.052	0.02	0.28	0.102	ND	0.454	-5.4
1A-3	16.0	0.72	0.132	0.05	0.51	0.119	ND	0.810	12.4
1A-4	21.3	0.96	0.160	0.07	0.61	0.181	ND	1.022	6.4
1A-5	26.7	1.2	0.288	0.11	0.70	0.175	ND	1.275	6.3

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
1A-1	11.9	6.3	61.9	19.9	0.0
1A-2	11.4	5.4	60.8	22.4	0.0
1A-3	16.4	6.5	62.5	14.7	0.0
1A-4	15.7	6.6	60.0	17.7	0.0
1A-5	22.6	8.6	55.1	13.7	0.0

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
1A-1	538.7	24.24	0.04	0.02	3.02	20.6	ND	23.681	-2.3
1A-2	538.7	24.24	0.04	0.03	3.56	18.5	ND	22.129	-8.7
1A-3	538.7	24.24	0.02	0.03	4.49	17.5	ND	22.055	-9.0
1A-4	538.7	24.24	0.09	0.03	4.25	17.9	ND	22.270	-8.1
1A-5	538.7	24.24	0.04	0.06	3.78	19.6	ND	23.490	-3.1

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
1A-1	0.2	0.1	12.7	87.0	ND
1A-2	0.2	0.1	16.1	83.6	ND
1A-3	0.1	0.2	20.3	79.4	ND
1A-4	0.4	0.1	19.1	80.4	ND
1A-5	0.2	0.3	16.1	83.4	ND

Calcium Mass Balances

	mg Mass Ca Added	Mass Ca Solution	Mass Ca Fraction (i)	Mass Ca Fraction (ii)	Mass Ca Fraction (iii)	Mass Ca Fraction (iv)	Total Mass Ca Measured	%error
2A-1	40	33.6	3.4	0.28	0.08	ND	37.3	-6.7
2A-2	40	33.9	3.9	0.42	0.09	ND	38.3	-4.3
2A-3	40	34.2	3.6	0.33	0.06	ND	38.2	-4.4
2A-4	40	33.8	4.0	0.45	0.12	ND	38.4	-4.0
2A-5	40	33.4	3.8	0.29	0.05	ND	37.6	-6.0

Percent Measured Ca in each fraction

	solution	i	ii	iii	iv
A-1	89.9	9.1	0.8	0.2	ND
A-2	88.4	10.2	1.1	0.2	ND
A-3	89.6	9.4	0.9	0.2	ND
A-4	88.1	10.4	1.2	0.3	ND
A-5	88.9	10.2	0.8	0.1	ND

Experimental Conditions: NaOH Treatment, No Added Iron, Zinc Variable

Zinc Mass Balances

	Initial Conc (mg/L) Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
A-1	5.3	0.24	0.24	ND	0.00	0.00	0.00	0.245	2.0
A-2	10.7	0.48	0.50	ND	0.00	0.00	0.00	0.499	4.0
A-3	16.0	0.72	0.72	ND	0.00	0.00	0.00	0.728	1.1
A-4	21.3	0.96	0.97	ND	0.00	0.00	0.00	0.980	2.1
A-5	26.7	1.2	0.67	ND	0.34	0.01	0.00	1.018	-15.2

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
A-1	99.2	ND	0.2	0.6	0.1
A-2	99.3	ND	0.2	0.4	0.2
A-3	99.3	ND	0.4	0.2	0.0
A-4	99.3	ND	0.5	0.2	0.0
A-5	65.4	ND	33.6	1.0	0.1

Experimental Conditions: NaOH Treatment, TOTFe = 2.4 mg, Zinc Varaible

Zinc Mass Balances

	Initial Conc (mg/L) Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
A-1	5.3	0.24	0.06	0.06	0.07	0.04	0.0	0.22	-7.7
A-2	10.7	0.48	0.18	0.09	0.13	0.04	0.0	0.45	-5.9
A-3	16.0	0.72	0.31	0.11	0.21	0.05	0.0	0.68	-5.7
A-4	21.3	0.96	0.50	0.14	0.23	0.04	0.0	0.92	-4.0
A-5	26.7	1.2	0.77	0.14	0.22	0.04	0.0	1.16	-3.3

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
A-1	26.9	25.0	30.6	17.0	0.5
A-2	39.8	20.9	29.9	9.3	0.2
A-3	46.2	16.0	30.9	6.8	0.1
A-4	54.6	15.3	25.4	4.6	0.1
A-5	66.0	11.7	19.0	3.2	0.1

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
2A-1	62.2	2.80	0.097	0.019	0.20	2.10	0.03	2.45	-12.4
2A-2	62.2	2.80	0.088	0.031	0.42	1.90	0.02	2.46	-12.2
2A-3	62.2	2.80	0.120	0.061	0.41	1.76	0.01	2.36	-15.6
2A-4	62.2	2.80	0.083	0.028	0.59	1.64	0.01	2.35	-16.0
2A-5	62.2	2.80	0.148	0.032	0.81	1.38	0.02	2.39	-14.6

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
A-1	4.0	0.8	8.2	85.7	1.3
A-2	3.6	1.2	17.1	77.4	0.7
A-3	5.1	2.6	17.4	74.4	0.5
A-4	3.5	1.2	25.0	69.7	0.6
A-5	6.2	1.3	33.9	57.8	0.7

Experimental Conditions: NaOH Treatment, TOTFe = 24 mg, Zinc Variable

Zinc Mass Balances

	Initial Conc (mg/L) Zn in soln	mg Mass Zn Added	Mass Zn in Solution	Mass Zn Fraction (i)	Mass Zn Fraction (ii)	Mass Zn Fraction (iii)	Mass Zn Fraction (iv)	Total Mass Zn Measured	%error
A-1	5.3	0.24	0.01	0.03	0.09	0.09	0.00	0.220	-8.3
A-2	10.7	0.48	0.01	0.08	0.19	0.16	0.00	0.436	-9.2
A-3	16.0	0.72	0.01	0.10	0.30	0.23	0.00	0.650	-9.7
A-4	21.3	0.96	0.08	0.20	0.36	0.24	0.00	0.883	-8.0

Percent Measured Zn in each fraction

	solution	i	ii	iii	iv
A-1	2.4	13.2	40.5	43.0	0.8
A-2	2.9	18.5	42.5	35.6	0.5
A-3	1.9	15.4	46.8	35.4	0.4
A-4	8.5	23.2	41.1	26.9	0.3

Iron Mass Balances

	(mg/L) Concentration Fe in soln	mg Mass Fe Added	Mass Fe in Solution	Mass Fe Fraction (i)	Mass Fe Fraction (ii)	Mass Fe Fraction (iii)	Mass Fe Fraction (iv)	Total Mass Fe Measured	%error
2A-1	620	27.9	0.29	0.07	0.67	23.29	0.37	24.7	-11.5
2A-2	620	27.9	0.13	0.05	0.66	22.23	0.27	23.3	-16.3
2A-3	620	27.9	0.06	0.04	0.82	23.35	0.27	24.5	-12.1
2A-4	620	27.9	0.15	0.04	0.92	23.13	0.27	24.5	-12.1

Percent Measured Fe in each fraction

	solution	i	ii	iii	iv
A-1	1.2	0.3	2.7	94.4	1.5
A-2	0.5	0.2	2.8	95.2	1.2
A-3	0.2	0.2	3.4	95.2	1.1
A-4	0.6	0.2	3.8	94.4	1.1

APPENDIX B

This appendix contains the data from the replicate experiments. The experimental treatment in all cases was $CaCO_3$. Values for the average and standard deviation between the replicates are given. All values are given in terms of mass present in each fraction in milligrams.

All values represent averages for the mass of the metal in the specified fraction. All units in mg.

Zinc Replicates

TOTFe = 2.4mg

Mass Zn	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.24	0.07	0.02	0.010	0.001	0.130	0.005	0.014	0.005
0.72	0.36	0.04	0.029	0.003	0.290	0.012	0.017	0.009
1.2	0.71	0.01	0.048	0.005	0.426	0.042	0.018	0.008

TOTFe = 24mg

Mass Zn	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.24	0.024	0.009	0.040	0.02	0.141	0.012	0.059	0.008
0.72	0.116	0.02	0.144	0.08	0.434	0.064	0.132	0.013
1.2	0.267	0.02	0.280	0.15	0.649	0.051	0.178	0.010

Iron Replicates for Variable Zinc Experiments

Mass Zn	Mass Fe	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Added	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.24	2.4	0.043	0.03	0.033	0.006	1.27	0.05	0.9	0.1
0.72	2.4	0.033	0.02	0.027	0.004	1.51	0.1	0.6	0.2
1.2	2.4	0.035	0.01	0.026	0.004	1.81	0.3	0.5	0.2

Mass Zn	Mass Fe	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.24	24.3	0.098	0.05	0.06	0.03	2.2	0.7	22.0	1.2
0.72	24.3	0.077	0.05	0.05	0.02	2.8	1.5	21.3	3.3
1.2	24.3	0.082	0.03	0.05	0.01	2.6	1.0	21.5	1.6

Nickel Replicates

TOTFe = 2.8mg

Mass Ni	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.26	0.165	0.004	0.023	0.01	0.038	0.027	0.021	0.01
0.78	0.545	0.03	0.047	0.04	0.087	0.056	0.044	0.04
1.3	1.023	0.04	0.025	0.02	0.133	0.104	0.031	0.02

TOTFe = 28mg

Mass Ni	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.26	0.044	0.02	0.056	0.03	0.065	0.020	0.081	0.01
0.78	0.205	0.008	0.146	0.08	0.187	0.047	0.182	0.02
1.3	0.317	0.1	0.223	0.09	0.282	0.050	0.261	0.03

Iron Replicates for Variable Nickel Experiments

Mass Ni	Mass Fe	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.26	2.8	0.058	0.029	0.018	0.01	0.038	0.430	0.021	0.60
0.78	2.8	0.043	0.02	0.018	0.01	0.087	0.489	0.044	0.53
1.3	2.8	0.048	0.01	0.014	0.00	0.133	0.606	0.031	0.69

Mass Ni	Mass Fe	Solution		Easily Exchangeable		Carbonate Associated		Iron Associated	
Added (mg)	Added (mg)	Average	STDEV	Average	STDEV	Average	STDEV	Average	STDEV
0.26	28	0.062	0.02	0.055	0.00	1.513	0.307	23.390	2.09
0.78	28	0.131	0.003	0.051	0.01	1.702	0.415	22.033	1.13
1.3	28	0.107	0.0	0.046	0.01	1.673	0.280	22.669	1.81

APPENDIX C

This appendix contains raw data from the bench scale passive system. This includes the metal concentrations and pH values from each sampling event, as well as tracer test data and elution curves.

For the metal concentrations, each sample was given a name beginning with the date the sample was taken, and followed by a number. The code for what each number represents is as follows:

01- Grab sample of soluble metals from the 0.75" limestone reactor

02- Grab sample of total metals from the 0.75" limestone reactor

03- Grab sample of soluble metals from the 1.5" limestone reactor

04- Grab sample of total metals from the 1.5" limestone reactor

05- Composite sample of combined effluent from both reactors, soluble metals

06- Composite sample of combined effluent from both reactors, total metals

07- Grab sample of soluble metals in the influent water

08- Grab sample of total metals in the influent water

The analyte and wavelength analyzed on the ICP-OES are in the far left column. Scandium and argon are used as internal standards, and do not represent an actual concentration. All units for metal concentrations are in mg/L. BDL means below detection limit.

Also included are metal concentrations from the pulsed limestone treatment system. All concentrations are in mg/L. The sample name consists of a date and a code related to the sample locations given below:

IS = Influent Sump

ES = Effluent Sump

ES AS = Effluent Sump Post Air Stripping

	2-17-05-01	2-17-05-02	2-17-05-03	2-17-05-04	2-17-05-05	2-17-05-06	2-17-05-07	2-17-05-08
Sc 361.383	1.03		0.990		1.06		1.08	
Ag 328.068	0.0150	0.00843	0.00887	BDL	0.0102	0.00798	BDL	BDL
Al 308.215	0.418	2.73	2.58	5.30	5.90	5.30	18.60	16.70
As 193.696	BDL	BDL.	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.101	0.310	BDL	BDL	BDL	0.158	BDL	BDL
Ba 455.403	0.0242	0.0171	0.0159	0.0201	0.0263	0.0161	0.0107	0.00790
Be 313.107	0.00246	0.00199	0.00248	0.00342	0.00383	0.00357	0.0103	0.00935
Ca 317.933	500	442	492	435	455	414	297	274
Cd 214.440	0.0722	0.0721	0.0827	0.0766	0.0854	0.0790	0.122	0.115
Co 228.616	0.111	0.0988	0.100	0.0903	0.108	0.0967	0.122	0.118
Cr 205.560	0.00370	BDL	BDL	0.00869	0.00352	BDL	0.009582	0.0115
Cu 324.752	0.386	0.640	1.49	1.68	1.83	1.68	4.76	4.26
Fe 238.204	0.00560	5.85	0.230	46.7	0.0846	0.498	57.3	100
K 766.490	3.67	3.31	3.96	3.51	4.08	3.88	3.44	3.22
Li 670.784	0.0514	0.0586	0.0418	0.0503	0.0400	0.0482	0.0371	BDL
Mg 279.553		95.4		99.9		100		94.5
Mn 257.610	75.8	67.7	72.8	65.0	76.4	70.2	80.3	75.0
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	60.9	52.9	60.4	52.3	60.6	54.3	57.4	52.0
Ni 231.604	0.161	0.144	0.185	0.167	0.178	0.164	0.211	0.195
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	688	618	712	637	688	630	664	622
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026		0.0938	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	12.6	11.8	16.2	14.8	15.6	14.2	22.1	20.1
Sn 189.927	0.0945	0.092	0.0924	0.0839	0.0847	0.0820	0.0854	0.0891
Sr 421.552	1.47	1.30	1.46	1.28	144	1.31	1.35	1.24
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	28.4	24.9	32.5	28.3	32.0	28.7	40.3	36.5

	2-24-05-01	2-24-05-02	2-24-05-03	2-24-05-04	2-24-05-05	2-24-05-06	2-24-05-07	2-24-05-08
Sc 361.383	1.09	1.02	0.981	0.999	1.02	0.997	1.03	
Ag 328.068	0.0104	0.00880	0.00802	0.00915	0.00990	0.00913	BDL	BDL
Al 308.215	0.430	2.42	0.709	3.48	4.76	4.99	18.8	16.6
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	BDL	BDL	BDL	BDL	0.105	0.186	BDL	BDL
Ba 455.403	0.0207	0.0154	0.0135	0.0128	0.0143	0.120	0.00724	0.00557
Be 313.107			0.00139	0.00222	0.00384	0.00382	0.0103	0.00921
Ca 317.933	481	445	488	439	461	420	298	267
Cd 214.440	0.0695	0.0661	0.0773	0.0700	0.0876	0.0815	0.123	0.114
Co 228.616	0.108	0.102	0.0935	0.0840	0.109	0.101	0.123	0.116
Cr 205.560	0.00316	BDL	BDL	BDL	BDL	BDL	0.00969	0.0146
Cu 324.752	0.445	0.702	1.13	1.27	1.78	1.65	4.73	4.20
Fe 238.204	0.0113	3.41	0.075	3.70	0.0183	3.04	53.2	118
K 766.490	3.46	3.23	3.77	3.32	3.97	3.55	3.50	3.07
Li 670.784	0.0346	BDL	0.0344	BDL	0.0446	0.0449	0.0372	BDL
Mg 279.553		98.4		99.2		101		91.8
Mn 257.610	73.8	68.9	70.5	63.9	76.9	70.9	80.9	73.2
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	57.8	52.8	57.5	51.1	60.0	53.8	57.0	50.2
Ni 231.604	0.162	0.152	0.178	0.161	0.180	0.163	0.213	0.192
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	695	653	714	645	730	664	706	635
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	12.5	12.1	14.5	13.4	15.6	14.3	22.4	19.8
Sn 189.927	0.0815	0.105	0.0978	0.0845	0.0897	0.0910	0.0759	0.0735
Sr 421.552	1.39	1.30	1.38	1.25	1.43	1.30	1.34	1.19
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.00668
Zn 213.857	27.8	26.0	30.6	27.3	32.8	29.4	40.3	35.8

	3-31-05-01	3-31-05-02	3-31-05-03	3-31-05-04	3-31-05-05	3-31-05-06	3-31-05-07	3-31-05-08
Sc 361.383	1.01	0.97	1.01	1.01	1.03	1.05	1.06	1.07
Ag 328.068	0.00870	0.00764	0.00828	BDL	0.00839	0.00742	0.00475	BDL
Al 308.215	0.247	5.55	0.140	6.59	0.113	1.48	10.4	9.16
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.0556	BDL	0.0561	0.250	0.0909	0.160	0.0623	BDL
Ba 455.403	0.0113	0.00787	0.0119	0.0132	0.0114	0.0142	0.00421	0.00814
Be 313.107	0.000412	0.00250	0.000330	0.00329	0.000340	0.000903	0.00589	0.00509
Ca 317.933	432	392	450	402	443	393	330	291
Cd 214.440	0.0447	0.0430	0.0407	0.0383	0.0506	0.0450	0.0682	0.0645
Co 228.616	0.0621	0.0568	0.0551	0.0501	0.0686	0.0559	0.0708	0.0701
Cr 205.560	BDL	BDL	BDL	BDL	BDL	BDL	0.00401	0.00634
Cu 324.752	0.192	1.22	0.243	0.983	0.179	0.469	2.27	2.02
Fe 238.204	0.00584	4.28	0.0165	6.47	BDL	1.20	11.2	142
K 766.490	4.13	3.79	4.21	3.87	4.22	3.66	4.27	3.67
Li 670.784	0.0354	0.0348	0.0339	0.0688	0.0456	0.0510	0.0425	0.0440
Mg 279.553		70.7		72.1		73.7		63.3
Mn 257.610	47.4	43.8	44.7	40.3	50.4	44.9	47.7	42.6
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	184	164	172	149	168	145	192	166
Ni 231.604	0.0752	0.0724	0.101	0.0940	0.105	0.0914	0.120	0.106
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	670	615	686	623	715	619	665	608
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	0.0404	0.0809	BDL	BDL	0.0474	BDL	BDL	BDL
Si 251.611	8.06	9.10	8.56	8.91	8.88	8.21	13.2	11.7
Sn 189.927	0.0833	0.0701	0.0784	0.0778	0.0827	0.0692	0.0786	0.0519
Sr 421.552	1.30	1.19	1.29	1.14	1.35	1.18	1.29	1.14
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.00984
Zn 213.857	13.0	13.6	15.8	14.8	17.1	15.0	23.4	20.3

	4-7-05-01	4-7-05-02	4-7-05-03	4-7-05-04	4-7-05-05	4-7-05-06	4-7-05-07	4-7-05-08
Sc 361.383	1.11	1.05	1.11	1.09	1.10	1.11	1.16	1.15
Ag 328.068	0.00800	BDL	0.00780	BDL	0.00814	0.00800	0.00527	BDL
Al 308.215	0.138	14.1	0.206	13.5	0.0826	1.22	10.5	9.38
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.0720	0.109	0.0722	BDL	0.0728	0.132	0.124	0.123
Ba 455.403	0.0171	0.0163	0.0162	0.0195	0.0143	0.0214	0.0117	0.0160
Be 313.107	0.000311	0.00624	0.000544	0.00581	BDL	0.000751	0.00841	0.00528
Ca 317.933	419	386	426	387	426	399	316	286
Cd 214.440	0.0447	0.0465	0.0405	0.0400	0.0471	0.0439	0.0731	0.0668
Co 228.616	0.0612	0.0588	0.0522	0.0493	0.0634	0.0603	0.0736	0.0649
Cr 205.560	BDL	0.00650	BDL	0.00618	BDL	BDL	0.00465	BDL
Cu 324.752	0.143	2.41	0.344	2.24	0.0761	0.380	2.80	2.54
Fe 238.204	0.00984	11.3	0.0403	14.9	BDL	0.999	11.5	63.7
K 766.490	4.16	3.85	4.09	3.74	4.01	3.67	4.07	3.70
Li 670.784	0.0365	0.0353	0.0330	0.0316	0.0334	0.0315	0.0524	0.0510
Mg 279.553		68.6		67.6		72.9		63.2
Mn 257.610	45.3	42.5	42.5	39.2	47.1	44.6	47.2	43.2
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	184	165	174	154	167	153	178	159
Ni 231.604	0.0790	0.0796	0.100	0.0943	0.0957	0.0911	0.137	0.121
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	681	621	675	618	697	641	668	607
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	0.0441	BDL
Si 251.611	8.30	11.7	8.56	10.5	8.34	8.32	13.2	11.9
Sn 189.927	0.0789	0.0781	0.0780	0.0654	0.0846	0.0786	0.0741	0.0623
Sr 421.552	1.27	1.17	1.22	1.11	1.27	1.20	1.24	1.13
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	13.5	16.4	15.6	15.7	15.4	14.6	23.1	20.6

	4-15-05-01	4-15-05-02	4-15-05-03	4-15-05-04	4-15-05-05	4-15-05-06	4-15-05-07	4-15-05-08
Sc 361.383	1.01	0.970	1.04	1.05	1.07	1.06	1.12	1.17
Ag 328.068	BDL	0.00669	0.00610	BDL	0.00403	BDL	BDL	BDL
Al 308.215	0.142	12.0	0.303	16.3	0.0787	0.898	11.2	10.1
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.147	0.296	0.0958	0.225	0.0900	0.241	0.0811	0.104
Ba 455.403	0.0148	0.0162	0.0165	0.0258	0.0194	0.0264	0.0127	0.0357
Be 313.107	0.000974	0.00626	0.000974	0.00771	0.000215	0.000790	0.00664	0.00636
Ca 317.933	451	409	436	404	446	402	339	314
Cd 214.440	0.0509	0.0519	0.0484	0.0473	0.0519	0.0490	0.0780	0.0736
Co 228.616	0.0674	0.0599	0.0560	0.0569	0.0629	0.0614	0.0734	0.0751
Cr 205.560	BDL	BDL	BDL	0.00859	BDL	BDL	0.00515	0.0118
Cu 324.752	0.173	2.34	0.510	2.75	0.0855	0.338	2.95	2.72
Fe 238.204	0.00232	8.5	0.0630	12.5	BDL	0.777	11.3	88.9
K 766.490	4.51	4.28	4.53	4.37	4.45	4.15	4.50	4.20
Li 670.784	0.0579	0.0588	0.0450	0.0459	0.0414	0.0402	0.0385	0.0353
Mg 279.077	82.8	72.0	84.0	78.3	88.3	79.5	86.9	82.9
Mn 257.610	48.9	45.2	46.4	43.4	48.8	44.7	51.0	47.6
Mo 202.031	0.0218	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	192	173	184	169	192	171	188	171
Ni 231.604	0.0955	0.0970	0.114	0.111	0.108	0.101	0.142	0.135
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	663	602	655	608	666	606	649	607
Sb 217.582	BDL	0.0185	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	8.94	11.8	9.29	11.7	8.92	8.38	13.5	12.4
Sn 189.927	0.101	0.0953	0.0829	0.0781	0.0954	0.0947	0.0914	0.102
Sr 421.552	1.42	1.30	1.35	1.26	1.41	1.28	1.38	1.27
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	16.0	18.9	17.8	18.2	16.1	15.3	24.7	22.4

	4-22-05-01	4-22-05-02	4-22-05-03	4-22-05-04	4-22-05-05	4-22-05-06	4-22-05-07	4-22-05-08
Sc 361.383	1.19	1.21	1.25	1.17	1.21	1.24	1.29	1.13
Ag 328.068	0.00416	0.0114	0.00440	BDL	0.00555	0.00794	BDL	BDL
Al 308.215	0.142	9.61	0.317	7.88	0.0789	0.283	11.9	10.9
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.107	0.234	0.121	0.271	0.207	0.394	0.156	0.0914
Ba 455.403	0.0293	0.0514	0.0327	0.0437	0.0303	0.0550	0.0248	0.0301
Be 313.107	0.000737	0.00637	0.00106	0.00409	0.000615	0.000872	0.00712	0.00680
Ca 317.933	446	414	447	413	442	413	335	312
Cd 214.440	0.0539	0.0538	0.0501	0.0489	0.0525	0.0493	0.0807	0.0803
Co 228.616	0.0731	0.0692	0.0626	0.0573	0.0675	0.0663	0.0820	0.0869
Cr 205.560	0.00298	BDL	BDL	0.00299	BDL	BDL	0.00341	0.00899
Cu 324.752	0.219	2.29	0.506	1.33	0.0926	0.183	3.00	2.87
Fe 238.204	0.0113	7.51	0.0726	7.10	BDL	0.208	13.5	213
K 766.490	4.53	4.33	4.66	4.39	4.62	4.48	4.40	4.18
Li 670.784	0.0375	0.0328	0.0348	0.0311	0.0516	0.0474	0.0410	0.0406
Mg 279.077	100	93.5	104	88.5	101	95.9	103	83.7
Mn 257.610	50.1	47.1	48.4	45.1	49.5	46.5	53.7	50.8
Mo 202.031	BDL	BDL	BDL	BDL	0.0226	BDL	BDL	BDL
Na 589.592	183	166	181	163	188	172	174	161
Ni 231.604	0.104	0.106	0.120	0.111	0.111	0.106	0.148	0.143
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.139
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	654	604	660	602	662	617	648	619
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	9.32	11.8	9.58	10.0	9.04	8.55	14.3	13.4
Sn 189.927	0.0961	0.0737	0.105	0.0916	0.0874	0.0964	0.0903	0.0818
Sr 421.552	1.41	1.32	1.39	1.28	1.42	1.32	1.37	1.29
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0146
Zn 213.857	17.9	20.4	18.9	17.6	16.5	15.2	26.1	24.0

	4-29-05-01	4-29-05-02	4-29-05-03	4-29-05-04	4-29-05-05	4-29-05-06	4-29-05-07	4-29-05-08
Sc 361.383	1.14	1.16	1.18	1.20	1.21	1.17	1.23	1.04
Ag 328.068	0.00435	BDL	0.00446	BDL	0.00541	BDL	BDL	BDL
Al 308.215	0.201	4.56	0.216	4.10	0.0639	0.169	11.9	11.2
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.198	0.397	0.199	0.394	0.196	0.414	0.181	BDL
Ba 455.403	0.0262	0.0428	0.0305	0.0506	0.0302	0.0437	0.0211	0.0161
Be 313.107	0.000767	0.00354	0.000732	0.00278	BDL	0.000463	0.00714	0.00661
Ca 317.933	455	413	460	419	449	416	334	316
Cd 214.440	0.0536	0.0520	0.0467	0.0453	0.0515	0.0478	0.0790	0.0861
Co 228.616	0.0680	0.0689	0.0580	0.0553	0.0639	0.0640	0.0799	0.0875
Cr 205.560	0.00308	BDL	BDL	BDL	BDL	BDL	0.00391	0.0117
Cu 324.752	0.228	1.29	0.293	0.943	0.0568	0.109	2.99	2.94
Fe 238.204	0.0142	3.67	0.0271	4.61	BDL	0.0801	13.1	299
K 766.490	4.59	4.14	4.46	4.21	4.57	4.39	4.60	4.78
Li 670.784	0.0400	0.0364	0.0373	0.0338	0.0367	0.0349	0.0359	0.0364
Mg 279.077	96.7	89.9	98.5	91.9	101	90.9	98.9	79.2
Mn 257.610	51.0	46.6	48.6	44.9	49.5	46.6	53.8	51.0
Mo 202.031	BDL	BDL	BDL	BDL	BDL	0.0204	BDL	BDL
Na 589.592	181	160	180	160	187	169	174	165
Ni 231.604	0.102	0.0986	0.113	0.110	0.109	0.107	0.145	0.139
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.172
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	663	608	653	604	656	609	651	639
Sb 217.582	BDL	0.0208	BDL	BDL	BDL	0.0152	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	8.78	9.52	9.07	9.25	8.75	8.21	14.3	13.5
Sn 189.927	0.102	0.108	0.0773	0.0861	0.0956	0.115	0.0794	0.0885
Sr 421.552	1.43	1.29	1.40	1.28	1.41	1.31	1.37	1.31
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0261
Zn 213.857	16.4	17.2	17.7	16.8	15.7	14.5	26.1	24.4

	5-9-05-01	5-9-05-02	5-9-05-03	5-9-05-04	5-9-05-05	5-9-05-06	5-9-05-07	5-9-05-08
Sc 361.383	1.01	1.12	1.10	1.07	1.12	1.08	1.15	1.12
Ag 328.068	0.00793	0.00941	0.0120	0.00777	0.00776	0.0111	BDL	BDL
Al 308.215	0.252	12.2	0.317	11.5	0.124	0.596	18.6	17.1
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.160	0.471	0.142	0.434	0.154	0.423	0.137	0.423
Ba 455.403	0.0148	0.0372	0.0230	0.0319	0.0233	0.0300	0.0158	0.0267
Be 313.107	BDL	BDL	BDL	BDL	BDL	BDL	0.00451	BDL
Ca 317.933	470	433	480	439	478	437	323	301
Cd 214.440	0.0615	0.0539	0.0593	0.0518	0.0489	0.0384	0.115	0.102
Co 228.616	0.0845	0.0787	0.0778	0.0748	0.0679	0.0613	0.125	0.109
Cr 205.560	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu 324.752	0.313	2.80	0.423	2.67	0.0475	0.217	4.06	3.76
Fe 238.204	BDL	13.6	0.00920	16.4	BDL	0.497	52.2	84.5
K 766.490	4.20	3.31	4.13	3.61	4.15	3.43	3.71	2.93
Li 670.784	0.0327	0.0207	0.0312	0.0248	0.0313	0.0214	0.0379	0.0291
Mg 279.077	98.2	97.6	108	96.2	98.4	88.1	127	114
Mn 257.610	64.4	60.3	65.0	59.7	54.1	50.4	86.5	81.7
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	0.0230	BDL
Na 589.592	137	123	140	126	185	168	97.4	88.2
Ni 231.604	0.121	0.115	0.143	0.127	0.115	0.101	0.200	0.183
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	639	585	652	596	658	608	657	619
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	0.0849	0.0420	BDL
Si 251.611	11.2	13.5	11.9	13.6	9.32	8.87	21.2	19.6
Sn 189.927	0.0989	0.103	0.102	0.0931	0.0933	0.108	0.0881	0.102
Sr 421.552	1.43	1.31	1.45	1.32	1.43	1.32	1.46	1.35
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	24.0	26.4	26.6	27.0	16.7	16.8	41.9	38.5

	5-17-05-01	5-17-05-02	5-17-05-03	5-17-05-04	5-17-05-05	5-17-05-06	5-17-05-07	5-17-05-08
Sc 361.383	1.10	1.07	1.08	0.97	1.14	1.11	1.14	1.21
Ag 328.068	0.0105	0.0107	0.0114	0.0153	0.0105	0.00935	BDL	BDL
Al 308.215	0.184	1.62	0.198	1.29	0.132	2.05	18.6	16.8
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.198	0.523	0.229	0.580	0.207	0.477	0.135	0.292
Ba 455.403	0.0216	0.0266	0.0206	0.00891	0.0262	0.0345	0.0139	0.0384
Be 313.107	BDL	BDL	BDL	BDL	BDL	BDL	0.00414	BDL
Ca 317.933	488	457	501	463	494	460	324	299
Cd 214.440	0.0692	0.0581	0.0603	0.0502	0.0613	0.0524	0.118	0.101
Co 228.616	0.102	0.0916	0.0854	0.0726	0.0943	0.0836	0.127	0.113
Cr 205.560	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu 324.752	0.159	0.626	0.179	0.387	0.0398	0.542	4.06	3.72
Fe 238.204	BDL	1.11	BDL	3.19	BDL	2.92	46.1	91.8
K 766.490	3.85	3.15	3.98	3.71	3.86	2.84	3.55	2.58
Li 670.784	0.0338	0.0270	0.0314	0.0284	0.0334	0.0216	0.0301	0.0220
Mg 279.077	119	106	120	99.6	122	109	126	122
Mn 257.610	75.5	71.1	74.1	69.2	72.7	68.7	86.8	81.1
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	110	100	112	103	116	105	97.6	87.2
Ni 231.604	0.139	0.127	0.148	0.129	0.144	0.127	0.203	0.182
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	655	607	667	622	670	610	657	614
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	0.0963	0.0723	BDL	BDL	BDL
Si 251.611	11.2	10.9	10.9	10.4	9.95	10.6	21.3	19.4
Sn 189.927	0.105	0.0823	0.0912	0.112	0.110	0.0929	0.0938	0.106
Sr 421.552	1.52	1.40	1.51	1.38	1.50	1.39	1.47	1.34
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	25.6	24.5	25.0	23.5	17.8	21.4	42.1	38.1

	5-23-05-01	5-23-05-02	5-23-05-03	5-23-05-04	5-23-05-05	5-23-05-06	5-23-05-07	5-23-05-08
Sc 361.383	1.15	1.12	1.15	1.11	1.05	0.96	1.01	0.98
Ag 328.068	0.0118	0.0116	0.0133	0.0106	0.00851	0.00782	BDL	BDL
Al 308.215	0.378	17.2	0.301	5.30	0.111	1.66	18.9	17.2
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.205	0.443	0.206	0.465	0.234	0.562	0.180	0.329
Ba 455.403	0.0247	0.0376	0.0268	0.0346	0.0177	0.00679	0.00236	BDL
Be 313.107	BDL	BDL	BDL	BDL	BDL	BDL	0.00424	BDL
Ca 317.933	482	445	499	455	498	460	327	306
Cd 214.440	0.0706	0.0657	0.0627	0.0565	0.0614	0.0539	0.117	0.103
Co 228.616	0.103	0.0928	0.0853	0.0818	0.0919	0.0820	0.125	0.108
Cr 205.560	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Cu 324.752	0.370	2.84	0.255	1.55	0.0384	0.516	4.12	3.78
Fe 238.204	0.0463	20.8	0.0106	12.4	BDL	2.40	41.8	145
K 766.490	3.65	2.98	4.23	3.36	3.84	3.19	3.76	3.14
Li 670.784	0.0299	0.0209	0.0300	0.0223	0.0304	0.0229	0.0307	0.0238
Mg 279.077	128	113	130	115	117	97.5	112	101
Mn 257.610	78.2	72.7	76.0	71.2	75.9	71.1	88.1	82.9
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	103	92.8	104	93.7	113	102	99.7	91.3
Ni 231.604	0.135	0.129	0.145	0.134	0.139	0.125	0.200	0.180
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	640	603	652	614	656	611	659	621
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	0.0843	BDL	BDL	0.0484	BDL
Si 251.611	11.4	15.5	10.7	11.9	9.9	10.6	21.6	19.7
Sn 189.927	0.0906	0.133	0.0976	0.0985	0.0987	0.0916	0.0759	0.0984
Sr 421.552	1.51	1.38	1.52	1.39	1.54	1.41	1.49	1.38
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	26.8	28.0	25.6	26.3	19.7	23.3	42.9	38.9

	7-11-05-01	7-11-05-02	7-11-05-03	7-11-05-04	7-11-05-05	7-11-05-06	7-11-05-07	7-11-05-08
Sc 361.383	1.08	1.01	1.06	1.00	1.08	1.01	1.08	1.01
Ag 328.068	0.00862	0.00668	0.00833	BDL	0.00824	0.00868	BDL	BDL
Al 308.215	1.32	4.32	0.354	21.6	0.0774	0.677	15.0	13.9
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.110	0.145	0.115	0.139	0.118	0.149	0.125	0.0797
Ba 455.403	0.0172	0.0133	0.0174	0.0145	0.0183	0.0150	0.00899	0.00616
Be 313.107	0.00192	0.00288	0.00105	0.00964	0.000550	0.000925	0.00835	0.00781
Ca 317.933	405	374	427	391	473	428	281	261
Cd 214.440	0.0726	0.0684	0.0706	0.0685	0.0789	0.0734	0.0961	0.0935
Co 228.616	0.0852	0.0798	0.0839	0.0793	0.0993	0.0877	0.0935	0.0915
Cr 205.560	BDL	BDL	BDL	0.00776	BDL	BDL	BDL	0.00761
Cu 324.752	1.14	1.44	0.648	3.35	0.231	0.497	3.97	3.68
Fe 238.204	0.121	1.47	0.0121	16.5	BDL	0.603	5.18	99.7
K 766.490	3.86	3.37	3.58	3.30	3.68	3.40	3.48	3.28
Li 670.784	0.0288	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Mg 279.077	103	86.2	100	85.1	117	98.6	89.9	77.0
Mn 257.610	52.1	48.4	52.8	48.3	64.3	58.5	50.7	49.6
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	197	181	199	179	133	119	245	225
Ni 231.604	0.119	0.109	0.141	0.130	0.147	0.135	0.153	0.145
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	625	567	621	572	645	591	597	564
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	10.5	9.97	11.0	14.5	11.1	10.3	15.9	14.7
Sn 189.927	0.0882	0.0741	0.0741	0.0898	0.0877	0.0885	0.0753	0.0753
Sr 421.552	1.27	1.19	1.30	1.19	1.42	1.30	1.22	1.14
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	22.4	20.4	25.5	24.8	27.5	24.9	31.2	28.3

	7-19-05-01	7-19-05-02	7-19-05-03	7-19-05-04	7-19-05-05	7-19-05-06	7-19-05-07	7-19-05-08
Sc 361.383	1.09	1.03	1.10	1.02	1.08	1.01	1.09	1.06
Ag 328.068	0.00952	0.00706	0.00853	0.00895	0.00781	0.00728	0.00685	2.81
Al 308.215	0.200	22.5	0.185	20.4	0.109	0.349	16.6	15.9
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.131	0.142	0.132	0.149	0.137	0.148	0.141	0.0622
Ba 455.403	0.0196	0.0170	0.0201	0.0170	0.0190	0.0154	0.0139	0.0151
Be 313.107	0.000800	0.0116	0.000915	0.00973	BDL	BDL	0.00976	0.00906
Ca 317.933	407	373	411	390	417	391	334	300
Cd 214.440	0.0666	0.0657	0.0686	0.0688	0.0666	0.0639	0.111	0.103
Co 228.616	0.0848	0.0815	0.0818	0.0818	0.0857	0.0769	0.104	0.101
Cr 205.560	BDL	0.00579	BDL	0.00351	BDL	BDL	BDL	0.00715
Cu 324.752	0.439	4.65	0.533	4.39	0.0742	0.179	4.44	4.07
Fe 238.204	0.0137	7.13	BDL	5.33	0.0246	0.161	0.873	80.7
K 766.490	3.94	3.54	3.51	3.39	3.68	3.39	3.68	3.44
Li 670.784	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Mg 279.077	102	86.0	101	86.7	103	88.1	99.8	87.7
Mn 257.610	50.9	46.2	51.9	49.0	52.7	49.4	57.1	56.2
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	196	176	206	190	216	199	151	135
Ni 231.604	0.109	0.114	0.136	0.138	0.125	0.116	0.176	0.161
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	609	555	603	582	634	595	572	540
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Si 251.611	9.86	15.4	10.8	14.4	9.51	8.97	18.7	17.5
Sn 189.927	0.0765	0.0769	0.0796	0.0805	0.0832	0.0782	0.0773	0.0639
Sr 421.552	1.27	1.15	1.27	1.21	1.31	1.23	1.26	1.14
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	20.4	24.6	24.6	27.8	19.5	18.5	36.5	32.4

	8-5-05-01	8-5-05-02	8-5-05-03	8-5-05-04	8-5-05-05	8-5-05-06	8-5-05-07
Sc 361.383	0.976	0.901	0.922	0.864	0.945	0.934	1.005
Ar 420.069	0.998	0.974	0.994	0.981	0.999	0.969	0.983
Ag 328.068	0.012	0.011	0.012	0.014	0.009	0.013	0.010
Al 308.215	0.087	9.245	0.117	28.245	0.073	0.142	0.153
As 193.696	-0.091	-0.107	-0.122	-0.101	-0.124	-0.126	-0.149
B 249.772	0.130	0.125	0.109	0.141	0.115	0.145	0.129
Ba 455.403	0.012	0.008	0.006	0.002	0.009	0.009	0.004
Be 313.107	0.001	0.005	0.000	0.012	0.000	0.000	0.000
Ca 317.933	424.082	380.525	396.409	366.052	416.317	395.302	307.380
Cd 214.440	0.048	0.047	0.072	0.072	0.069	0.065	0.135
Co 228.616	0.069	0.072	0.104	0.097	0.088	0.081	0.146
Cr 205.560	0.002	0.004	0.001	0.006	0.001	0.003	0.002
Cu 324.752	0.056	3.487	0.145	4.016	0.053	0.102	0.379
Fe 238.204	0.001	3.755	-0.001	2.542	-0.004	0.032	-0.003
K 766.490	3.537	3.189	3.810	3.368	3.536	3.248	3.458
Li 670.784	0.092	0.060	0.062	0.050	0.054	0.048	0.046
Mg 279.553		83.019				84.098	
Mn 257.610	49.782	44.664	61.433	56.795	54.545	51.208	71.932
Mo 202.031	0.041	0.022	0.013	0.010	0.013	0.012	0.007
Na 589.592	191.610	168.922	202.259	183.308	195.874	181.343	222.966
Ni 231.604	0.067	0.105	0.159	0.165	0.126	0.118	0.244
P 177.434	-0.780	-0.568	-0.286	-1.273	-0.561	-1.596	-0.804
Pb 220.353	-0.053	-0.040	-0.047	-0.036	-0.048	-0.049	-0.046
S 180.669	677.916	636.543	711.539	657.920	715.492	679.272	725.582
Sb 217.582	-0.015	-0.001	-0.027	-0.008	-0.017	-0.016	-0.027
Se 196.026	-0.006	-0.016	-0.004	0.018	0.017	-0.001	0.009
Si 251.611	6.173	9.359	8.787	14.987	9.788	9.201	12.735
Sn 189.927	0.085	0.077	0.081	0.080	0.084	0.089	0.086
Sr 421.552	1.266	1.129	1.269	1.168	1.295	1.215	1.231
Ti 334.940	-0.013	0.044	-0.013	-0.012	-0.014	-0.012	-0.010
V 292.402	-0.002	-0.002	-0.005	-0.003	-0.003	-0.002	-0.003
Zn 213.857	9.185	21.349	23.514	29.250	18.963	17.676	43.796

	8-26-05-01	8-26-05-02	8-26-05-03	8-26-05-04	8-26-05-05	8-26-05-06	8-26-05-07	8-26-05-08
Sc 361.383	1.11	1.03	1.14	1.07	1.14	1.05	1.16	1.09
Ag 328.068	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Al 308.215	0.845	26.8	0.179	19.7	0.0947	0.133	14.2	12.6
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.142	0.131	0.159	0.173	0.178	0.205	0.156	0.0922
Ba 455.403	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Be 313.107	0.000622	0.0117	BDL	0.00878	BDL	BDL	0.00719	0.00644
Ca 317.933	469	446	487	444	499	455	396	354
Cd 214.440	0.0655	0.0690	0.0595	0.0581	0.0694	0.0635	0.0936	0.0845
Co 228.616	0.0746	0.0806	0.0694	0.0697	0.0793	0.0746	0.0889	0.0807
Cr 205.560	BDL	0.0151	BDL	0.00703	BDL	0.00544	0.00506	0.00719
Cu 324.752	0.611	5.70	0.236	4.27	0.120	0.153	3.40	3.04
Fe 238.204	0.0654	37.4	0.0340	13.8	BDL	0.0568	18.4	89.6
K 766.490	3.13	2.96	3.47	3.23	3.34	2.95	3.24	2.82
Li 670.784	0.0343	0.0324	0.0346	0.0301	0.0357	0.0330	0.0328	0.0293
Mg 279.553		80.8		80.7				74.0
Mn 257.610	49.2	47.6	50.4	45.7	53.5	48.5	53.3	48.0
Mo 202.031	0.0128	0.0131	BDL	BDL	0.0127	BDL	BDL	BDL
Na 589.592	64.6	61.4	76.1	68.1	78.3	70.1	57.8	51.2
Ni 231.604	0.0935	0.111	0.105	0.117	0.105	0.0962	0.143	0.126
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	609	598	646	589	666	601	624	561
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	0.0551	0.0587	BDL	0.0487	BDL	BDL	0.0411	0.0608
Si 251.611	9.03	16.2	8.14	12.9	9.05	8.15	15.9	14.1
Sn 189.927	0.0631	0.0682	0.0931	0.0812	0.0925	0.0800	0.0785	0.0635
Sr 421.552	1.17	1.12	1.18	1.07	1.24	1.12	1.16	1.04
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	19.1	25.2	18.9	26.1	20.2	18.1	30.3	26.4

	9-15-05-01	9-15-05-02	9-15-05-03	9-15-05-04	9-15-05-05	9-15-05-06	9-15-05-07	9-15-05-08
Sc 361.383	1.01	1.00	1.05	1.00	1.06	1.05	1.13	1.06
Ag 328.068	0.0113	0.0107	0.00889	0.0112	0.0101	0.00917	BDL	BDL
Al 308.215	7.01	6.33	3.48	6.54	1.90	1.84	12.8	12.0
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.175	0.182	0.122	0.180	0.127	0.171	0.0664	0.0992
Ba 455.403	0.0125	0.0137	0.0152	0.0135	0.0166	0.0164	0.0147	0.0122
Be 313.107	0.00552	0.00456	0.00276	0.00513	0.00249	0.00249	0.00714	0.00685
Ca 317.933	535	499	528	504	515	474	389	372
Cd 214.440	0.0798	0.0720	0.0733	0.0757	0.0745	0.0690	0.0790	0.0760
Co 228.616	0.0889	0.0839	0.0788	0.0779	0.0829	0.0754	0.0808	0.0769
Cr 205.560	BDL	0.00394431	BDL	BDL	BDL	BDL	0.00624	0.00636
Cu 324.752	2.17	1.99	1.45	2.19	1.12	1.05	2.96	2.79
Fe 238.204	0.0203	0.102	0.0260	0.138	0.0125	0.113	40.2	59.2
K 766.490	3.99	3.66	4.51	3.57	3.73	3.36	3.39	3.35
Li 670.784	0.0724	0.0577	0.0530	0.0519	0.0480	0.0458	0.0401	0.0397
Mg 279.553		86.1		86.1		84.3	74.7	72.0
Mn 257.610	55.8	51.9	54.2	53.1	54.4	50.7	49.9	47.9
Mo 202.031	0.0627	0.0400	0.0199	0.0231	0.0162	0.0172	BDL	0.0150
Na 589.592	67.4	61.8	67.5	64.3	74.3	67.5	55.6	52.5
Ni 231.604	0.127	0.116	0.121	0.123	0.115	0.108	0.125	0.120
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	686	634	671	650	665	620	605	579
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	0.0661	BDL	0.0481	BDL	BDL	BDL	BDL	BDL
Si 251.611	13.2	12.0	11.7	12.4	10.7	9.78	14.5	13.6
Sn 189.927	0.100	0.101	0.101	0.0903	0.107	0.0922	0.0951	0.0778
Sr 421.552	1.50	1.41	1.46	1.43	1.44	1.33	1.27	1.22
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	27.5	24.5	26.2	26.0	24.6	22.2	26.3	24.4

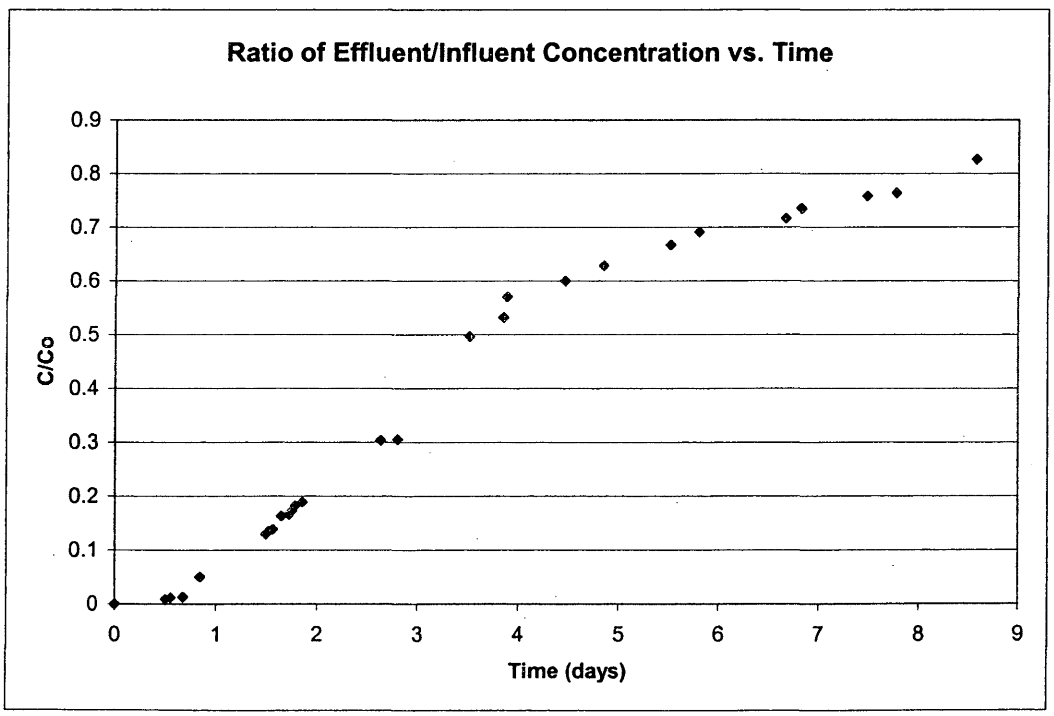
	10-11-05-01	10-11-05-02	10-11-05-03	10-11-05-04	10-11-05-05	10-11-05-06	10-11-05-07	10-11-05-08
Ag 328.068	0.012	BDL	0.012	BDL	0.014	0.010	0.005	BDL
Al 308.215	3.678	7.331	4.747	9.132	5.059	4.489	13.408	11.953
As 193.696	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
B 249.772	0.375	0.345	0.372	0.370	0.379	0.386	0.371	0.378
Ba 455.403	0.013	0.013	0.011	0.009	0.013	0.011	0.007	BDL
Be 313.107	0.001	0.002	0.002	0.003	0.002	0.002	0.006	0.005
Ca 317.933	552.860	436.491	519.328	482.820	533.413	481.712	421.635	376.799
Cd 214.440	0.074	0.060	0.073	0.070	0.074	0.067	0.085	0.077
Co 228.616	0.087	0.071	0.078	0.074	0.084	0.073	0.086	0.074
Cr 205.560	BDL	0.011	BDL	0.018	BDL	BDL	0.006	0.007
Cu 324.752	1.274	1.413	1.712	1.921	1.760	1.564	3.163	2.838
Fe 238.204	0.151	39.595	0.271	54.928	0.018	0.117	32.079	71.500
K 766.490	3.746	2.964	3.632	3.233	3.723	3.283	3.579	3.105
Li 670.784	0.037	0.029	0.035	0.031	0.036	0.032	0.034	0.030
Mg 279.553		72.454						74.063
Mn 257.610	54.193	42.709	51.313	47.886	53.696	48.532	53.526	48.167
Mo 202.031	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Na 589.592	61.307	47.365	57.279	52.674	60.760	54.111	57.317	50.649
Ni 231.604	0.127	0.105	0.129	0.126	0.132	0.120	0.142	0.129
P 177.434	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Pb 220.353	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
S 180.669	707.485	573.943	666.255	622.221	695.376	626.487	673.542	613.116
Sb 217.582	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Se 196.026	0.061	0.064	0.074	0.088	0.086	BDL	0.083	0.080
Si 251.611	11.322	10.037	11.793	11.951	11.949	10.591	15.066	13.415
Sn 189.927	0.075	0.065	0.070	0.067	0.070	0.077	0.078	0.065
Sr 421.552	1.405	1.102	1.305	1.217	1.354	1.229	1.282	1.154
Ti 334.940	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
V 292.402	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zn 213.857	25.460	20.125	25.816	23.702	26.353	23.281	27.876	24.518

pH Readings From Limestone Pretreatment System

Date taken	Days elapsed 'om 12-16-04	Time	5" Limestone	5" Limestone	! Mine Water	
12/16/2004	0	11:05am	6.26	6.88	2.6	
12/20/2004	4	10:15am	6.22	6.82	2.7	
12/21/2004	5	12:30pm	6.25	6.7	2.7	
12/28/2004	12	9:10am	7.019	6.79	2.755	
12/29/2004	13	10:30am	7.04	6.806	2.746	
12/30/2004	14	2:40pm	6.96	6.764	2.7	
1/3/2005	18	2:10pm	ND	6.924	2.73	ND=no data
1/4/2005	19	10:00am	ND	6.77	2.71	ND=no data
1/6/2005	21	10:30am	ND	6.85	2.685	ND=no data
1/17/2005	32	3:55pm	5.652	6.237	2.543	
1/21/2005	36	10:00am	4.104	6.38	2.851	
1/25/2005	40	12:00pm	5.017	6.477	2.794	
1/27/2005	42	6:10pm	6.154	6.071	2.715	
1/31/2005	46	3:10pm	5.495	5.712	2.774	
2/3/2005	49	10:00am	5.493	5.588	2.566	
2/7/2005	53	3:40pm	5.262	6.088	2.621	
2/11/2005	57	10:15am	5.217	6.369	2.681	
2/17/2005	63	5:30pm	5.079	6.602	2.718	
2/24/2005	70	10:00am	5.984	6.255	2.620	
3/1/2005	75	10:15am	4.982	6.561	2.618	
3/4/2005	78	7:30pm	5.272	6.245	2.553	
3/10/2005	84	1:00pm	5.07	6.109	2.832	
3/15/2005	89	11:00am	5.811	6.574	2.954	
3/20/2005	91	3:00pm	5.591	6.763	2.792	
3/31/2005	102	1:30pm	6.366	6.308	2.762	
4/7/2005	109	9:30am	6.176	6.510	2.762	
4/15/2005	117	4:00pm	6.036	6.471	2.767	
4/22/2005	124	1:50pm	6.035	6.622	2.710	
5/4/2005	136	9:15am	6.039	6.37	2.666	
5/9/2005	141	11:45am	6.033	6.276	2.706	
5/17/2005	147	3:00pm	6.688	6.853	2.696	
5/23/2005	153	11:30am	6.273	6.054	2.624	
5/31/2005	161	2:35pm	5.98	6.23	2.66	
6/9/2005	170	4:45pm	5.56	6.17	2.71	
6/17/2005	176	12:00pm	5.93	5.87	2.83	
6/28/2005	186	7:30pm	5.65	5.48	2.71	
7/11/2002	199	4:15pm	6.08	5.53	2.87	
7/19/2005	206	8:00pm	6.31	6.24	3.31	
8/5/2005	223	11:00am	6.27	6.38	5.44	
8/26/2005	244	2:00pm	6.13	5.58	2.68	
9/15/2005	264	3:00pm	5.01	4.64	2.7	<= Failure begins here
10/12/2005	291	2:30pm	4.06	4.47	2.55	
Average pH in each reactor before failure:			5.35	6.15	2.72	

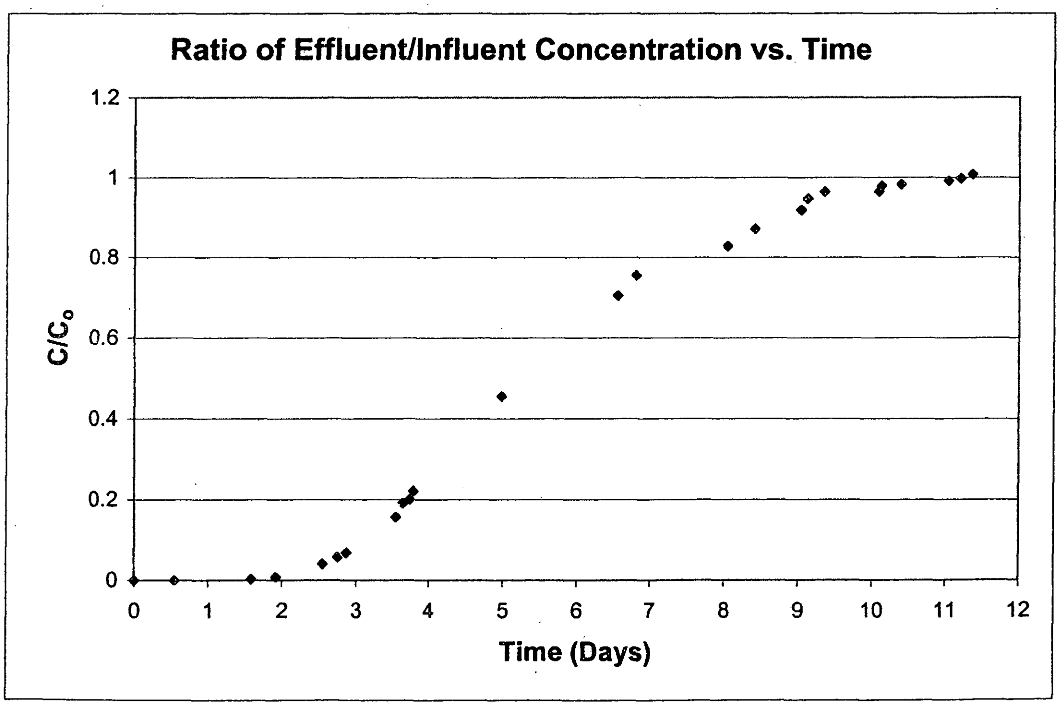
Tracer Test Data for the 0.75" limestone reactor

Date	Time	Elapsed Time (hours)	Elapsed Time (days)	Conductance	Corrected Conductance	Conc. (M) based on corrected conductance	Volume Additions (mL)	Cumulative volume (mL)	Flow rate (mL/day)
11/9/2005	8:45 PM	0.0	0.00	3.3	0	0			
11/10/2005	8:30 AM	12.0	0.50	4.1	0.8	0.009			
	9:50 AM	13.3	0.56	4.4	1.1	0.012			
	12:45 PM	16.2	0.68	4.5	1.2	0.013			
	4:50 PM	20.3	0.85	7.9	4.6	0.051			
11/11/2005	8:20 AM	35.8	1.49	15.1	11.8	0.130			
	9:00 AM	36.5	1.52	15.6	12.3	0.135			
	10:00 AM	37.5	1.56	15.9	12.6	0.138			
	12:00 PM	39.5	1.65	18.1	14.8	0.163			
	1:45 PM	41.2	1.72	18.4	15.1	0.166			
	2:30 PM	42.0	1.75	19	15.7	0.173			
	3:45 PM	42.7	1.78	19.9	16.6	0.182			
	4:30 PM	43.5	1.81				365	365	201
	5:30 PM	44.5	1.85	20.5	17.2	0.189			
11/12/2005	12:10 PM	63.2	2.63	30.9	27.6	0.303			
	4:15 PM	67.2	2.80	31.1	27.8	0.305	170	535	170
11/14/2005	9:30 AM	84.5	3.52	48.5	45.2	0.497	320	855	444
	5:30 PM	92.5	3.85	51.7	48.4	0.532			
	6:45 PM	93.2	3.89	55.2	51.9	0.570			
11/15/2005	8:30 AM	107.0	4.46	57.9	54.6	0.600			
	5:45 PM	116.2	4.84	60.5	57.2	0.629			
11/16/2005	10:00 AM	132.5	5.52	64	60.7	0.667	380	1235	190
	4:45 PM	139.2	5.80	66.2	62.9	0.691			
11/17/2005	1:35 PM	160.0	6.67	68.5	65.2	0.716			
	5:20 PM	163.8	6.82	70.2	66.9	0.735			
11/18/2005	9:00 AM	179.5	7.48	72.3	69	0.758			
	4:00 PM	186.5	7.77	72.8	69.5	0.764	360	1595	160
11/21/2005	11:30 AM	206.0	8.58	78.5	75.2	0.826	500	2095	163
11/22/2005	9:30 AM	228.0	9.50	80.1	76.8	0.844			
	5:40 PM	236.1	9.84	80.9	77.6	0.853	220	2315	175



Tracer Test Data for the 1.5" Limestone Reactor

Elapsed Time (hours)	Elapsed Time (days)	Conductance	Corrected Conductance	Conc. (M) based on corrected conductance	Volume Additions (mL)	Cumulative volume (mL)	Flow rate (mL/day)
0	0	2.8	0	0	(475)		
13.2	0.55	2.8	0.0	0.000			
38.2	1.59	3.1	0.3	0.003			
46.2	1.92	3.5	0.7	0.008	320	320	166
61.2	2.55	6.5	3.7	0.041			
65.9	2.75	8.0	5.2	0.057			
68.9	2.87	9.0	6.2	0.068			
85.2	3.55	17.0	14.2	0.156			
87.5	3.64	20.2	17.4	0.191			
89.6	3.73	21.0	18.2	0.200	320	640	177
90.9	3.79	22.9	20.1	0.221			
119.4	4.98	44.2	41.4	0.455	210	850	169
157.4	6.56	66.9	64.1	0.704			
163.4	6.81	71.5	68.7	0.755	325	1175	177
192.9	8.04	78.2	75.4	0.829			
201.9	8.41	82.1	79.3	0.871			
216.8	9.03	86.4	83.6	0.919			
218.8	9.12	89.0	86.2	0.947			
224.3	9.35	90.6	87.8	0.965	355	1530	140
241.8	10.08	90.6	87.8	0.965			
242.8	10.12	91.9	89.1	0.979			
249.3	10.39	92.2	89.4	0.982			
264.8	11.03	93.0	90.2	0.991			
268.8	11.20	93.6	90.8	0.998			
272.8	11.37	94.5	91.7	1.008	340	1870	164



Metal concentrations from the pulsed limestone bed system

Analyte Name	7/8/05 IS	7/8/05 ES	7/8/05 ES AS
Al 308.215	20.848	1.686	0.141
Ca 317.933	321.391	444.737	469.651
Cu 324.752	5.237	1.723	0.092
Fe 238.204	95.554	0.352	1.676
Mn 257.610	71.918	61.829	63.692
Ni 231.604	0.228	0.172	0.212
S 180.669	624.524	574.738	590.476
Zn 213.857	41.821	35.357	28.205

Analyte Name	7/11/05 IS	7/11/05 ES	7/11/05 ES AS
Al 308.215	15.310	0.314	0.109
Ca 317.933	311.710	433.595	448.218
Cu 324.752	3.874	0.332	0.023
Fe 238.204	50.849	0.228	0.220
Mn 257.610	55.157	54.634	55.901
Ni 231.604	0.161	0.152	0.149
S 180.669	570.635	574.685	590.917
Zn 213.857	32.291	29.255	17.146

Analyte Name	7/13/05 IS	7/13/05 ES	7/13/05 ES AS
Al 308.215	13.681	0.087	0.067
Ca 317.933	305.735	445.005	427.600
Cu 324.752	3.537	0.089	0.018
Fe 238.204	8.243	B.D.L.	B.D.L.
Mn 257.610	50.308	54.765	52.510
Ni 231.604	0.139	0.145	0.075
S 180.669	540.504	568.113	553.702
Zn 213.857	28.613	24.617	10.785

Analyte Name	IS 7-14-05	ES 7-14-05	ES AS 7-14-05
Al 308.215	16.6	0.194	0.0712
Ca 317.933	339	422	422
Cu 324.752	4.17	0.307	0.0457
Fe 238.204	3.97	0.00649	0.00991
Mn 257.610	54.9	50.9	51.3
Ni 231.604	0.166	0.143	0.139
S 180.669	546	507	522
Zn 213.857	33.8	27.0	21.0

Analyte Name	7/15/05 IS	7/15/05 ES	7/15/05 ES AS
Al 308.215	18.233	0.909	0.083
Ca 317.933	320.661	460.522	456.855
Cu 324.752	4.501	0.989	0.102
Fe 238.204	70.397	0.538	0.099
Mn 257.610	63.472	66.180	65.413
Ni 231.604	0.181	0.181	0.186
S 180.669	604.729	607.661	609.501
Zn 213.857	B.D.L.	36.580	31.029

Analyte Name	7/18/05 IS	7/18/05 ES	7/18/05 ES AS
Al 308.215	18.746	0.503	0.090
Ca 317.933	295.398	429.127	434.782
Cu 324.752	4.713	0.536	0.036
Fe 238.204	19.012	0.575	0.143
Mn 257.610	64.172	58.025	57.937
Ni 231.604	0.189	0.166	0.159
S 180.669	628.775	611.284	622.987
Zn 213.857	39.908	31.741	16.603

Analyte Name	IS 7-19-05	ES 7-19-05	ES AS 7-19-05
Al 308.215	18.1	3.35	1.97
Ca 317.933	273	370	374
Cu 324.752	4.57	2.64	2.16
Fe 238.204	54.2	0.0231	0.0190
Mn 257.610	65.6	60.6	61.8
Ni 231.604	0.182	0.169	0.169
S 180.669	575	550	547
Zn 213.857	36.2	33.0	34.3

Analyte Name	7/20/05 IS	7/20/05 ES	7/20/05 ES AS
Al 308.215	16.511	0.645	0.074
Ca 317.933	292.491	444.005	442.553
Cu 324.752	4.037	0.680	0.023
Fe 238.204	58.059	0.373	0.093
Mn 257.610	59.675	59.796	59.702
Ni 231.604	0.166	0.164	0.165
S 180.669	599.047	614.579	620.510
Zn 213.857	34.640	32.595	15.114

Analyte Name	7/21/05 IS	7/21/05 ES	7/21/05 ES AS
Al 308.215	15.918	0.510	0.076
Ca 317.933	298.315	398.035	397.838
Cu 324.752	4.152	0.522	0.047
Fe 238.204	12.061	B.D.L.	0.024
Mn 257.610	61.664	62.621	61.917
Ni 231.604	0.180	0.179	0.180
S 180.669	592.401	598.961	596.243
Zn 213.857	38.233	36.722	25.807

Analyte Name	7/22/05 IS	7/22/05 ES	7/22/05 ES AS
Al 308.215	17.441	0.212	0.085
Ca 317.933	310.190	413.930	415.037
Cu 324.752	4.926	0.317	0.031
Fe 238.204	1.131	0.014	0.023
Mn 257.610	72.980	75.270	73.733
Ni 231.604	0.213	0.213	0.203
S 180.669	607.771	627.096	625.141
Zn 213.857	45.945	41.283	27.937

Analyte Name	IS 7-25-05	ES 7-25-05	ES AS 7-25-05
Al 308.215	15.61	0.136	0.0924
Ca 317.933	282	362	384
Cu 324.752	4.32	0.228	0.0259
Fe 238.204	28.6	0.0283	0.00503
Mn 257.610	77.6	77.0	80.1
Ni 231.604	0.226	0.221	0.219
S 180.669	563	573	609
Zn 213.857	44.7	40.8	26.4

Analyte Name	7/27/05 IS	7/27/05 ES	7/27/05 ES AS
Al 308.215	16.800	0.970	0.151
Ca 317.933	278.448	382.727	385.597
Cu 324.752	4.088	1.037	0.250
Fe 238.204	48.870	0.209	0.099
Mn 257.610	61.069	59.075	59.536
Ni 231.604	0.167	0.158	0.159
S 180.669	590.758	590.975	595.164
Zn 213.857	36.559	33.097	31.661

Analyte Name	IS 8-1-05	ES 8-1-05	ES AS 8-1-05
Al 308.215	9.257	0.090	0.083
Ca 317.933	344.784	384.715	373.159
Cu 324.752	3.389	0.087	BDL
Fe 238.204	0.021	BDL	BDL
Mn 257.610	68.997	66.588	61.799
Ni 231.604	0.192	0.172	0.137
S 180.669	672.704	717.781	712.162
Zn 213.857	43.308	33.177	12.588

Analyte Name	IS 8-2-05	ES 8-2-05	ES AS 8-2-05
Al 308.215	15.040	0.766	0.075
Ca 317.933	437.452	566.275	562.251
Cu 324.752	3.728	0.762	0.027
Fe 238.204	43.545	BDL	BDL
Mn 257.610	58.485	59.167	58.438
Ni 231.604	0.152	0.155	0.149
S 180.669	717.547	751.818	750.339
Zn 213.857	34.487	33.337	22.549

Analyte Name	IS 8-3-05	ES 8-3-05	ES AS 8-3-05
Al 308.215	14.287	1.123	0.088
Ca 317.933	328.638	422.080	422.633
Cu 324.752	3.568	1.138	0.123
Fe 238.204	33.341	0.544	0.060
Mn 257.610	56.611	58.757	58.570
Ni 231.604	0.150	0.151	0.150
S 180.669	747.108	756.573	761.226
Zn 213.857	33.943	33.328	30.076

APPENDIX D

This appendix contains the chemical equations and thermodynamic values used, as well as the source of each of the values. Equations are denoted as to when it was used. For example, many of the equations and species used in the PHREEQC modeling were also used to create the solubility diagrams in Chapter One. There is also a copy of the PHREEQC input code for the batch reactor modeling. The code shown is for experiments related to variable zinc experiments with TOTFe = 2.4mg.

Soluble Species:

1.) $Zn^{+2} + H_2O = ZnOH^+ + H^+$
log_k -8.96
delta_h 13.4 kcal

2.) $Zn^{+2} + 2\ H_2O = Zn(OH)_2 + 2\ H^+$
log_k -16.9

3.) $Zn^{+2} + 3\ H_2O = Zn(OH)_3^- + 3\ H+$
log_k -28.4

4.) $Zn^{+2} + 4\ H_2O = Zn(OH)_4^{-2} + 4\ H+$
log_k -41.2

5.) $Zn^{+2} + CO_3^{-2} = ZnCO_3$
log_k 5.3

6.) $Zn^{+2} + 2\ CO_3^{-2} = Zn(CO_3)_2^{-2}$
log_k 9.63

7.) $Zn^{+2} + HCO_3^- = ZnHCO_3^+$
log_k 2.1

8.) $Zn^{+2} + SO_4^{-2} = ZnSO_4$
log_k 2.37
delta_h 1.36 kcal

9.) $Zn^{+2} + 2\ SO_4^{-2} = Zn(SO_4)_2^{-2}$
log_k 3.28

10.) $Ni^{+2} + H_2O = NiOH^+ + H^+$
log_k -9.86

11.) $Ni^{+2} + 2\ H_2O = Ni(OH)_2 + 2H^+$
log_k -19.0

12.) $Ni^{+2} + 3\ H_2O = Ni(OH)_3^- + 3H^+$
log_k -30.00

13.) $Ni^{+2} + CO_3^{-2} = NiCO_3$
log_k 6.87

14.) $Ni^{+2} + 2\ CO_3^{-2} = Ni(CO_3)_2^{-2}$
log_k 3.24

15.) $Ni^{+2} + SO_4^{-2} = NiSO_4$
log_k 2.29

16.) $Ni^{+2} + 2\ SO_4^{-2} = Ni(SO_4)_2^{-2}$
log_k -1.27

Sources for thermodynamic values for the soluble species:
All equations and values for the zinc soluble species are in the default database of PHREEQC available online January 1, 2006.
All equations and values for the nickel soluble species are from Benjamin 2002.

Solid Species:

17.) Calcite
$CaCO_{3(s)} = CO_3^{-2} + Ca^{+2}$
log_k -8.48
delta_h -2.297 kcal

18.) Zn(OH)2(s)
$Zn(OH)_{2(s)} + 2\ H^{+} = Zn^{+2} + 2\ H_2O$
log_k 11.5

19.) Smithsonite
$ZnCO_{3(s)} = Zn^{+2} + CO_3^{-2}$
log_k -10.0
delta_h -4.36 kcal

20.) Hydrozincite
$Zn(OH)_{1.2}(CO_3)_{0.4(s)} + 2H^{+} = Zn^{+2} + 1.6\ H_2O + 0.4\ CO_2$
log_k 9.18

21.) Nickel_Hydroxide
$Ni(OH)_{2(s)} = Ni^{+2} + 2\ OH^{-}$
log_k -17.2

22.) Nickel_Carbonate

$NiCO_{3(s)} = Ni^{+2} + CO_3^{-2}$

log_k -6.84

Sources for thermodynamic values for the solid species:
Calcite, Zn(OH)2(s), and Smithsonite are in the default database of PHREEQC.
Hydrozincite value from Zachara 1988.
Nickel Hydroxide and Nickel Carbonate are from Benjamin 2002.

Use of the solid and soluble species equations:

- To create the $Zn(OH)_2$ solubility curve in Chapter One, equations 1-4, 8,9, and 18 were used.
- To create the $ZnCO_3$ solubility curve in Chapter One, equations 5-9, and 19 were used.
- To create the $Ni(OH)_2$ solubility curve in Chapter One, equations 10-12, 15, 16, and 21 were used.
- To create the $NiCO_3$ solubility curve in Chapter One, equations 13-16, and 22 were used.

Surface Interactions:

Strong binding site--Hfo_s

$Hfo\_sOH + H+ = Hfo\_sOH^{2+}$

log_k 7.29

$Hfo\_sOH = Hfo\_sO^{-} + H^{+}$

log_k -8.93

Weak binding site--Hfo_w

$Hfo\_wOH \quad + H+ = Hfo\_wOH^{2+}$

log_k 7.29

$Hfo\_wOH = Hfo\_wO^{-} + H^{+}$

log_k -8.93

Calcium

$Hfo\_sOH + Ca^{+2} = Hfo\_sOHCa^{+2}$

log_k 4.97

$Hfo\_wOH + Ca^{+2} = Hfo\_wOCa^{+} + H^{+}$
log_k -5.85

Zinc

$Hfo\_sOH + Zn^{+2} = Hfo\_sOZn^{+} + H^{+}$
log_k 0.99

$Hfo\_wOH + Zn^{+2} = Hfo\_wOZn^{+} + H^{+}$
log_k -1.99

$Limestone + Zn^{2+} = LimestoneZn^{2+}$
log_k 2.17

$Limestone + ZnOH^{+} = LimestoneZnOH^{+}$
log_k 2.17

Nickel

$Hfo\_sOH + Ni^{+2} = Hfo\_sONi^{+} + H^{+}$
log_k -0.37

$Limestone + Ni^{2+} = LimestoneNi^{2+}$
log_k 2.17

Sulfate

$Hfo\_wOH + SO_4^{-2} + H^{+} = Hfo\_wSO_4^{-} + H_2O$
log_k 7.78

$Hfo\_wOH + SO_4^{-2} = Hfo\_wOHSO_4^{-2}$
log_k 0.79

Carbonates

$Hfo\_wOH + CO_3^{-2} + H+ = Hfo\_wCO_3^{-} + H_2O$
log_k 12.56

$Hfo\_wOH + CO_3^{-2} + 2H^{+} = Hfo\_wHCO_3 + H_2O$
log_k 20.62

Sources for the surface interaction equations and values:

All the Hfo related equations are in the PHREEQC default database except for the nickel value. The Hfo_s/nickel value is from Dzombak and Morel 1990.

Values for surface interaction between both zinc and nickel with limestone are from Zachara 1991.

PHREEQC Input File for Zinc experiments

```
TITLE Zinc Batch Reactor Model

Surface_master_species
   Limestone  Limestone

SURFACE_SPECIES
  Limestone = Limestone
     log_k 0.0

  Limestone + Zn+2 = LimestoneZn+2
     log_k 2.17

  Limestone + ZnOH+ = LimestoneZnOH+
     log_k 2.17

SURFACE 1
     Hfo_sOH     4.8e-5    600    0.0024
     Hfo_wOH     1.92e-3   600    0.0024
     -diffuse_layer  10e-8
     -only_counter_ions

Phases
   Hydrozincite
   Zn(OH)1.2(CO3)0.4 + 2H+ = Zn+2 + 1.6H2O + 0.4CO2
   log_k  9.18

SOLUTION 1
     -units  ppm
     pH     1.9
     Zn     5.3
     S(6)   1100
```

```
End

SOLUTION 2
	-units ppm
	pH	1.9
	Zn	10.7
	S(6)	1100
End

SOLUTION 3
	-units ppm
	pH	1.9
	Zn	16.0
	S(6)	1100

End

SOLUTION 4
	-units ppm
	pH	1.9
	Zn	21.3
	S(6)	1100

End

SOLUTION 5
	-units ppm
	pH	1.9
	Zn	26.7
	S(6)	1100

End

USE surface none

SELECTED_OUTPUT
	-file high iron zinc.sel
	-molalities	Hfo_wOZn+	Hfo_sOZn+ Zn+2 ZnSO4 Zn(SO4)2-2 ZnOH+
	ZnHCO3+ ZnCO3 Zn(OH)2 Zn(CO3)2-2 Zn(OH)3- CO3-2
	Zn(OH)4-2 Ca+2 CaSO4 CaHCO3+ CaCO3 CaOH+ CaHSO4+
```

```
    -saturation_indices Smithsonite Zn(OH)2(e) Hydrozincite  Calcite Gypsum
    Siderite

USE solution 1
USE surface 1
EQUILIBRIUM_PHASES 1
    Calcite   -0.2 1.0
    CO2(g)     -1.5
END

USE solution 2
USE surface 1
EQUILIBRIUM_PHASES 1
    Calcite   -0.2 1.0
    CO2(g)     -1.5
END

USE solution 3
USE surface 1
EQUILIBRIUM_PHASES 1
    Calcite   -0.2 1.0
    CO2(g)     -1.5
END

USE solution 4
USE surface 1
EQUILIBRIUM_PHASES 1
    Calcite   -0.2 1.0
    CO2(g)     -1.5
END

USE solution 5
USE surface 1
EQUILIBRIUM_PHASES 1
    Calcite   -0.2 1.0
    CO2(g)     -1.5
END
```