MECHANISMS OF NICKEL AND ZINC REMOVAL IN OXIC LIMESTONE SYSTEMS AND THE APPLICATION TO METAL MINE DRAINAGES[1]

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Abstract. Limestone systems are generally used for acid neutralization of mining impacted waters. However they can also be designed to remove heavy metal constituents. The issues surrounding the design of a limestone system for metal removal are different from the issues involved in acid neutralization. Experiments were carried out to explore these issues by evaluating the interaction of $CaCO_3$ with solutions containing a primary metal (Fe, Al), and a secondary metal (Zn, Ni). The fate of the secondary metals and their removal as a function of pH, alkalinity, and primary metal concentration are reported. Although these parameters by themselves are not necessarily good indicators of secondary metal removal, when coupled with the influent primary:secondary metal ratio, trends become apparent that can be used as design parameters. Zinc and Ni removals appear to be a function of Fe^{+3} concentrations and removals are shown to be as high as 97% and 87%, respectively, at near neutral pH values. The removal reaches a saturation point at an Fe:Zn ratio of 50:1, and for Ni the saturation ratio is 45:1 Zinc and Ni removals with Al gave ambiguous results.

Additional key words: co-precipitation, sorption, heavy metals, limestone drains

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Background

Acid mine drainage (AMD) causes two main problems in ecological systems: acidity, and dissolved metals. The acidity affects the pH of receiving waters and has a negative impact on living systems in that water. The dissolved metals have a two-fold effect. First effect is the hydrolysis and precipitation of the metal species. This process will liberate protons and further decrease the pH of the water (Benner et al., 1999). The second effect is the toxicity of the metals themselves. Many of the metals present in AMD are required nutrients for most types of life. However, at the elevated concentrations present in many mine waters, they can have negative effects. Thus for both of the above reasons, the goals in AMD treatment are neutralization and metal removal.

Mainly due to economic concerns the preferred treatment methods are generally passive in nature. Passive treatment systems (PTS) allow for minimized man power and inexpensive treatment materials (Wu et al., 2003, Benner et al., 1999). Also, due to the fact that many mines are located in remote areas where both access and space for a PTS are limited, the desired system is a small low-maintenance reactor. In order to minimize the footprint of a PTS, it must be operating at its optimum. Therefore understanding the chemical processes in a PTS is of utmost importance.

One type of PTS treatment material that is commonly used is limestone (Watzlaf et al., Ziemkiewicz et al., 1997, Skousen, 1991, Ziemkiewicz et al., 1994, Cravotta and Trahan, 1999). The dissolution of limestone by AMD waters proceeds by reactions 1, 2, and 3, with the effect of consuming protons and thus increasing both alkalinity and pH, which can lead to a neutralized discharge that is net alkaline.

$$CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-} \tag{1}$$

$$H^+ + CO_3^{2-} \leftrightarrow HCO_3^- \tag{2}$$

$$HCO_3^- + H^+ \leftrightarrow CO_{2(g)} + H_2O \tag{3}$$

There are two major types of limestone systems commonly in use that have different chemistry and also different mechanisms for metal removal. Anoxic limestone systems (ALS) are used when the mine water to be treated is in a chemically reduced state, with little to no dissolved O_2, or if the water can be intercepted before being exposed to atmospheric conditions (Skousen, 1991). The anoxic water conditions force the metals present to stay in their reduced forms. Most importantly Fe will be predominantly present in the Fe^{+2} state, and Mn in the Mn^{+2} state. These reduced forms of metals do not precipitate as hydroxides or oxides until a pH of 8 or 9, respectively, and because ALS can usually only attain an effluent pH of approximately 6, the iron and manganese pass through the limestone system generally unaffected (Watzlaf, et al., 2004). Aluminum is not affected by the redox potential of the water. It is only affected by the pH change caused by the limestone. For waters with a pH greater than about 4.5, the Al changes from dissolved to particulate. However, typically the flocs remain suspended and are flushed out of the drain as the systems are designed to have a large flow velocity. By forcing the metals through the drain, the amount of armoring on the limestone surface and clogging of the drain are both reduced. These common problems are most often caused by the primary metal precipitates.

The goal of the ALS is the dissolution of the limestone leading to higher pH and alkalinity in the effluent, while the metal removal is accomplished by a subsequent oxidation and hydrolysis process that is separate from the limestone system. Because the ALS is not open to the atmosphere, there is also an increase in dissolved CO_2 concentration, which can help to dissolve the remaining limestone (Cravotta and Trahan, 1999). When the effluent reaches the oxidation stage, the excess CO_2 is released to the atmosphere giving an average discharge pH of ~7.

The other main type of limestone systems are systems that are open to the atmosphere or for waters with large amounts of oxidized metal species, and are thus called oxic limestone systems (OLS) (Ziemkiewicz, et al., 1997, Ziemkiewicz, at al., 1994, Cravotta and Trahan, 1999). In this type of system the pH and alkalinity additions happen concurrently with metal precipitation. As the pH in an OLS increases Fe^{+3} and Al will precipitate, and can accumulate on the limestone surface thus forming an armored coating. Although the armoring does not stop limestone dissolution completely, it can slow the rate of dissolution which, if not taken into account in the design of the OLS, can cause a drain to fail (Ziemkiewicz et al., 1997, Letterman, 1995). Also, the conglomeration of Fe^{+3} and Al precipitates in the drain can cause clogging, preferential flow paths, and short-circuiting. In order to minimize these problems, the recommendation is to design the OLS with a sufficient water velocity, or to have some sort of periodic flushing mechanism to both scour the surface of the limestone, and flush the precipitates out of the system (Ziemkiewicz, at al., 1994). This flushing is not necessary, however if the iron and aluminum concentrations are near zero.

The majority of research on limestone systems has been conducted on coal mine drainages, where total metal concentrations are generally low and limited to the primary metals Fe, Al, and Mn (Cravotta, this volume). In metal mine drainages, however, the metal concentrations can be orders of magnitude higher, and the species with significant concentrations can include the primary metals, and many secondary metals such as Zn, Cu, Ni, Cd, Cd, and Cr (Lee et al., 2002, Okumura and Kitano, 1986, Wildeman and Schmiermund, 2004). Because limestone research has centered on coal mine drainages, the fate of the primary metals in oxic limestone systems is well documented (Ziemkiewicz et al., 1994, Cravotta and Trahan, 1999). Concentrations of Fe^{+3} and Al in the effluent are near zero (~100% removal). For the pH range of an average oxic limestone system effluent (~6-7), it is expected that these two metals precipitate as metal hydroxides. Iron(II), is not typically removed in limestone drains, unless sufficient O_2 is present or added to oxidize the Fe^{+2} to Fe^{+3}. Manganese, for many different reasons, is generally conserved and removals are modest (<10%). On the fate of secondary metals however, the data is sparse (Cravotta and Trahan, 1999), and the application of the data to design of a limestone drain for metal mine drainages is difficult due to two major issues.

The first issue is that available removal data for secondary metals is generally for the lower concentrations found in coal mine drainages (<1mg/L) (Watzlaf et al. 2004, Cravotta and Trahan, 1999). At such low levels it is difficult to judge whether the effluent metal concentration constitutes a removal or if that concentration is dictated by the water chemistry. For example, if an influent Zn concentration is 0.5 mg/L, and the effluent concentration is 0.4 mg/L, it is impossible to say whether that removal is the maximum percent removal possible or whether an influent concentration of 5.0 mg/L would also be reduced to 0.4 mg/L based on the pH, alkalinity, and primary metal concentrations. Therefore these previous studies are directly applicable to coal mine drainages, but not to metal mine drainages where metal concentrations can be much higher.

The second concern with available data is the retention time of the limestone drains currently in use. Current literature values for retention times on limestone systems range from 1-109 hours, and the majority of reported retention times are less than 24 hours (Watzlaf et al., Ziemkiewicz et al., 1997, Cravotta and Trahan, 1999). The large range of variability is due mainly to both whether the limestone system is oxic or anoxic, and also on influent water conditions. In general the more acidic the water is the longer the retention time needs to be. The other major consideration in deciding on a retention time is the treatment goals of the limestone drain. In many instances the goal is acid neutralization only, and the metals removal is a by-product of the system. In these instances shorter retention times are all that are needed to achieve the stated goal of acid neutralization. Alternatively, if the treatment goal is metal precipitation within the limestone system, retention times need to be much longer to account for the stated problem of armoring and the slower limestone dissolution rate that it can cause, and also to allow for sorption and co-precipitation reactions of the secondary metals. It has been shown that Ni and Zn sorption require 19 and 30 hours, respectively, to maximize sorption to hydrous ferric oxides at pH 7 (Trivedi and Axe, 2001). Therefore, to design an oxic limestone system with the stated goal of metals removal, retention times should be on the order of days as opposed to hours. Also, as the goal is metals removal in the limestone system itself, periodic maintenance or flushing would be required to maintain system permeability and treatment efficacy.

There are three main fates for the secondary metals in limestone systems. They can precipitate as a discrete hydroxide or carbonate, sorb to either a mineral surface or a primary metal precipitate surface, or co-precipitate within the primary metal precipitates or in the calcite itself. Because of the high solubilities of the secondary metal-hydroxides (Fig. 1), precipitation as a metal-hydroxide would not be expected for typical values of pH and metal concentration that occur in a limestone drain. Metal carbonate precipitation is more difficult to predict as it is both pH and alkalinity dependant (Cravotta, this volume). Nevertheless, it is possible to determine if hydroxide precipitation or carbonate precipitation is favored for a given set of water quality data based on the effluent of a limestone drain. In cases where secondary metals removal is observed, but undersaturation with the hydroxide or carbonate phases is indicated, sorption and co-precipitation reactions could be the major mechanism for secondary metal removals (Lee et al., 2002, Okumura and Kitano, 1986, Al et al., 2000, Cravotta and Trahan, 1999). The difference between sorption and co-precipitation is a question of degrees. Sorption is generally defined in the literature as an accumulation of metals on any available surface (metal precipitate or mineral). Co-precipitation is generally defined as an accumulation of metals on an available surface that become part of the primary metal mineral lattice, and are thus not easily reversible (Lee et al., 2002, Zachara et al., 1988). To separate the two fates, an operational decision is made to change solution conditions in some way and measure how much metal re-solubilizes. Different researchers have accomplished this in different ways. Zachara et al., 1988, changed the pH and dissolved CO_2 concentrations. Karthikeyan et al., 1997, added dilute EDTA to differentiate between the fractions. Some researchers did not differentiate between sorbed and co-precipitated metals (Lee et al., 2002, Trivedi and Axe, 2001). The operational definition does affect the applicability of the results, but must be made to separate the different fates.

In this study, batch reactors were used to mimic the treatment of a metal mine drainage in an oxic limestone system. This was accomplished by adding solid phase $CaCO_3$ to synthetic mine waters containing a primary metal and a secondary metal. The concentrations of these metals are in the range seen in metal mine drainages. The solutions and $CaCO_3$ mixtures were allowed to react for four days, and the fate of the secondary metals was measured. These experiments will help to establish factors that should be considered when designing a limestone drain for metal removal. They may also have implications on metal loading and thus sizing requirements of subsequent treatment systems.

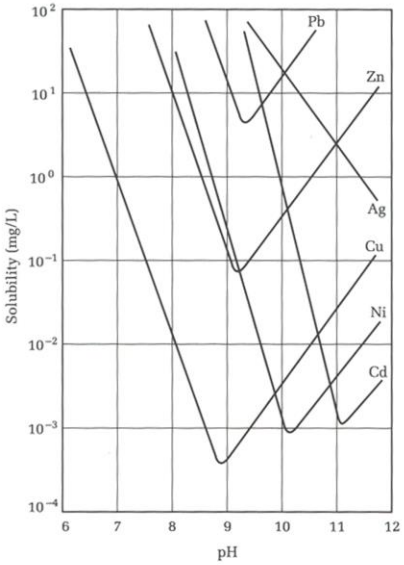

Figure 1 -pC/pH diagram for metal hydroxide precipitation of selected metals (Davis and Cornwell, 1998)

Methods

Solutions/Chemicals

The synthetic mine waters were made with metal sulfate salts and diluted with 0.02 N H_2SO_4 (final pH ~2.1). For Fe, $FeSO_4$ was used, and a small amount of H_2O_2 was added to oxidize the Fe^{+2} to Fe^{+3}. The reason for this was to minimize the amount of redox chemistry that was taking place in the reactor vials. The target concentrations for the metals in the reactors were: Fe:0-500mg/L, Al: 0-300mg/L, Ni: 0-200mg/L, and Zn: 0-200mg/L. In order to achieve the specific desired concentration in each reactor, the 0.02 N H_2SO_4 was used for dilution to maintain the low pH.

The solution used for the metal sorption extraction was a dilute ($3.4*10^{-4}$M) EDTA solution. A 5%(v/v) HNO_3 solution was used to completely dissolve the precipitates for the co-precipitated/precipitated fraction.

All chemicals listed above, and the calcium carbonate used, were reagent grade or better.

Process:

The procedural part of these experiments was modified from Karthikeyan et al. (1997). Different experiments were conducted where the primary metals concentrations, the secondary metals concentrations, and the amount of $CaCO_3$ were variable. The reason for varying the amount of $CaCO_3$ was to achieve different pH and alkalinity levels. Solutions containing the primary metal, the secondary metal and, if needed, the 0.02 N H_2SO_4 were added to 50-mL centrifuge tubes. To that solution powdered calcium carbonate was added. These reactor vessels were capped, and shaken by hand to suspend the $CaCO_3$. Within five minutes the vials were un-capped to vent the CO_2 to the atmosphere. The vials were then re-capped, and placed on a shaker table in an upright position. The upright position helped to minimize leakage as CO_2 pressure built up in the vial. Once the initial, vigorous dissolution of the $CaCO_3$ had ceased (after approximately 12 hours), the vials were vented, re-capped, and placed back on the shaker table in a horizontal position. The horizontal position maximized the surface area exposed to the headspace gases to allow for an efficient gas exchange across the liquid/gas interface. The vials remained on the shaker table for a total of four days being vented twice daily to the atmosphere. It is assumed that the continuous venting maintained gases in the headspace that mimicked atmospheric conditions.

At the end of four days, the vials were removed from the shaker table and the pH of each solution was measured. The vials were then centrifuged (10,000g for 20 minutes) to separate the precipitates from the supernatant solution. The supernatant was sampled for metals analysis and a colorimetric alkalinity titration was performed using a Hach digital titrator. In some of the vials, the $CaCO_3$ completely dissolved and there was no visible precipitate. In these vials essentially all of the metal was present in the solution phase. However, these vials were treated as though there was a precipitate, and were subsequently taken through the entire process. A measured volume of the dilute EDTA solution was added to the precipitate. The solution and precipitate were shaken vigorously by hand to re-suspend the precipitate, and then placed on the shaker table for one hour. These solutions were again centrifuged, and the supernatant was sampled for metals analysis (sorbed fraction). The 5% HNO_3 was added to the remaining precipitate until complete dissolution was achieved. A sample was taken from this solution for metals analysis (precipitated fraction).

Each of the metal analysis samples were acidified with a few drops of concentrated HNO_3. The metals were then analyzed on a Perkin Elmer 3000 ICP-OES for the constituents of concern.

Results

All alkalinity values are reported as mg/L as $CaCO_3$. Unless otherwise specified metal concentrations are in mg/L, and total metal masses are in mg.

Figures 2 and 3 represent the results from experiments with influents containing Fe and Zn. Figures 4 and 5 are the results from influents containing Fe and Ni. These figures show the distribution of the secondary metal fates as a function of pH and alkalinity. For each of these figures the primary metal to secondary metal ratio is specified. It can be seen that there is a definite increase in secondary metal removal (smaller percents in solution) for higher iron to secondary metal ratios. Figures 6 and 7 show the Zn distributions for influents containing Al and ZN at different Al:Zn ratios, while Fig. 8 and 9 show the distributions of Ni for influents containing Al and Ni at different Al:Ni ratios. As with the Fe experiments there are higher secondary metal removals with increasing Al to secondary metal ratios.

The percent error in the mass balances for secondary metal recovery was generally less than five percent. Negative percent values, values greater than one hundred percent, and total percents that do not add up to one hundred percent for the three fractions are artifacts from error in the recovery of the secondary metal.

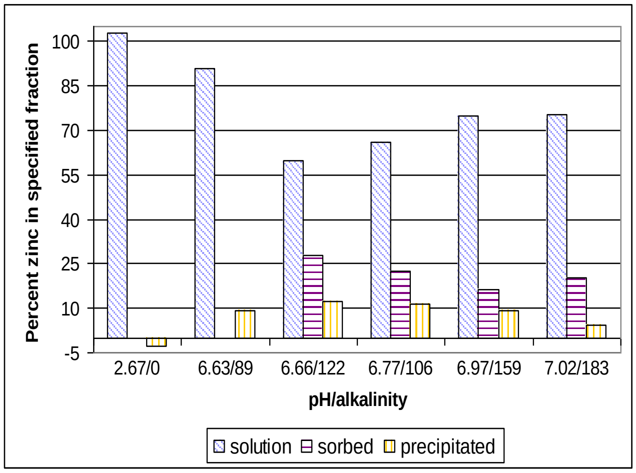

Figure 2-Zinc distribution vs. pH and alkalinity for an Fe:Zn ratio of 0.2

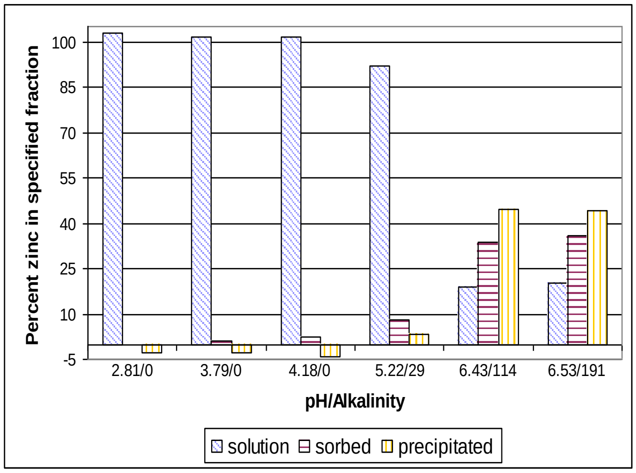

Figure 3-Zinc distribution vs. pH and alkalinity for an Fe:Zn ratio of 20

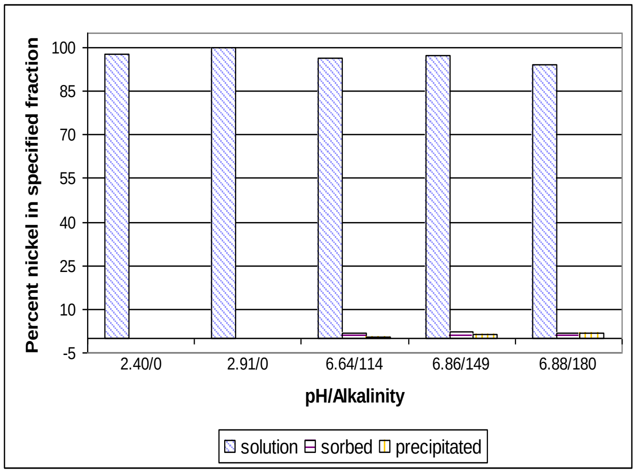

Figure 4-Nickel distribution vs. pH and alkalinity for an Fe:Ni ratio of 0.2

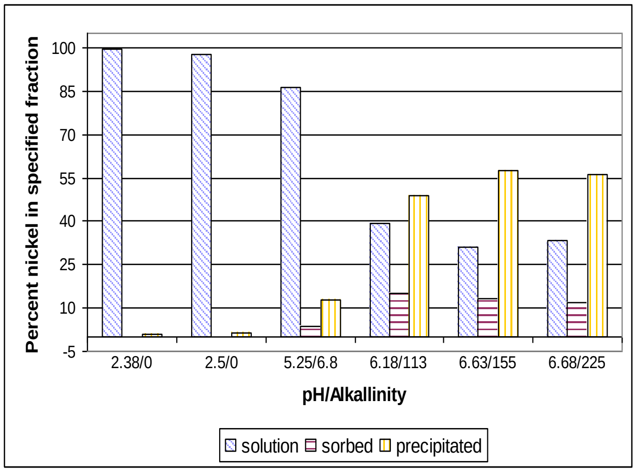

Figure 5- Nickel distribution vs. pH and alkalinity for an Fe:Ni ratio of 20

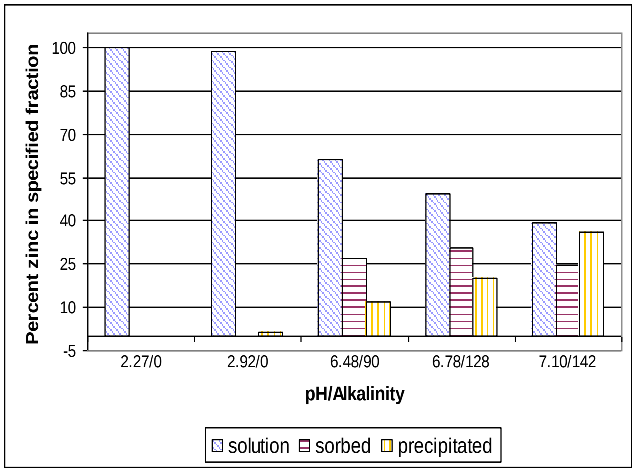

Figure 6-Zinc distribution vs. pH and alkalinity for an Al:Zn ratio of 0.1

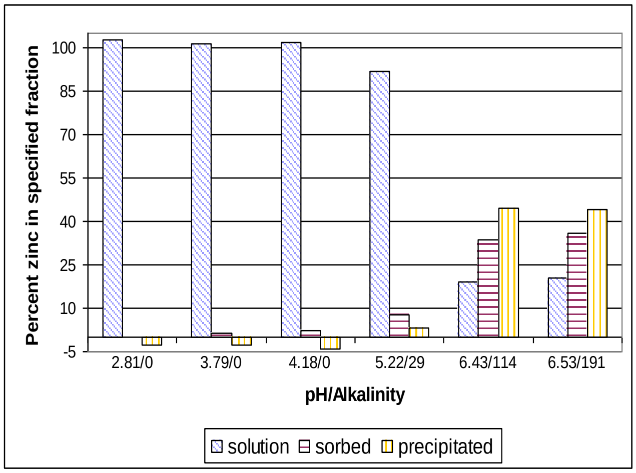

Figure 7-Zinc distribution vs. pH and alkalinity for an Al:Zn ratio of 10

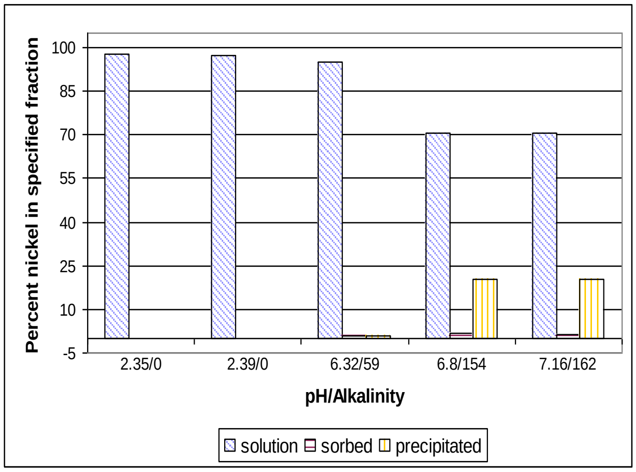

Figure 8-Nickel distribution vs. pH and alkalinity for an Al:Ni ratio of 0.1

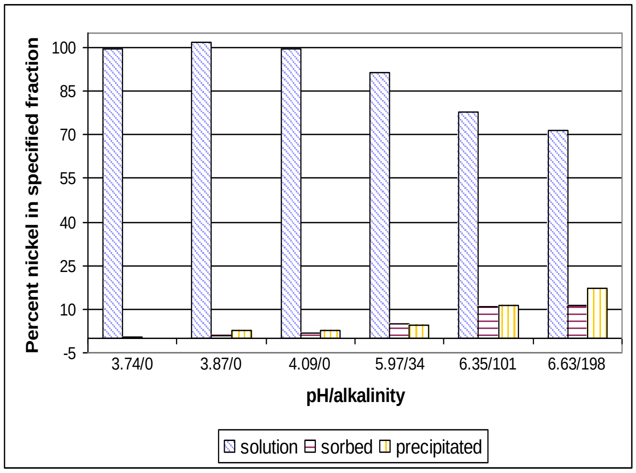

Figure 9-Nickel disribution vs. pH and alkalinity for an Al:Ni ratio of 10

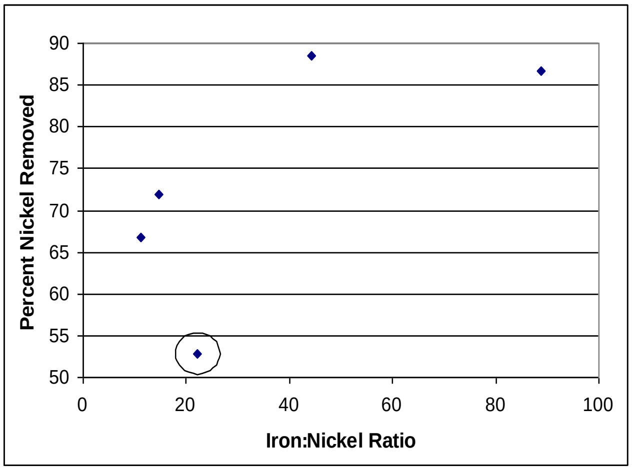

Figure 10-Percent Ni removed vs. Fe:Ni ratio, pH:6.7±0.15, alkalinity: 120±15. The outlier point is circled (pH=6.3 and alkalinity=47).

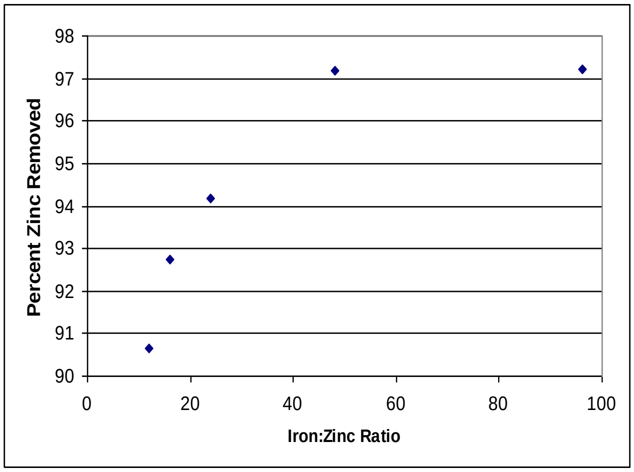

Figure 11-Percent Zn removal vs. Fe:Zn ratio, pH:6.7±0.1, alkalinity:125±7

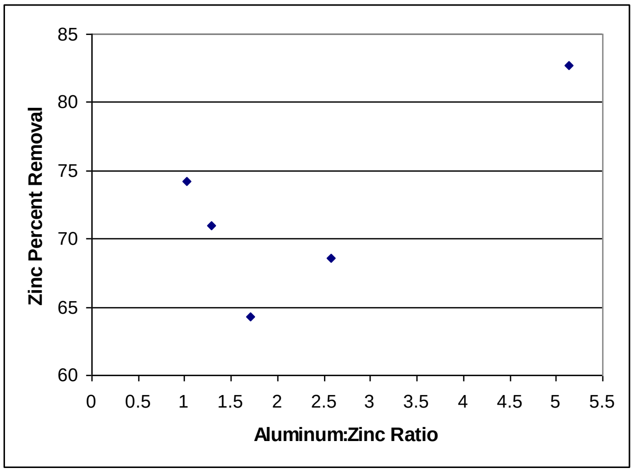

Figure 12-Percent Zn removal vs. Al:Zn ratio, pH:6.9±0.15, alkalinity:130±15

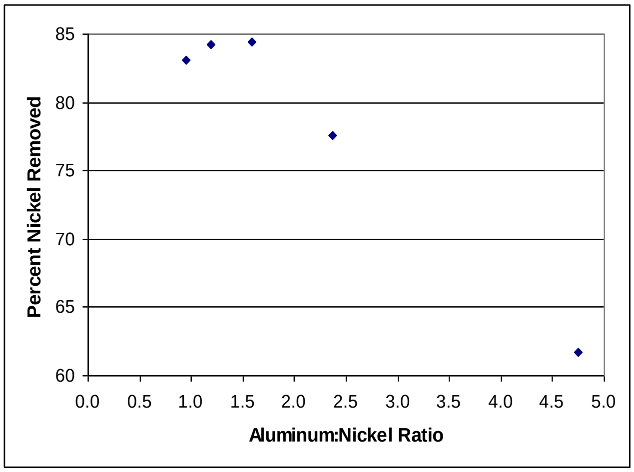

Figure 13-Percent Ni removal vs. Al: Ni ratio, pH:6.8±0.15, alkalinity:130±20

Figures 10 through 13 were generated by comparing conditions with different primary to secondary metal ratios but similar pH and alkalinity values. Figures 10 and 11 represent secondary metal removal when combined with iron at different ratios. From Fig. 10 it can be seen that there is a saturation point where higher Fe to Ni ratios do not lead to higher percent removals. This saturation ratio is 45:1 Fe:Ni, and maximizes at a nickel removal of approximately 87%. An explanation of the implications of the outlier value is left for the discussion section. Figure 11 shows zinc removal as a function of the Fe:Zn ratio. Again a saturation type curve is seen, with the Fe:Zn ratio at saturation being 50:1, and a Zn removal of approximately 97%.

Figures 12 and 13 are graphs of the secondary metal removal as a function of the Al to secondary metal ratio. The same type of saturation-like curves that were seen for the mixing of iron with the secondary metals is not at all seen for Al. The reasons for this are not entirely clear, and a discussion of possible reasons is left to the discussion section.

Dissolved Ca concentrations for all the reactor vials ranged from ~220 to 720mg/L. For many of the vials in the lower end of the range (<350mg/L) complete dissolution of the added $CaCO_3$ was observed. In these vials, the pH did not sufficiently increase to allow for significant metal precipitation (pH<3.5). For vials where the pH was higher than 3.5, and Fe and Al were visibly precipitating, the Ca^{+2} ion concentrations were at the higher end of the range (>350-720mg/L). For these vials, the calculated amount of Ca added as a solid phase was always higher than the amount measured in solution. Thus there was still un-dissolved $CaCO_3$ in the reactor vials.

Discussion

In comparing and contrasting Fig. 2 through 9, it can be seen that Zn has higher removals as a function of primary metal concentration and pH than does Ni. However, varying the primary metal concentration has a larger effect on Ni than it does on Zn (Fig. 10 and 11). For both Zn and Ni, it can be seen that there is generally higher removal efficiencies with increasing pH. This is consistent with sorption mechanisms of cations onto an $Fe(OH)_3$ surface. It is also possible that there is more discrete precipitation of the secondary metals as the pH and alkalinity increase.

Over the pH ranges presented, there is not an obvious trend in the sorbed and precipitated fractions. This may be due to the ion exchange that is occurring between the protons and Ca ions. In these simulated limestone drains, the increase in pH (decrease in proton concentration) is caused by the dissolution of $CaCO_3$ (increase in Ca concentration). Protons and Ca^{+2} ions will both compete with the secondary metal for possible sorption sites on any given surface. Therefore, the added sorption and co-precipitation that is generally expected at higher pH, is not readily seen in these systems. It could also be that the narrow pH range is not wide enough to capture significant differences in the amount of sorption and co-precipitation.

From Fig. 10 and 11 it is easy to interpolate the amount of secondary metal removed given influent metal concentrations, and effluent pH and alkalinity values. The problem with this method however, is that many curves would need to be produced, and each would only be valid for the pH and alkalinity ranges given. For example, in Fig. 9, the outlier point has a pH that falls well out of the range of the other points making up the curve. Because the removal mechanisms of the secondary metals are pH dependant, it is not surprising that a pH difference leads to a different metal removal. If it is assumed that the saturation like quality of these graphs is conserved, a line of a similar shape to the curve created by the other points could be drawn through this outlier point. That new line would have the same predictive power but would be for a pH of approximately 6.3 and an alkalinity of 49. Much more work would need to be done in order to confirm that the saturation shape of these curves is consistent, and also to determine the maximum values at saturation.

A final comment on the shape of these saturation curves: the ratio of primary:secondary metal concentrations at saturation and the removal percent at which these curves maximize, are a function of the four day reaction time of the experiment and do not necessarily represent the maximum amount that can be expected if time is variable. A possible mechanism to account for secondary metal sorption to an Fe or Al precipitate includes a migration of the secondary metal from the outer surface into the inner pore spaces of the Fe/Al precipitate (Trivedi and Axe, 2001). This migration takes time. With this in mind, it is entirely possible that as the reaction time increases, the saturation curves will move up (higher percent removals), and to the left (lower saturation ratios). Likewise, as the reaction time goes to zero the curves will move down (lower percent removals) and to the right (higher saturation ratios). This re-emphasizes the importance of retention time in a limestone drain when designing for metal removal. Kinetic work with these systems would have to be completed to fully explore this idea.

Figures 12 and 13 are far more difficult to interpret as they are contradictory in nature. It was assumed that the Al precipitates would lead to more secondary metal removal than the Fe precipitates on a mass to mass basis due to the fact that the average hydrated aluminum oxide has larger pore volumes and surface areas than a hydrated iron oxide (Trivedi and Axe, 2001). Because of this the ratio of secondary metal to Al was much lower in these experiments, but the results were expected to be similar. As can be seen in Fig. 12 and 13, the results do not mimic the results for Fe, and are not even self-consistent. The Zn removal in Fig. 12 minimizes at an Al:Zn ratio of about 1.8, and then increases without bound in the range studied. The Ni removal in Fig. 12, maximizes at a ratio of about 1.5, and then decreases without bound. A consistent mechanism to account for both of these removals is not immediately evident. One or the other response could be justified. Work is on-going to determine the cause of the shape of these graphs.

Conclusions

In all of these experiments the secondary metal removals are consistently lower than what would be predicted from only looking at the equilibrium chemistry in solution. The mechanisms to achieve these lower concentrations are sorption and co-precipitation, which occur to varying degrees, on and with the available surfaces present in solution. These same surfaces, or analogs thereof, are present in limestone drains, and other limestone neutralization systems. Therefore the mechanisms and amounts of secondary metal removal that took place in these experiments can also take place in limestone treatment systems. Knowing the primary:secondary metal ratio of the influent mine water is important when designing a drain for metal removal, or in order to predict the metal removal to design subsequent treatment systems. Limestone drains can be used not only for the neutralization of acid mine drainage with low metal loads, but also for the neutralization and subsequent removal of heavy metals, as long as the design of the system takes into account the mechanisms of removal, rates of limestone dissolution, and a method to flush precipitates from the drain in order to maintain permeability and a consistent retention time over the life of a drain.

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