

TREATMENT OF METAL-MINE EFFLUENTS BY LIMESTONE NEUTRALIZATION AND CALCITE CO-PRECIPIATION¹

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Abstract: The U.S. Geological Survey - Leetown Science Center and the Colorado School of Mines have developed a remediation process for the treatment of metals in circumneutral mining influenced waters. The process involves treatment with a pulsed limestone bed (PLB) system, followed by co-precipitation of metal-carbonate impurities. The PLB system is resistant to armoring through the action of intermittently pulsing fluids through beds of limestone. This imparts significant alkalinity to the water, especially when CO₂ has been added to enhance dissolution of the limestone. Then, product water is directed through an inclined channel containing limestone where co-precipitation of metal carbonates occurs, resulting in the removal of additional impurities, such as Zn, Cd and Mn. The maximum pH in the channel reaches 8.3, which is suitable for direct discharge into surface waters. The selectivity of the process results in lower reagent consumption and sludge volumes than would be expected with conventional lime or caustic treatment. The process was tested on four different hard-rock-mine-drainage effluents, and process performance and effluent composition were determined. If the water has only significant concentrations of zinc and minor concentrations of manganese, then removal of 90 % or more of the zinc is achieved. If the water has significant Mn concentration (≈ 50 mg/L) and minor Zn concentration, then removal of manganese is much more difficult and only after significant processing can the concentration of manganese be lowered to below 5 mg/L. Sludge volumes generated by the process are significantly smaller, only 10 % of those generated by hydroxide precipitation.

Additional Key Words: water treatment, carbon dioxide, pulsed limestone bed, aquatic chemistry, mine drainage, manganese, zinc, AMD

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Introduction

Many mining-related sites have discharges that are not acidic at all, but are circumneutral in pH (Rose and Cravotta, 1998). However, these circumneutral waters often contain elevated concentrations of metals potentially harmful to aquatic life, including zinc (Zn), cadmium (Cd) and manganese (Mn) (Wildeman and Schmiermund, 2004). The metals can be removed by addition of an alkaline agent to bring the pH to 10, followed by settling or filtration to remove the precipitates, and readjustment of the pH for discharge into the environment. This process has the drawback of generating voluminous sludges that require expensive handling and disposal. Reagent costs are high because lime ($\text{Ca}(\text{OH})_2$) or sodium hydroxide (NaOH) is typically required. In addition, the pH readjustment requires further processing of the solution. A method that would (1) remove these potentially harmful metals without requiring lime or sodium hydroxide addition, and (2) not generate large quantities of sludge and require pH readjustment would be a vast improvement in treatment technology. A process consisting of co-precipitation of the metals Zn, Cd, and Mn in a calcium-carbonate (CaCO_3 or calcite) matrix has been observed by one of the authors under natural conditions in the field. Preliminary laboratory tests on synthetic water containing Zn and Mn at 50 mg/L each has shown that this method of removal has promise (Sibrell et al., 2007). The purpose of this paper is to report on a recent laboratory testing program to try this co-precipitation process on four mining-influenced waters that have significant concentrations of Mn and/or Zn. The method uses a combination of a pulsed limestone bed (PLB; Sibrell, et al. 2000, 2003) and drainage channels lined with limestone for the co-precipitation process. The optimum conditions for metal removal were investigated and these conditions were used to test the water samples. Also, sludge volumes from the co-precipitation process and from traditional treatments are compared.

Test Sites and Methods

Test Sites

At least 40 liters of water from each of four sites were collected. To ensure that the chemistry of the water did not change, the containers were completely filled so that exposure to air was minimized. The conditions measured just prior to testing are shown in Table 1. The metals concentrations given throughout this paper were determined using inductively-coupled plasma, atomic emission spectroscopy (ICP-AES). Because the Wellington Oro water contained a significant concentration of iron, its chemistry changed after sample collection. At collection, the sample pH was 6.3 and the alkalinity was 29 mg CaCO_3/L ; however, the chemistry just prior to use is given in Table 1. A description of each of the sample sites is given below.

Table 1. Chemistry of the four mining-influenced waters that were tested. Concentrations are in mg/L, alkalinities are in mg CaCO₃/L, and pH is in standard units. The chemistry is from samples taken just prior to the start of experiments.

Constituents	Water concentrations in mg/L (pH in SU)			
	<i>Palmerton</i>	<i>Doe Run</i>	<i>Argo</i>	<i>Well. Oro</i>
pH	7.15	7.80	6.41	4.46
Alkalinity (mg/L CaCO ₃)	25	169	68	0.0-
[Ca]	373	254	545	261
[Mg]	272	91	114	102
[Mn]	56	0.40	55	46
[Zn]	328	7.8	24	117
[Fe]	BDL	BDL	0.035	83

Palmerton Site. The Palmerton site near Palmerton, Pennsylvania, was a Zn smelter that has operated in this location since the early 1900s, with a resulting pile of smelter slag and residue nearly one-mile long. Water infiltrating the pile has contaminated ground water in the area, and has prompted the listing of the site by the U.S. Environmental Protection Agency (U.S. EPA) on the National Priority List (NPL) for remediation. A sample was obtained at the Palmerton site in August of 2005 with the cooperation of site contractors and the U.S. EPA. This water was chosen for its very high Zn concentration.

Argo Tunnel Site. Currently, the State of Colorado and the U.S. EPA are operating a plant to treat up to 2650 L/min of acid-mine drainage (AMD) discharging from the Argo Tunnel site, in Idaho Springs, Colorado. Sodium hydroxide was initially used as the neutralizing agent, but now lime is being used as the neutralizing reagent. Treatment consists of adding lime to reach a pH value of 10, settling and filtration to remove the resulting solids, and reacidification to pH 8 with carbon dioxide. Although the process results in good effluent quality and metal removal, the operating costs are high due to the cost of lime and the handling and disposal of the solid precipitate, which tends to encapsulate large amounts of water. Consequently, limestone neutralization using a PLB reactor has been tested at this site for two reasons (Sibrell et al., 2005). First, the low cost of limestone typically makes it the cheapest agent for acid neutralization. Second, the resulting solid precipitate is usually denser and settles more rapidly than lime or hydroxide sludges, so handling and disposal costs would be decreased. The influent into the pilot PLB had a pH of around 3 and average Fe and Al concentrations of 35.2 and 11.5 mg/L. The water used in this study was the effluent from the PLB after it had been air stripped. Consequently for the water in Table 1, all of the Fe and Al are removed and there is alkalinity in the water. This water was chosen because it presented the possibility of determining whether the Mn and Zn could be removed from severe acid rock drainage by sending the water through a PLB for a second time.

Elvins-Rivermines Site. The Elvins-Rivermines site (Doe Run) is a closed 100-acre lead-mine-tailings basin about 60 miles southwest of St. Louis, Missouri. The surface of the tailings basin has been regraded and is being revegetated by the Doe Run Company. Currently, neutral-pH seepage from the toe of the main tailings embankment discharges from the site at about 150 gallons per minute and this flow is expected to decrease when the vegetation on the cover

matures. Dissolved Zn concentrations in the seepage range from about 18 to 24 mg/L. Doe Run Company, with assistance from the U.S. EPA, plans to construct a passive treatment system to receive the residual seepage. The primary components of the system will include a sulfate-reducing bioreactor (SRBR) followed by an aerobic polishing cell/wetland. This technology has been successfully treating 1,200 gpm of discharge at Doe Run's West Fork Unit since 1996. This water was chosen for study because it is a good example of circumneutral water that contains a significant concentration of Zn and minor Mn. Such water is quite prevalent in mined areas in the western United States such as the Coeur d'Alene Mining District in Idaho.

Wellington Oro Mine Site. The French Gulch Wellington Oro Mine is located one mile east of Breckenridge, Colorado. The majority of the lead-zinc-copper-silver sulfide ores were extracted between the 1880s and 1930s. During this period, the underground mine workings consisted of more than 12 miles of tunnels, adits, drifts, stopes, and crosscuts. Mining ceased in 1972 and the site was added to the U.S. EPA NPL list in 1988. Subsequently, the site was deeded to Summit County, and the Town of Breckenridge and the county have initiated a semi-passive treatment using the BioteQ® process, which uses sulfide generated by a sulfate reduction plant to precipitate Fe, Zn, and Cd. This water was chosen because it has a significant concentration of iron as well as Zn.

The Pulsed Limestone Bed (PLB) Process

The PLB was developed as an active method for remediation of mine-drainage sites (Sibrell, et al. 2000, 2003). Water is cycled through two columns filled with limestone and a third column injected with carbon dioxide, the carbonator column. The addition of CO₂ increases the solubility of calcite and the concentration of bicarbonate. After passing through the PLB, the water is air-stripped to remove excess CO₂ and this induces precipitation of calcite and the co-precipitation of metals into the calcite. A laboratory-sized PLB reactor was used, and the optimum operating conditions (determined in a previous study) were 0.25 L/min inflow, 0.50 L/min recycle flow, carbon dioxide pressure of between 34.5 and 104 kPa (5 to 15 lb/in²), and a carbonator water level of 23 cm (Sibrell et al., 2007). Also, in the previous study, the optimum finishing processes were determined to be air stripping for one hour to remove excess carbon dioxide, and then pumping the water through channels lined with crushed limestone. Unless noted, these conditions were used for all of the experiments in this study. Figure 1 is a diagram of the PLB system.

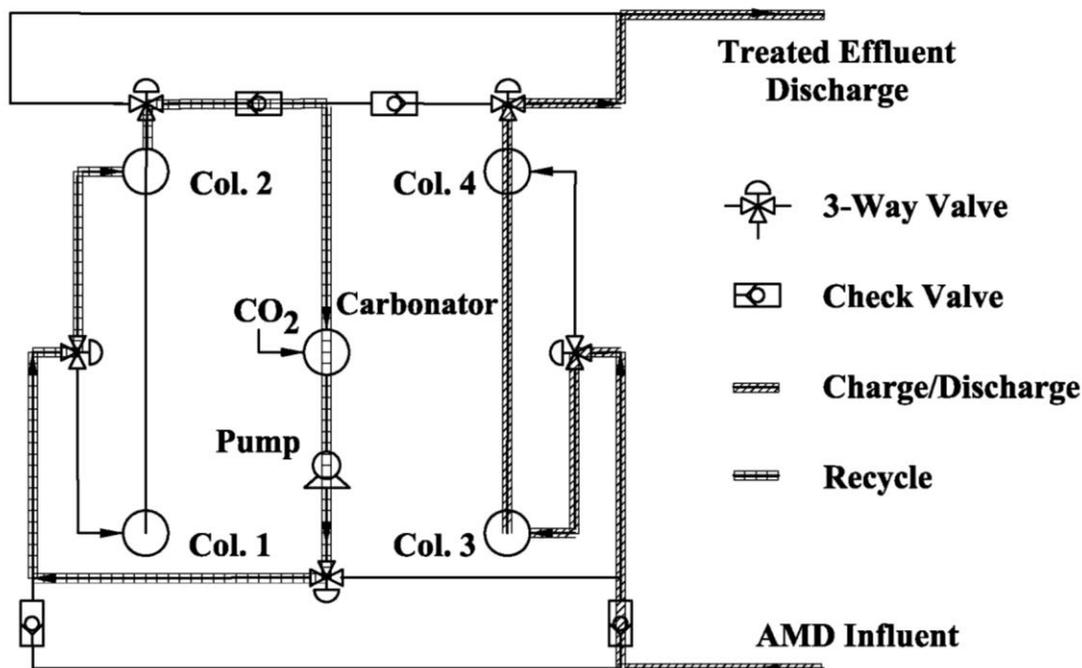


Figure 1. A schematic diagram of pulsed limestone bed (PLB) system.

Palmerton Experiments and Results

In a previous study on the Palmerton water, Mn and Zn were reduced to 24 and 5 mg/L, respectively, by cycling the solution through the PLB for two hours (Sibrell et al., 2007). The first objective of this study was to try to duplicate those removal results on the Palmerton water and to try to remove as much Zn and Mn as possible. In the replication, the water was diluted 1:1, the conditions stated above were used, the solution was cycled through the PLB for 24 minutes, the effluent was air stripped for one hour, and then run through the channel at 100 ml/min for 2 hours. The concentrations of Ca, Mn, and Zn are shown in Fig. 2, and Mn and Zn concentrations of 18 and 27 mg/L were achieved. The longer time in the PLB in the previous study increased the alkalinity to 315 mg CaCO₃/L as compared with 263 mg CaCO₃/L when the solution was in the PLB for 24 minutes. This also generated a higher pH of 7.8 after air stripping as compared with 7.5. Because it was determined in the previous study that the Zn precipitate is hydrozincite, Zn₅(OH)₆(CO₃)₂, an increase of pH will definitely decrease the concentration of Zn.

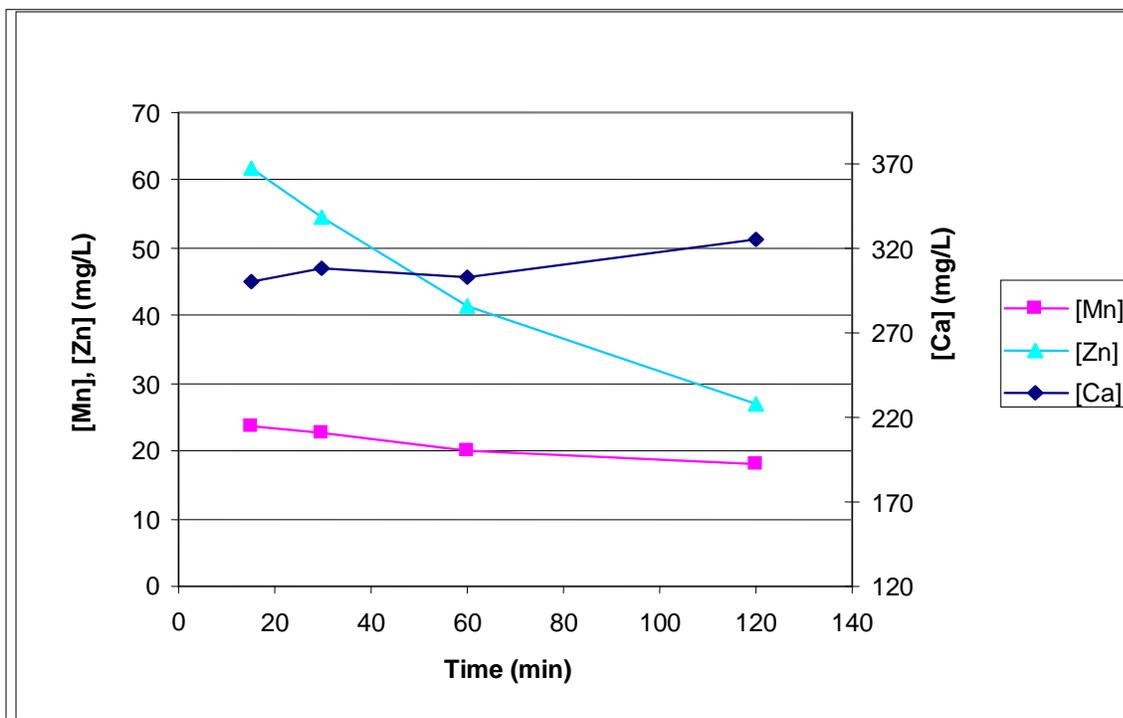


Figure 2. Concentration of Ca, Mn, and Zn after the PLB reactor, air stripping and limestone channel at the Palmerton site near Palmerton, Pennsylvania. The x axis is the time spent in the limestone channel after air stripping.

Recycle Experiments

In the previous study (Sibrell et al., 2007), the best results were achieved when the Palmerton water was recycled through the PLB until the alkalinity was high enough (600 mg CaCO₃/L) to chemically match the precipitation of Zn hydroxide. Thus, a series of recycle experiments were conducted to determine the maximum amount of Zn and Mn that can be removed from the Palmerton water. In the first experiment, Palmerton water was recycled through the PLB using the standard conditions for 145 minutes, raising the alkalinity to 678 mg CaCO₃/L. Then the effluent was air stripped, and run through the limestone channel for up to 120 minutes. The results for Mn, Zn and Ca concentrations are shown in Fig. 3. Removal for Mn and Zn was down to 37 and 10 mg/L; which are comparable to the results from the previous study.

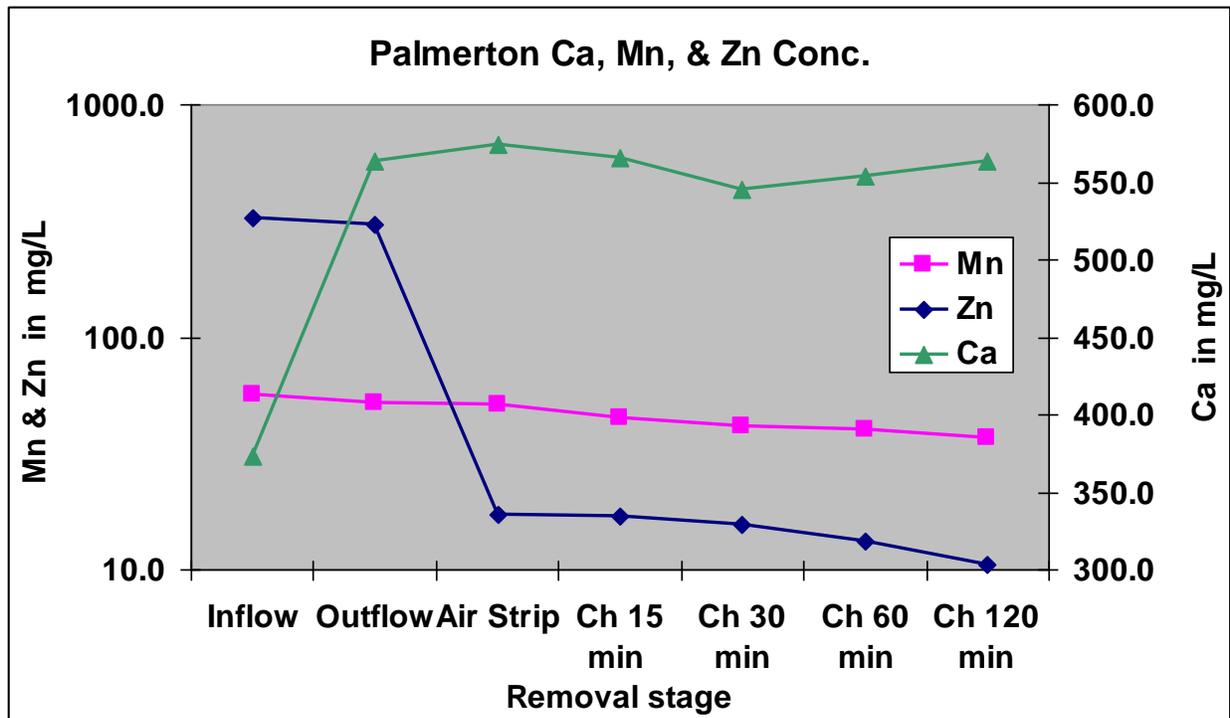


Figure 3. Mn, Zn, and Ca concentrations (mg/L) at various removal stages in the first recycle experiment using Palmerston water. The original concentrations are given in Table 1.

In the next recycle variation, water was continuously pumped from the PLB to the channels and then the channel effluent was directed back into the PLB feed. This variation was not effective in removing Zn or Mn. A sample of the effluent was taken after the run and air stripped, and only then did the Zn precipitate out of solution. It was determined that air stripping was necessary for the precipitation to occur. In the third recycle variation, an air-stripping container was placed between the PLB and the limestone channel, the water in the container was stirred at 300 rpm and decanted continuously into the channel, and the channel effluent was recycled into the PLB. The air stripping/stirring caused the Zn to precipitate; however, the precipitate was carried over to the limestone channel. The concentrations of Mn and Zn were again lowered to 35 and 11 mg/L, about the same as the first recycle experiment.

Finally, to ensure removal of Zn, a second limestone channel was added to the system, and the limestone in the channels was sculpted into small hills that caused the water to form ponds in the channels. This topography increased the retention time in the channel and gave a better removal of Mn from the water. Palmerston water was run through the PLB and was recycled until the alkalinity reached 634 mg/L. It continued to recycle while water was pumped to the channels at 29 ml/min. The system was run at these settings over the course of several days. The first two days the PLB was run and the system was stopped overnight. After the second day the PLB was not run but the channels continued and ran overnight for three more days to determine how much Mn and Zn can be removed. The results are summarized in Table 2.

Table 2. Ca, Mn and Zn concentrations, alkalinity, and pH for five consecutive days of treating Palmerston water.

	End of Day				
	1	2	3	4	5
PLB Run	Yes	Yes	No	No	No
Ca (mg/L)	620	706	672	580	580
Mn (mg/L)	49	29	12	5.5	5.7
Zn (mg/L)	49	7.1	1.20	1.05	1.23
Alk.(mg CaCO ₃ /L)	300	282	214	120	124
pH	7.5	7.9	8.0	8.0	8.1

Experiments and Results on the Other Waters

Standard Treatment Design

Based on the results of the previous year (Sibrell et al., 2007) and the experience with the Palmerton water, a standard treatment procedure for the other waters was determined. The PLB was run at the standard conditions previously described, the effluent was air stripped for one hour, and then the water was run through two limestone channels that had ponds built into them. Instead of continuously recycling the water, the water draining from the second channel was collected and then run through the PLB a second time, then again through the air stripper and two limestone channels.

Doe Run Water

Using the standard design, the water from the Elvins Rivermines (Doe Run) described in Table 1 was treated. The results are shown in Fig. 4. At the end of the second PLB and channel run, the concentrations of Mn and Zn had been reduced to 0.06 and 0.11 mg/L, the pH of the water was 7.8, and the alkalinity was 286 mg CaCO₃/L. Among the four waters tested, this constituted removal to the lowest concentrations of Mn and Zn.

Argo Tunnel Water

The Argo Tunnel water was collected as the effluent from the air stripper during a 48-hour run of the PLB at the Argo Tunnel in Idaho Springs, Colorado. The samples were collected at 24, 36, and 48 hours during the run and then combined. The chemistry of the water is described in Table 1. Except for an adjustment made at the end of the first PLB run, the standard treatment design was used. At the end of Run 1, after the water from channel 2 had been collected, it was run again through the limestone channels; it was collected again and run a third time through the limestone channels. The results are shown in Fig. 5 and 6; and the three times through the limestone channels are designated as Run 1 Ch2A, Run 1 Ch2B, and Run 1 Ch2C. When Run 2 through the PLB was started, there was still considerable residual water from the Run 1 in the columns, which is why the concentration of Mn and Zn in Run 2 effluent rose.

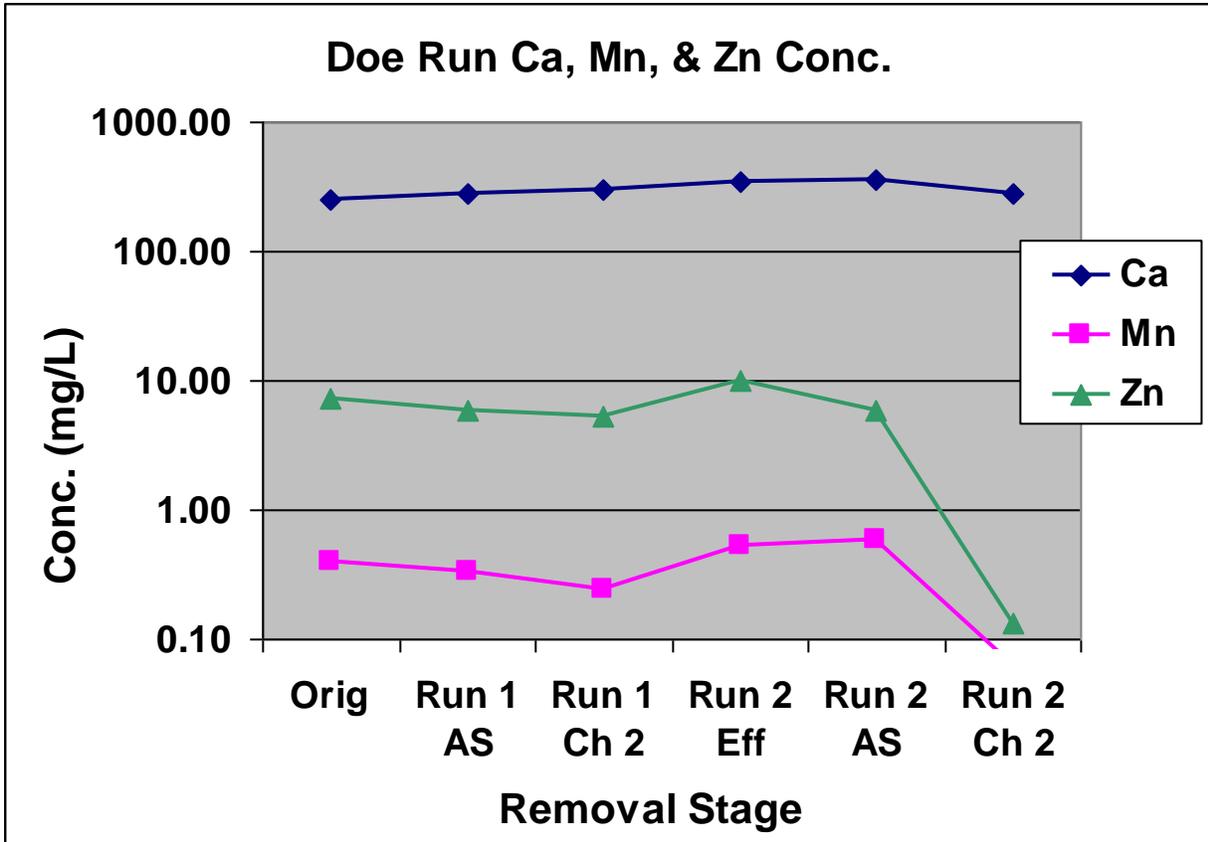


Figure 4. Concentrations of Ca, Mn, and Zn in mg/L for the Doe Run Water using the standard treatment method.

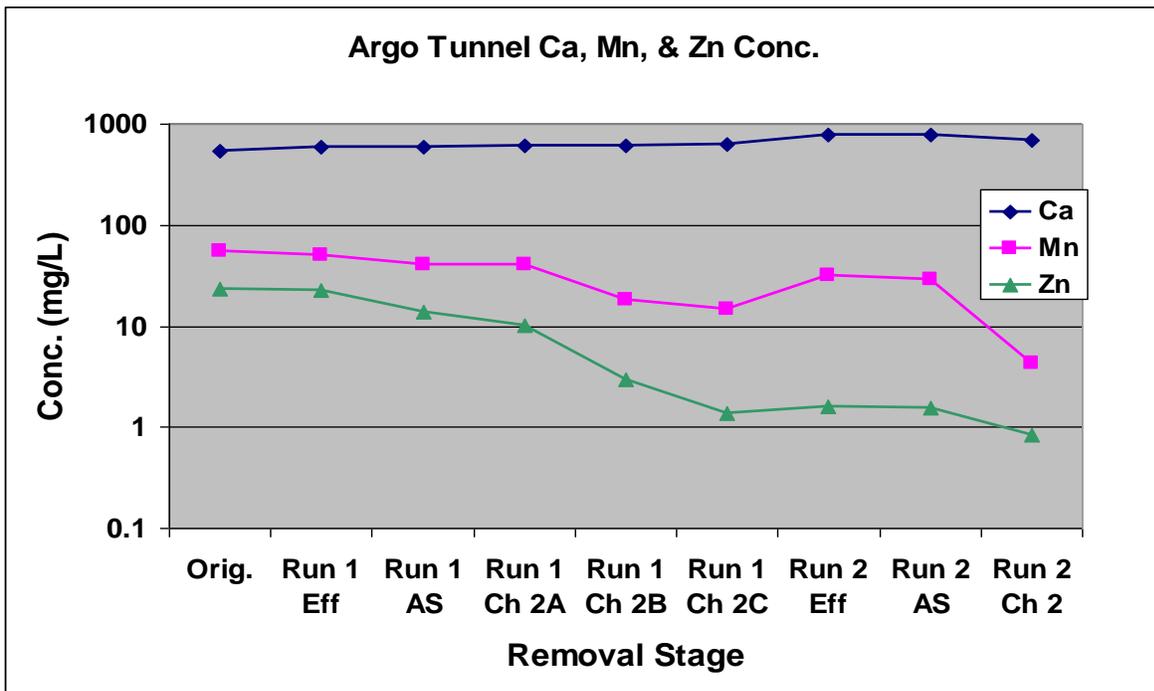


Figure 5. Concentrations of Ca, Mn, and Zn in mg/L for the Argo Tunnel Water using the standard treatment method.

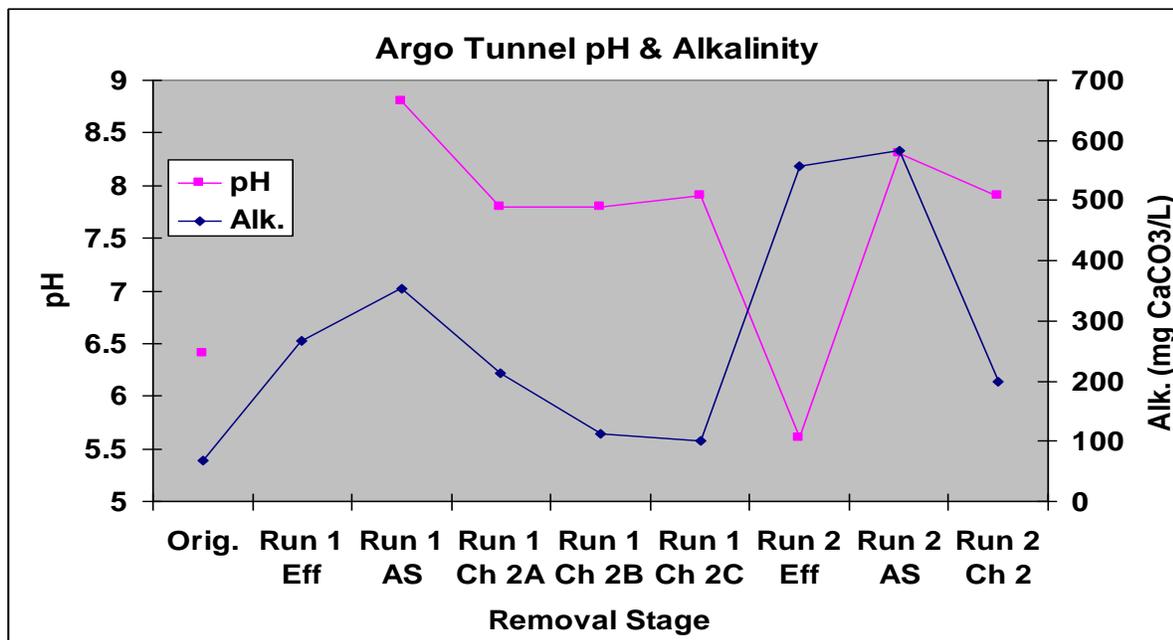


Figure 6. Alkalinity (mg CaCO₃/L) and pH for the Argo Tunnel Water using the standard treatment method.

Wellington Oro Water

Using the standard design, the water from the Wellington Oro Mine described in Table 1 was treated. The results are shown in Fig. 7 and 8. One reason this water was chosen was because it contained 83 mg/L of Fe. The Fe was completely removed in the air stripper during the first PLB run. Also, Wellington Oro water remaining in the PLB caused the concentration of Zn to increase in the effluent of Run 2.

Sludge Volume Measurements

Sludge volumes were measured using the Standard Methods for the Examination of Water and Wastewater method for settleable solids (APHA, 1995). For each treatment, 1 L of effluent was placed in an Imhoff cone and allowed to settle. After 45 minutes, the cone was gently turned to cause any solids collecting on the sides to fall to the bottom of the cone. The volume of settled solids was measured after one hour of settling (Table 3). Palmerton water had three sludge measurements from limestone treatments: 29, 18, and 11 ml/L. For comparison, sludge volumes generated by a titration of the water to a pH of 10 with sodium hydroxide were measured for the waters.

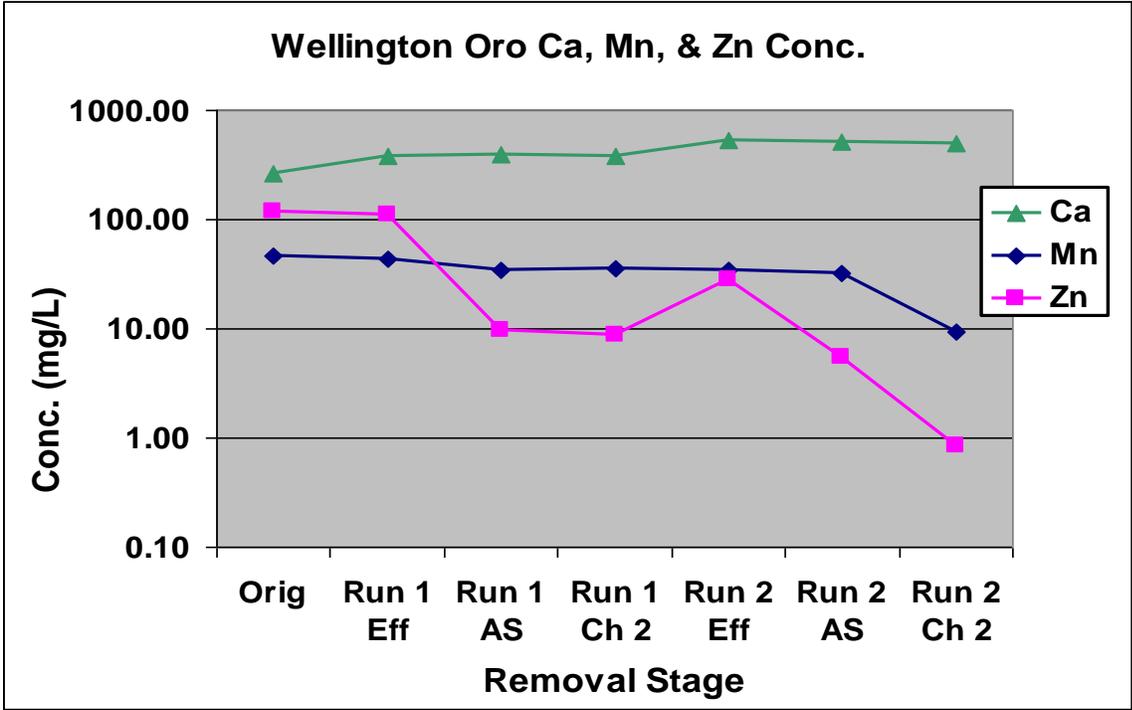


Figure 7. Concentrations of Ca, Mn, and Zn in mg/L for the Wellington Oro water using the standard treatment method.

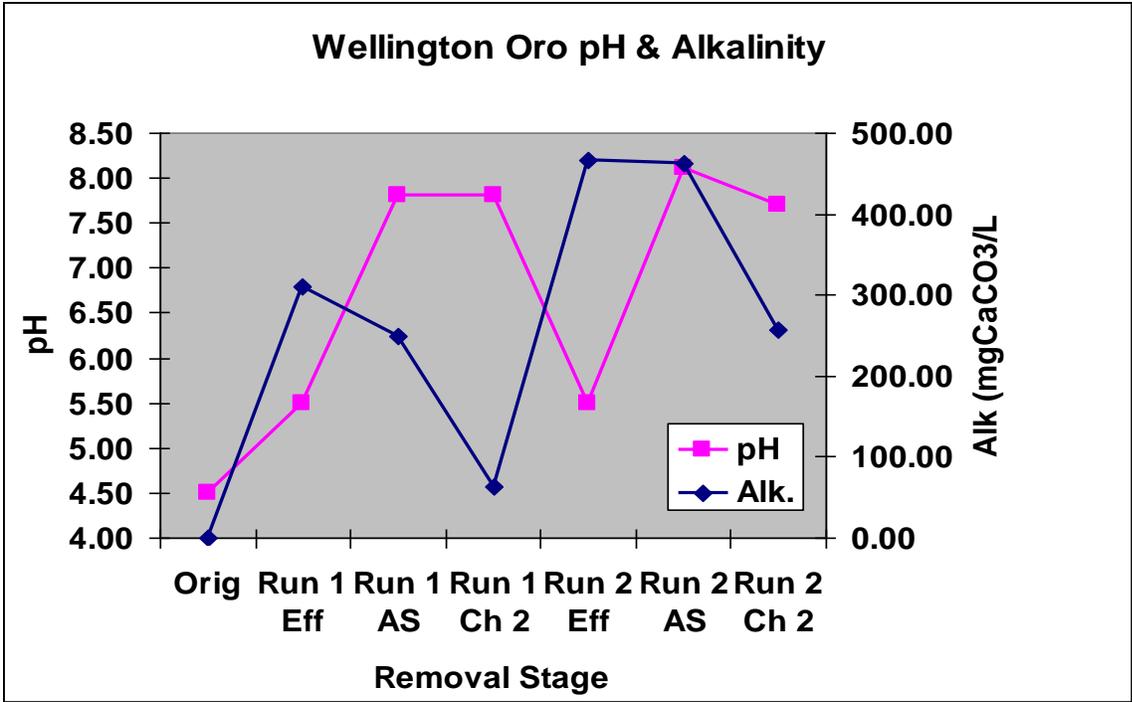


Figure 8. Alkalinity (mg CaCO₃/L) and pH for the Wellington Oro water using the standard treatment method.

Table 3. Comparison of sludge volumes from the PLB limestone precipitation versus titration with sodium hydroxide.

Sludge Volume Comparison			
Sample	Method	Sludge Volume (mL/L)	% Reduction
Doe Run	titration to pH 10 w/NaOH	3.25	
	limestone treatment	0.4	87.7%
Palmerton	titration to pH 10 w/NaOH	275	
	Average value of three limestone treatments	19	93.1%
Wellington Oro	titration to pH 10 w/NaOH	200	
	limestone treatment	23	88.5%

Discussion of Results

Manganese Removal

Water from the Palmerton site was used in method development of the PLB/limestone channel system. This previous testing achieved almost complete removal of Zn and 40% removal of Mn. This testing was continued to find conditions that increase Mn removal. Further development of the channels, including addition of ponds in the channels, has increased Mn removal to about 90 %. These results are shown in Table 4.

Table 4. Maximum removal of Mn in mg/L in the four waters tested.

Maximum Mn Removal			
Sample	Initial [Mn] (mg/L)	Final [Mn] (mg/L)	% Removed
Palmerton (previous study)	57	33	42
Palmerton (this study)	56	5.5	90.1
Doe Run	0.40	0.06	85
Argo	55	4.3	92
Wellington Oro	46	6.1	87

However, for coal mine drainages, the Mn criteria concentration limit is 2 mg/L, and that concentration was not achieved when dealing with these waters that had high initial concentrations. If further testing is done, it would be reasonable to try some coal-mine drainages that have Mn concentrations below 10 mg/L, a more typical concentration (Cravotta, 2006). Also, using limestone rock filters to remove moderate concentrations of Mn have met with success (Cravotta, and Trahan, 1999; Means and Rose, 2005). If the contaminated water was first sent through a PLB to remove iron and add alkalinity, and then was run through a limestone rock filter, the pH would rapidly rise to around 8.0 and Mn would rapidly be oxidized to Mn(IV) and precipitated as MnO₂ (Clayton et al., 1998). Also, in these limestone-rock filters, algae and manganese-oxidizing bacteria catalyze the Mn removal (Means and Rose, 2005); however, bacterial catalysis was not available in this laboratory study. Consequently, it appears at this time that if Mn removal from net alkaline waters is the objective, the best use of this technology is to run the water through the PLB and air stripper so that all other metals are removed and

considerable alkalinity is added to the water. Then, Mn removal in a limestone rock filter would be more efficient.

Finally, in the previous study, spectroscopic examination of the limestone from the channels revealed no discrete Mn minerals; however, Mn was found in the limestone that was used in the channels after the studies had been completed (Sibrell et al., 2007). This provides evidence that indeed co-precipitation of Mn into the calcite structure is the mechanism for removal. This mechanism is confirmed by the fact that, in this study, significant Mn removal in the limestone channels is accompanied by a decrease in the concentration of Ca.

Zinc Removal

For Zn removal, there are two distinct situations: when Zn is the dominant metal over Mn (best exemplified by the Doe Run water), and when Mn is the dominant metal over Zn (exemplified by the other three waters during late-stage removal). For the Doe Run water, Zn removal in the two-stage process was 97 % and was reduced to 0.11 mg/L, a value close to the 0.10 mg/L aquatic toxicity standard for water with a hardness of 100 mg CaCO₃/L (Colorado, 2006). In addition, considerable bicarbonate alkalinity has been added to the water and according to the Biotic Ligand Model this alkalinity complexes the remaining Zn and renders it unavailable for incorporation into aquatic organisms (Ranville et al., 2006). The results show that for waters where Zn is the predominant metal contaminant, the PLB process would be a good alternative to traditional hydroxide treatment. In addition, for the original Palmerton and Wellington Oro waters, where the Zn concentration is high and considerably greater than the Mn concentration, removal of the Zn in the air stripper after the first run through the PLB was about 90 %. This would be a good method for removing high concentrations of Zn so the water would be suitable to run through a sulfate-reducing bioreactor for removal of Zn down to aquatic toxicity limits (Gusek, 2004). In this mode, if the water were run through the PLB and then held in an aeration pond for several hours, Zn concentrations should decrease to around 10 mg/L.

In situations where the Mn concentration is over five times greater than the Zn, then Zn removal is controlled by Mn removal, which is controlled by calcite precipitation. This is seen in Table 2 for the Palmerton water and in Fig. 5 and 7 for the Argo and Wellington Oro waters where Mn and Zn concentrations are reduced when the Ca concentration decreases. Also, this situation is somewhat controlled by the pH. Making a simplifying assumption that zinc hydroxide is the precipitating phase and using a solubility product of 4.1×10^{-17} for Zn(OH)₂, the pH has to be 8.21 to drop the concentration of Zn to 1.0 mg/L. Also, without a further rise in the pH, only minor amounts of calcite precipitate. Consequently, when Mn is the dominant metal and the concentration of Zn is below 10 mg/L, calcite precipitations controls Mn and Zn removal.

It has been the experience of one of the authors that when the concentration of Zn in natural waters is significant, the Cd concentration in the water is 100 to 1000 times less than the Zn concentration. Table 5 gives the original Zn and Cd concentrations for each water and the lowest concentrations of Zn and Cd achieved during treatment. The aquatic toxicity standard for Cd is about 0.002 mg/L (Colo. Dept. Health and Environ., 2006). It appears that with this PLB co-precipitation process, if the Zn is removed to about 1.0 mg/L, then the Cd will be removed to close to the aquatic toxicity limits.

Table 5. Maximum amounts of Cd and Zn removed in mg/L in the four waters tested.

	Concentrations in mg/L			
	Zn Orig.	Cd Orig.	Zn Minimum	Cd Minimum
Palmerton	328	0.38	0.97	0.005
Doe Run	7.8	0.0082	0.11	0.0016
Argo	24	0.066	0.63	0.005
Wellington Oro	117	0.099	0.75	0.0029

Sludge Reduction

The use of limestone for removal produces significantly less sludge than traditional treatments, such as pH adjustment with hydroxide. As shown in Table 3, it was found that the use of limestone generated, on average, only 10 % of the sludge that titration with NaOH generated. The reason for this is likely due to the fact that with limestone precipitation hydrozincite is formed as compared with zinc hydroxide formation using hydroxide. In a previous study using hydroxide (Wildeman, personal communication), precipitation of Zn in the Wellington Oro water produced a hydroxide sludge that was over 90 % water. This significant reduction of sludge will be an economic advantage of this PLB system due to a decrease in the cost of sludge removal. In addition, because hydrozincite is formed, the sludge could be easily added to a Zn metallurgical processing circuit and the metal values recovered.

Conclusions

This follow-up study on the removal of Mn and Zn by co-precipitation using a PLB reactor has generated the following conclusions:

- For Mn, the macroscopic removal trends support the hypothesis that it is being removed by co-precipitation by calcite from a solution that was supersaturated by the dissolution of limestone in the PLB.
- For Zn, the macroscopic removal trends support the observation made in the previous study that it is being removed by precipitation of hydrozincite. This action results in a sludge reduction of about 90 %, and the generation of a residue that could be easily processed for Zn recovery.
- For waters that have high concentrations of Mn (≈ 50 mg/L or more), the best removal scenario would be to raise the alkalinity and remove all other metals so that the air-stripped water could easily reach a pH of 8 in a limestone filter. Waters with lower concentrations of Mn need to be tested to see if removal to a concentration below 2 mg/L is possible.
- For waters that have high Zn concentrations (> 100 mg/L), removal of Zn down to a concentration below 10 mg/L is possible using one pass through the PLB along with air stripping. The water should be recycled through the PLB until the alkalinity generated is greater than the acidity generated by the precipitation of zinc hydroxide.

- For waters with moderate Zn concentrations (< 20 mg/L) and low concentrations of Mn, removal of Zn to concentrations below 0.2 mg/L should be possible using 2 passes through the PLB reactor along with settling in the air stripper. In a full-scale system, this may require two PLB systems to be set up in series; a situation that would add to the capitol costs of the treatment system.

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