COMPARISON OF SLUDGE CHARACTERISTICS BETWEEN LIME AND LIMESTONE/LIME TREATMENT OF ACID MINE DRAINAGE[1]

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Abstract: The U.S. Geological Survey, in cooperation with the Colorado School of Mines and the U.S. Environmental Protection Agency, has demonstrated the application of pulsed limestone bed (PLB) treatment of acid mine drainage (AMD) at the Argo tunnel discharge near Idaho Springs, Colorado. Current technology for AMD treatment at the Argo facility is neutralization with lime. However, lime neutralization often results in large amounts of highly hydrated metal oxide sludge, leading to high disposal costs. Use of the PLB process as a pretreatment typically offers cost savings not only through lower reagent costs, but also through decreased sludge volume. In this study we compared the characteristics of sludges created using lime only to a sludge that was pretreated with the PLB, followed by lime treatment. Lime treatment was performed batch-wise in a 60 gallon cone-bottom stirred tank where the pH was elevated to 10, and held for an hour. A sample of sludge from the operating treatment plant was also tested for comparison. The PLB/lime treatment was accomplished by first passing the water through the PLB system, followed by batch lime treatment to pH 10 as before. The sludge qualities were evaluated through settled sludge volume, filterability through a bench-scale filter press, and the moisture percentage in the filter cake. The PLB/lime treatment resulted in a decrease in sludge volume of 34% after 24 hours, with good filtration performance, and a final cake solids content of 22% versus 19% for the lime sludge. A decrease in lime consumption of 45% was also obtained with the PLB pretreatment.

Additional Key Words: acid mine drainage, mining impacted water, treatment, fluidized bed reactor, limestone, sludge, filtration

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Background

Lime treatment of acid mine drainage (AMD) is the current treatment of choice at the Argo Tunnel in Idaho Springs, Colorado. Although lime as a treatment alternative can lead to good effluent water quality, it also can be quite expensive. The current full scale treatment plant has an average annual operating budget of about $0.9 million (Scott, 2005). Much of this expense is due to the costs for reagent and for sludge handling. From the perspective of both cost as well as a worker safety, limestone as a treatment material is much more desirable, and has been used in the treatment of AMD both in passive and active treatment trains (Cravotta and Trahan, 1999; Sibrell et al., 2005; Skousen, 1991; Watzlaf et al., 2004; Ziemkiewicz et al., 1994). However, operators have been hesitant to use limestone because of problems associated with slow dissolution rates and armoring of the limestone surface.

Another major issue in AMD is the high concentration of dissolved metals (Wildeman and Schmiermund, 2004). As the pH of an AMD source is increased from acidic to circum-neutral via limestone dissolution, the Fe^{3+} and Al are removed, predominantly as their respective hydroxides (Kairies et al., 2005; Cravotta, 2006). Other metals are removed with variable efficiencies and through several different possible mechanisms. These mechanisms can include discrete precipitation, sorption to, and co-precipitation with the Fe and Al precipitates or with calcite depending on the metal in question and conditions in the limestone system (Cravotta, 2006; Karthikeyan et al., 1997; Miller, 2006; Lee et al., 2002; Trivedi and Axe, 2001; Zachara et al., 1991). Two very problematic metals are Mn^{2+} and Zn. Neither of these metals will precipitate to dischargeable levels at the circum-neutral pH of the average limestone system effluent. Thus, a secondary treatment of some sort is needed, depending on influent water quality and discharge standards.

As a treatment process for neutralization and partial metal removal, the pulsed limestone bed (PLB) system has already been proven effective (Sibrell and Watten, 2003; Sibrell et al., 2003; Watten et al., 2004; Sibrell et al., 2005). One avenue that has yet to be explored with regard to the operating of this system is the characteristics of the sludge. The goal of this paper is to compare the sludge quality of the traditional lime-only treatment process, with that of the limestone/lime "mixed treatment". In a traditional lime treatment plant, the pH is raised to 10 to precipitate out all of the metals and the pH is re-adjusted with acid prior to discharge. Sequential limestone and lime treatment, using the limestone to neutralize pH and the lime to remove the remaining metals, will lead to water quality similar to that from lime treatment alone. The question that remains is whether this coupling of treatment technology will come at a lower overall cost. Due to the differing mechanisms of metal removal, as well as the different water chemistries involved in the different treatment processes, it was hypothesized that the sludge for the mixed treatment process would be more easily filterable, have less volume, and would lead to an overall reduction of lime consumption compared to traditional lime-only treatment.

Methods

Three sludges were compared for relative settling rates, filterability, and percent moisture in the filter cake. These sludges came from three different treatment methods of the same influent water: sludge from the full-scale, operating Argo plant, sludge from lime treatment of a PLB-treated effluent, and batch lime treatment of the Argo tunnel influent.

Influent Water Quality

Pertinent water quality data from the Argo Tunnel is summarized in Table 1. The high degree of variability in the water quality is caused by filter backwashing in the full scale plant. When the filters are backwashed, the backwash water is mixed with fresh influent in the equalization basins that feed the plant. The backwash water has a neutral-to-alkaline pH and, when mixed with the acidic influent, there is partial neutralization and metal removal.

Table 1. Influent water quality data for Argo Tunnel. Metal concentrations are in mg/L and pH is in standard units.

		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

Full-Scale Plant Sludge

The current treatment train in the lime-based operating plant can be summarized as follows. The influent accumulates in an equilibration basin before entering the plant. From there it is mixed with hydrated lime until a pH of 10 is achieved. This mixture is sent to a sludge thickener where the precipitates settle by the force of gravity from the water. Polymeric flocculant is added here to improve settling and filtration performance. The overflow water is polished using a sand filter, and then treated with HCl to achieve a discharge pH of 8.0-8.3. The precipitates are pumped from the bottom of the sludge thickener and then sent to a plate-and-frame filter press. The filter cake solids fraction is sent for disposal and the liquid is returned to the sand filter. The sludge for the experiments described here was taken from the bottom of the sludge thickener and tested in the "as-is" condition.

Mixed-Treatment Sludge

The PLB system has been well described in literature (Sibrell and Watten, 2003; Sibrell et al., 2003; Watten et al., 2004; Sibrell et al., 2005), and thus only a brief summary is presented here. The reactor system uses sand-size limestone as the major treatment material. The mine water is pumped upwards through the reactor columns, thus fluidizing the limestone to provide attrition for prevention of armoring of the limestone surface. Because the columns are closed to the atmosphere, the CO_2 released from the limestone dissolution remains dissolved in the water. Precipitates that may form are flushed out of the system by the active pumping. The mine water also passes through a packed-bed absorber where commercial CO_2 may be added to the water. The added CO_2 leads to more limestone dissolution, and thus potentially higher alkalinity and pH in the effluent. This gives the plant operator flexibility in the amount of alkalinity imparted to the water. For this series of tests, however, no additional CO_2 was added to the Argo water during the PLB pretreatment process. Excess CO_2 is stripped and recycled from the effluent to the influent. After treatment, there is still some residual dissolved CO_2 remaining in the water. This is removed from solution by stripping the water with air. Upon removal of the CO_2, the pH increases further.

To fully precipitate the metal contaminants from the water, a pH of 10 is required. Since limestone will give a maximum pH of 8.3, addition of lime was required after air stripping was completed. Subsequent lime treatment of the PLB effluent was performed in batches in a 60 gallon cone-bottom tank. Once the tank had been filled, the solution was air-stripped using a forced air diffuser until a constant pH was attained. The process took approximately one hour. A measured amount of the slaked lime slurry used by the full-scale treatment plant was added to the solution in the tank to achieve a pH of 10.0. This solution was constantly stirred and enough lime slurry was added to maintain a pH of 10.0 for one hour. Once the reaction time had elapsed, the stirring was ceased, and the sludge volume was recorded as a function of time as gravity settling proceeded. Initially, sludge settling rates were measured by taking a 1-L sample of stirred suspension and settling in an Imhoff cone. Readings were taken of the sludge volume after 30 minutes and after 24 hours. In later tests, the sludge volume was measured directly in the cone-bottom tank.

In order to get enough sludge to perform tests with a bench-scale filter press, this process had to be repeated several times (about five 60 gallon batches to create 10 gallons of settled sludge). Also, the sludge was not initially thick enough to be fed directly to the filter press, so it was allowed to gravity settle for 2-3 days. After this time, the supernatant was poured off and the filter press tests were performed on this gravity-thickened sludge.

Lime-Only Treatment

For the lime-only treatment sludge, the influent to the pilot plant was diverted to the 60 gallon cone-bottom tank. The rest of the process is identical to the lime treatment of the PLB effluent with the sole exception that it was unnecessary to air-strip the influent. The sludge as produced underwent the same solids concentration steps as the mixed treatment sludge.

Filter Press Procedure

The procedure for the filter press was identical for the three sludge types. Before subjecting the sludge to the filter press, measured volumes were taken (approximately 100 mL) and placed in an oven (105± 5°C) overnight to determine percent solids in the sludge. The filter press had a chamber volume of 44 in^3 (0.02 ft^3) and a filter area of 0.24 ft^2. The sludge was supplied to the press through a diaphragm pump, which was powered by an external air compressor. The pressure behind the sludge into the press was set at 60 lbs/in^2 for all experimental analyses. Effluent volume from the press was measured as a function of time. When the effluent flow out of the filter press had become minimal, the pump was stopped. Each filter press run was from 50 to 55 minutes long

The produced filter cake was placed on tared Al drying pans and dried at 105±5°C until a constant mass was achieved (approximately 22 to 24 hours) in order to determine the percent moisture of the filter cake.

Duplicates of this entire procedure were performed for the operating plant sludge (Argo 1 and 2) and the lime-only treatment sludge (Lime 1 and 2), while the mixed-treatment sludge filtering was performed in quadruplicate (PLB 1-4).

Results and Discussion

Lime Consumption and Sludge Settling

Lime consumption and sludge settling rates are shown in Table 2 for a series of tests conducted with the lime sludge and the PLB pretreated sludge.

Table 2. Lime consumption and sludge settling results. Values reported are means, with standard deviations in parentheses.

Treatment method	Lime Consumption (mL)	Settled volume- Imhoff cone (mL) **	
		30 min	24 hrs
Lime-only (4)*:	3008 (1361)	223 (21)	97 (6)
PLB/Lime (8)*:	1656 (492)	130 (58)	64 (16)

*Number of replicates in parentheses

**Settling values represent the settled volume (mL) at the time indicated

Lime consumption was decreased by 45% through the PLB pretreatment process, representing a potential cost savings to the operator. Some of these savings would be offset by limestone costs, but since limestone is much less expensive than lime, there would still be savings in reagent costs. For example, using a lime cost of $66/T and a limestone cost of $34/T, with a 45% decrease in lime consumption and a limestone consumption of 280 mg/L (as $CaCO_3$), the overall reagent cost reduction amounts to 24%. Significantly lower sludge volumes were also observed for the PLB treated sludge: 42% less after 30 minutes and 34% less after 24 hours of settling time. A decrease in sludge volume would result in smaller capital costs through decreased size of filters needed to process the sludge. Operating costs would be decreased as well. The Argo plant currently has two separate presses, and as many as five filter-press runs per day. A decrease in sludge volume would cut down on the number of press runs required per day, and also reduce labor requirements for plant operation.

The primary purpose of the 60-gallon cone bottom tank was generation of enough sludge for filtration testing, but some settling results were obtained during sludge processing. Figure 1 shows the comparative settling rates of the PLB-pretreated and lime sludges in the cone-bottom tank. Although there is some noise in the data, the PLB pretreated sludge, in general, settled more rapidly and to a smaller volume than the lime sludge. Design of the cone-bottom tank precluded accurate volumetric measurements below a volume of approximately 6 gallons, so no data was available for extended settling times. However, comparison of these results with those obtained with Imhoff cones (Table 2) after 30 minutes of settling shows roughly comparable results, with a settled sludge volume of 13 - 23% for the PLB-pretreated sludge versus 25 - 33% for the lime-only sludge. This suggests that the Imhoff cone results after 24 hr of settling, where there was still an advantage for the PLB sludge (6 vs. 10% sludge volume), could be successfully extrapolated to larger scales of operation.

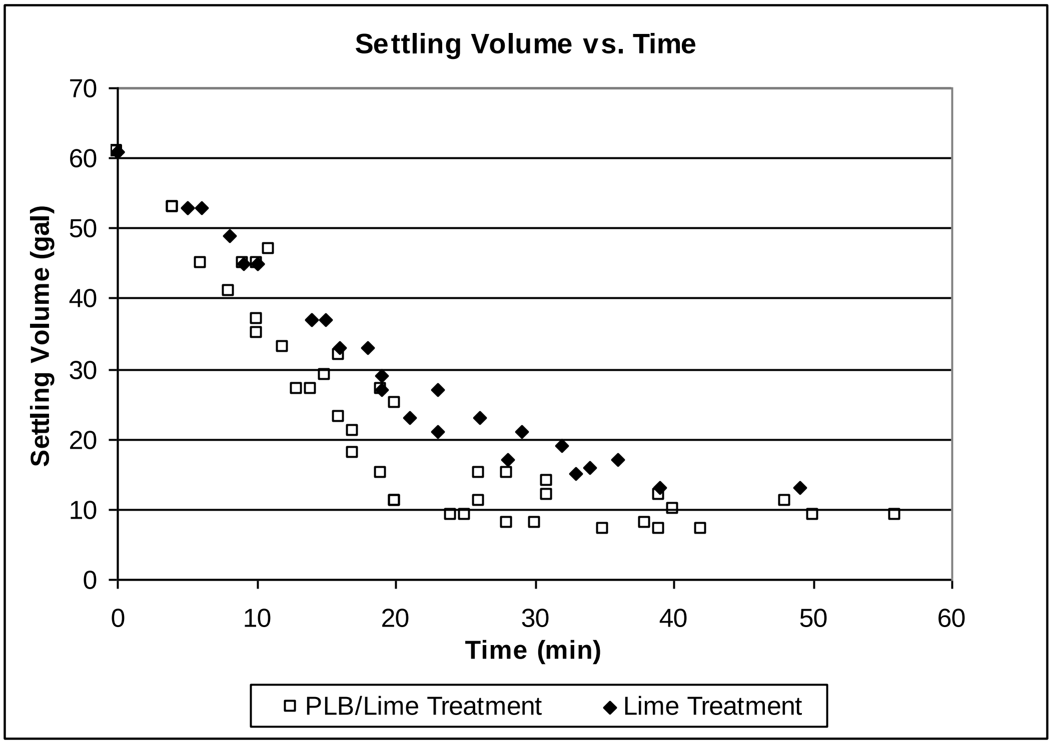

Figure 1. Settling rate comparison – cone bottom tank

Filtration results

Results for the plate-and-frame filter press are shown in Table 3. The filter loading results can be used to estimate the size of the filter press (by area, ft^2) required for full-scale processing based on the number of gallons of sludge per day to be processed. It can be seen that this figure is highly dependent upon the solids content of the feed slurry. The PLB pretreated and lime sludges had loadings of 4 to 7 gal/ft^2, while the Argo operating plant sludge had a loading of about 2 gal/ft^2, but the plant sludge had a much higher feed-solids content of about 6%. Alternatively, the filter press size (by volume, ft^3) can be estimated from the dry cake density. Here it is apparent that the treatment options were more equal, but again the PLB pretreatment gave the highest loading.

In the end, however, it is the solids content of the sludge that determines sludge disposal costs. At the Argo plant, approximately 21,000 pounds of sludge per day are generated and require landfill disposal. Even a small decrease in the water content of the filter cake would pay dividends in decreasing sludge disposal costs. All filtration treatments were for the same period of time, yet the PLB pretreated sludge gave the highest solids content of the three methods tested, at nearly 22% solids. The lime sludge gave about 19% solids, and the operating plant sludge gave 21%, despite starting with a greater initial solids content. It is apparent that the solids content of the feed affects the final cake solids. Since the PLB-pretreated sludge generally gave a higher solids content after settling (Table 2 and Fig. 1), this advantage would carry over into filtration as well, resulting in a higher cake solids content. The plant sludge appears to be a special case, however, because even after starting with a much higher feed solids concentration, the final cake solids content was less than the PLB-pretreated sludge. This may be related to the addition of polymer in the full scale operating plant, which often results in greater moisture retention. Overall, these results indicate that the PLB pretreatment confers an advantage in the filterability of the AMD sludge over conventional lime treatment alone.

Conclusions

Pilot-scale PLB pretreatment of AMD was tested at the Argo treatment plant in Idaho Springs, Colorado. The PLB pretreatment process gave a 45% decrease in the amount of lime required for neutralization to pH 10. Reagent cost would decrease by 24% once limestone consumption and cost were taken into account. No CO_2 was added in these tests, but CO_2 addition generally results in greater alkalinity, and gives the plant operator flexibility in the level of treatment imparted to the water. PLB pretreatment also resulted in faster sludge settling rates and decreases in sludge volume. This would lead to capital cost savings through decreased size of settling basins and filter presses required. At the Argo plant, where the equipment is already in place, decreasing sludge volumes would decrease labor costs, by decreasing the number of filter press runs required each day. The PLB pretreated sludge was readily filtered using a standard plate-and-frame filter press to a cake solids content of 22%, versus 19% for the lime-only treatment, thus indicating improved filterability. In summary, the PLB process offers a robust alternative to conventional lime processing, with advantages with respect to treatment flexibility, and savings in both reagent cost and sludge handling labor costs.

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Table 3. Filtration results

Run ID	Feed Solids (%)	Filtrate Volume (mL)	Wet Cake Weight (g)	Wet Cake Density (lb/ft^3)	Dry Cake Weight (g)	Cake Solids (%)	Dry Cake Density (lb/ft^3)	Filter Loading (gal/ft^2)
PLB-1	3.10	3970.00	647.60	71.38	143.20	22.11	15.78	5.08
PLB-2	1.61	5623.00	586.60	64.66	99.90	17.03	11.01	6.93
PLB-3	3.39	3575.00	629.60	69.40	142.60	22.65	15.72	4.64
PLB-4	4.04	3375.00	638.70	70.40	162.20	25.40	17.88	4.41
Averages:						**21.80**	**15.10**	**5.26**
Lime 1	2.73	3730.00	613.60	67.64	118.40	19.30	13.05	4.81
Lime 2	2.46	4195.00	611.30	67.38	118.20	19.34	13.03	5.33
Averages:						**19.32**	**13.04**	**5.07**
Argo-1	6.46	1535.00	629.00	69.33	139.80	22.23	15.41	2.35
Argo-2	5.93	1413.00	622.50	68.62	120.80	19.41	13.32	2.22
Averages:						**20.82**	**14.36**	**2.28**

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