Mine Water Treatment with Cement Kiln Dust (CKD)

Allison Mackie, Heather Farmer, Margaret Walsh

Dalhousie University, Department of Civil and Resource Engineering, 1360 Barrington Street, Halifax, Nova Scotia, B3J 1Z1, Canada

Abstract Bench-scale treatment trials were performed to determine the efficacy of active mine water treatment using slurries made from four different cement kiln dust (CKD) samples. The results of the study showed that zinc and iron precipitation and removal with all of the CKD slurry samples were statistically comparable to those achieved with quicklime, the industry standard. Total suspended solids (TSS) were found to be elevated in the low free lime CKD-treated samples, but an increase in settling time reduced TSS levels to be comparable to quicklime, along with further reducing metals concentrations.

Key Words Cement Kiln Dust, Quicklime, Mine Water, Acid Rock Drainage, Wastewater Treatment

Introduction

Water that comes into contact with sulphide minerals exposed due to mining activities can be highly acidic and contain elevated amounts of dissolved metals and sulphate. Metal ores in the form of sulphides like pyrite (FeS_2) and sphalerite (ZnS) release acidity and metal ions when exposed to water and oxygen (Evangelou 1995). Conventional active treatment of this contaminated water, termed acid rock drainage (ARD), involves neutralization by alkaline addition and subsequent sedimentation. When quicklime is used as an alkaline reagent, it is first slaked with water in order to hydrate the lime (CaO) to form calcium hydroxide ($Ca(OH)_2$), which then dissociates into hydroxide (OH^-) and calcium (Ca^{++}) ions (Boynton 1980). This highly alkaline slurry is then mixed with the mine water, where the hydroxide ions can combine with dissolved metal ions to precipitate solid metal hydroxides. A polymer flocculant is usually added and treated effluent is then sent to either a clarifier or settling pond to allow precipitated metals and other particulates to settle out and be removed as sludge.

Cement kiln dust (CKD) is a byproduct of cement manufacturing that can contain from 8 to 61 % total CaO, and from zero to 37 % free lime, varying by cement kiln (Mackie et al. 2010). Free lime is the amount of lime that is available for reactions, and is a good indicator of how reactive a CKD will be. This lime content makes it attractive for use as a neutralization/precipitation agent (Mackie et al. 2010). Current reuse options for CKD include soil stabilization, fertilization of crops, solidification and stabilization (S/S) of hazardous wastes, and as a concrete additive, among other applications (Adaska and Taubert 2008). Previous studies have looked at CKD use in removing metal ions from various effluents. Pigaga et al. (2005) evaluated a low free lime content (3 – 7 %) CKD to demontrate metal ion removal from synthetic solutions of Cu, Ni, Pb, Co, and Cd. Zaki et al. (2007) investigated the filtrate of CKD solutions (free lime = 14.8 %), or leachate, to demonstrate removal of Cu, Ni, and Zn ions in synthetic solutions. El-Awady and Sami (1997) studied the treatment of tannery wastewater with CKD in order to remove Cr, Zn, Cd, Cu, Pb, Ni, Fe, and Mn. Close to 100 % removal efficiencies were found at optimum testing conditions in all studies.

The objective of this study was to determine if CKD can be used as an alternative to quicklime in the treatment of ARD. Tests were undertaken to compare the performance of CKD to that of quicklime in precipitating and removing metals, specifically zinc and iron, from the effluent of a lead/zinc mine. The impacts of settling time and slurry concentration on metals removal were also investigated.

Materials and Methods

Slurries of four different CKD samples and one quicklime sample were used to treat 1 litre samples of mine effluent from a lead/zinc mine in a standard jar tester (Phipps and Bird, Fisher Scientific). Key characteristics of the CKD and quicklime samples used in this study are listed in Table 1, with further characteristics presented in Mackie et al. (2010). Lime (CaO) is the main constituent of quicklime and its main active ingredient. Other oxides such as those of Al, K, Mg, Na, Si, and S make up the majority of the remaining constituents in the CKD samples.

***Table 1** Key characteristics of CKD and quicklime samples used in this study*

Sample ID	Free Lime (wt %)	Total Lime (wt %)	Specific Surface Area (m^2/g)	Median Particle Size (µm)
CKD-A	15.0	44.2	0.502	8.5
CKD-B	8.8	47.8	0.350	15.9
CKD-C	5.0	40.3	0.500	20.5
CKD-F	37.0	57.2	0.400	21.2
QUICKLIME	87.0	90.1	0.164	32.0

Mine effluent samples were obtained from a lead-zinc mine located in northeastern New Brunswick, Canada. Effluent treated at this mine's wastewater treatment plant comes from three separate streams: the underground mine itself, an abandoned open pit mine on the site, and runoff and seepage from the tailings pile. The average pH of the collective mine effluent is 2.5 ± 0.1, average total iron is 410 ± 80 mg/L (soluble = 370 ± 80 mg/L), and average total zinc is 117 ± 8 mg/L (soluble = 109 ± 8 mg/L). The pH and metal concentrations of the sampled effluent were measured during each jar test in order to accurately calculate removal percentages.

Calcium hydroxide slurries were made using a modified mixing apparatus designed to simulate slaking. For the 25 % slurries, 1 L of Milli-Q water was added to 250 grams of CKD or quicklime and mixed for a minimum of five minutes. Five percent slurries were made using 50 grams of material per 1 L of water. The appropriate volume of slurry was added to 1 L of mine effluent in order to raise the pH to 9.5, targeting the minimum solubility of zinc. The samples were then rapid mixed at 150 rpm for one minute, at which time 1 mg/L of polymer was added (POLYFLOC AE1138, GE), followed by an additional 30 seconds of rapid mixing. Mixing speed was then reduced to 50 rpm and samples flocculated for 2 minutes. Treated mine effluent samples were allowed to settle quiescently for 30 minutes before settled water was sampled. Four replicates of the batch tests were performed for each of the 25 % slurries, and three for each of the 5 % ones.

Samples of the treated mine effluent were taken at the coagulation stage just prior to polymer addition, and after the settling period. The pH of coagulation and final samples was measured with variable temperature electrodes (accuFlow, Fisher Scientific) using an XL50 meter from Fisher Scientific. Coagulation and final samples were analyzed for total and soluble iron and zinc using an atomic absorption spectrometer (AAnalyst 200, PerkinElmer). Total suspended solids (TSS) concentrations of the settled treated effluent was measured according to Standard Methods for the Examination of Water and Wastewater (APHA et al. 2005). Sludge volumes generated in each of the jar tests were estimated from gradations on the jars of the jar tester.

Statistical comparisons of the CKD treated samples to the quicklime treated sample were performed using Dunnett's method (Mac Berthouex and Brown 2002; Dunnett 1964) and analysis of variance (ANOVA) at both the 95 % and 99 % (if warranted) confidence intervals (CI). Dunnett's method is a way of comparing k means with the mean of a control (i.e. the quicklime slurry-treated samples).

Results and Discussion

Higher addition volumes of the 25 % calcium hydroxide slurries were required to raise the pH of the mine effluent to the target of 9.5 for CKD-A, CKD-B, and CKD-C (low free lime content CKDs) than for CKD-F or quicklime. Specifically, CKD-A required 55 ml; CKD-B, 70 ml; CKD-C, 120 ml; CKD-F, 13 ml; and 8 ml were required for quicklime. The slurry volume added varied proportionately with the free lime content of the CKD sample used to make the calcium hydroxide solution (R^2 = 0.99). These results are similar to results of previous work that found pH achieved in synthetic acid solutions per gram of material added was dependent on free lime content (Mackie et al. 2010).

Treatment of the mine effluent samples with all of the CKD-generated slurry samples, along with the quicklime-generated slurry sample, resulted in efficient precipitation of metals in the coagulation stage. Specifically, over 99 % of soluble iron and zinc in the raw mine effluent was transformed into insoluble compounds (precipitates) within the one minute coagulation (rapid mix) period. Removal of the precipitated metals after settling was also evaluated for both the CKD and quicklime treated mine effluent. Zinc was removed (i.e. settled out) by an average of greater than 98 % for all samples, with no statistically significant difference between the removal efficiency of the CKD and quicklime treated samples at the 95 % CI. Iron was removed at greater than 97 % efficiency for all samples. Slightly lower, but significant, removal of iron was found for CKD-A and CKD-B at the 95 % CI when compared to quicklime, with no significant differences between any samples at the 99 % CI.

TSS concentrations were found to be much higher in the low free lime content CKD-treated samples (i.e. CKD-A, CKD-B, and CKD-C) than in the CKD-F and quicklime-treated mine effluent samples (tab. 2). As shown in Table 1, CKD-A and CKD-B have a smaller mean particle size than CKD-F and quicklime, which may have impacted settling velocities according to Stokes' law. CKD-C has particles similar in size to CKD-F but also required much greater slurry addition. The additional mass of particles added in the CKD-C treated mine effluent may have resulted in the elevated TSS concentrations found in this study. Table 2 also includes the average volume of sludge generated after 30 minutes of settling in the batch treatment tests. All CKD samples were found to generate considerably less sludge than the quicklime sample, even with the higher volume addition of slurry required for treatment and pH target achievement. These are interesting results, in that they indicate lower sludge volumes could be generated through the use of CKD slurry treatment compared to traditional quicklime treatment. Preliminary particle analysis indicates that CKD slurries generate smaller, denser particles during treatment of mine water than quicklime slurries. Further study is required to investigate the potential implications to dewatering processes.

Total and soluble metal concentrations show that the remaining metals are mainly in the particulate (i.e. precipitated) form, except in the case of quicklime (tab.2). Note that when final soluble metals concentrations were found to be below the method detection limit (MDL), a value of half the MDL was substituted for those tests (0.00652 mg/L for zinc and 0.0245 mg/L for iron). This data, along with the TSS data discussed above, indicate that further settling is required for increased metal removal with lower free lime CKDs. Increasing the settling time from 30 minutes to 60 minutes for CKD-B decreased the settled water metal concentrations considerably, to an average of 1.3 ± 0.2 mg/L total iron and 0.18 ± 0.03 mg/L total zinc. The increased settling time had little effect on the settled water samples treated with the CKD-F and quicklime slurries (other CKD samples were not studied). Treatment with the CKD-B slurry was found to remove slightly more zinc (99.87 %) from the mine effluent than quicklime (99.38 %) after 60 minutes of settling, confirmed using Dunnett's method, while CKD-F performed equally to quicklime. Settled water TSS concentrations were also significantly decreased with the additional settling time for the samples treated with the CKD-B slurry, by an average of 86%. No difference in settled water TSS concentrations was found between the 30 and 60 minute settling times with CKD-F or quicklime slurry treatment. However, settled water TSS concentrations were found to be comparably low with the 30 minute settling time experiments for both CKD-F and quicklime. No significant change in sludge volume was noted with increased settling for any of the three slurries.

To investigate the effect of the solids concentration in the CKD and quicklime slurries on contaminant removal, batch treatment trials were performed using 5 % slurries and compared with those performed using 25 % slurries. Table 3 shows that the volumes of 5 % CKD slurry required to raise the pH of the effluent to 9.5 were much higher than the 25 % slurries, but that the actual amount of material added is higher for the 25 % CKD slurries. Overall, the percent zinc and percent iron removal in the treated mine effluent was found to decrease with treatment with the lower

Table 2 *Average settled water total suspended solids (TSS) concentration, volume of sludge generated, and total and soluble metals. Error terms represent one standard deviation*

Sample ID	TSS (mg/l)	Sludge generation (ml/l)	Zinc (mg/l)		Iron (mg/l)	
			Total	Soluble	Total	Soluble
CKD-A	260 ± 104	160 ± 10	2.1 ± 1.2	0.1 ± 0.1	11.8 ± 6.9	0.2 ± 0.2
CKD-B	300 ± 120	153 ± 5	2.8 ± 1.5	0.1 ± 0.1	14.4 ± 7.7	0.1 ± 0.1
CKD-C	310 ± 71	170 ± 20	2.4 ± 1.2	0.2 ± 0.1	8.3 ± 1.4	0.2 ± 0.4
CKD-F	50 ± 20	148 ± 5	0.9 ± 0.2	0.1 ± 0.1	4.6 ± 2.9	0.1 ± 0.2
QUICKLIME	60 ± 20	280 ± 60	1.0 ± 0.3	0.5 ± 0.6	2.9 ± 0.5	1.5 ± 2.3

Table 3 *Comparison of average low and high concentration slurry batch test data. Standard deviations have been omitted for brevity*

Sample ID	Slurry added (ml)		Material added (g)		Zinc removal (%)		Iron removal (%)		TSS (mg/l)		Sludge (ml/l)	
Slurry (%)	**5**	**25**	**5**	**25**	**5**	**25**	**5**	**25**	**5**	**25**	**5**	**25**
CKD-A	200	55	10.0	13.4	78.9	98.2	71.0	96.8	103	262	200	160
CKD-B	220	70	11.0	17.5	85.8	97.6	66.1	96.7	195	302	150	150
CKD-C	350	120	17.5	28.7	84.6	97.9	84.4	97.7	146	310	200	170
CKD-F	55	13	2.7	3.2	87.1	99.0	75.4	98.9	121	48	160	150
QUICKLIME	45	8	2.2	2.0	87.1	99.1	74.7	99.3	25	61	180	280

slurry concentration (tab. 3). No significant difference in TSS concentration or sludge volume generated was found between the 5 % slurry and 25 % slurry treated samples.

Conclusions

The results of this study show that CKD has the potential to replace quicklime in the active treatment of acidic mine effluent. The CKD-generated calcium hydroxide slurries evaluated in this study were found to be effective at neutralizing acidic mine water to raise its pH and remove target metals through precipitation and settling mechanisms. Compared to control experiments with quicklime, higher volumes of the CKD slurries were required proportional to the free lime content of the CKD to achieve the target pH of 9.5 in the mine water samples. However, considerably less sludge by volume was generated in tests with the CKD treatment compared to quicklime treatment, indicating potential benefits of CKD over traditional quicklime. Analysis of the settled water found TSS concentrations were higher in the low free lime content-treated samples (CKD-B) than for CKD-F and quicklime. Increasing the settling time significantly reduced the average TSS concentration of the CKD-B treated mine water, as well as decreasing the average total metal concentrations remaining in solution. Decreasing the CKD and quicklime slurry concentration from 25 % to 5 % significantly decreased the treatment efficiency in terms of metals removal.

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