

UTILIZING INDUSTRIAL WASTES AND ALTERNATIVE REAGENTS TO TREAT ACIDIC DRAINAGE¹

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Abstract: Waste by-products from various industries can be successfully applied to treat acidic drainage. The advantages of utilizing waste material for treatment of other wastes include cost savings, greenhouse gas reduction (from lime) and reduced waste management requirements. Several waste products and their treatment effectiveness were evaluated. The performance of papermill sludge, cement kiln dust (CKD), lime kiln dust (LKD), and calcium magnesium hydrate (CMH) were assessed in terms of treatment efficiency and environmental performance. This study found that these alternative reagents could be used to replace lime in mine water treatment. Significant greenhouse gas (GHG) and reagent cost savings could be realized if lime was replaced with 'waste' or alternative low cost reagents.

Additional Key Words: lime treatment, high density sludge process, cement kiln dust, lime kiln dust, papermill sludge, calcium magnesium hydrate, climate change, greenhouse gas emissions

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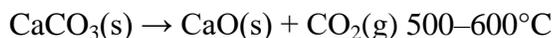
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Introduction

Lime neutralization is the most accepted and commercially used method for removing metals from acidic metal-bearing effluents, plating and bleed streams. Lime is an effective amendment for contaminated soils, acid generating tailings and waste rock. However, the production of lime generates CO₂, contributing to climate change effects. In an attempt to reduce greenhouse gas emissions from reduced lime production/usage, this study was initiated to evaluate the potential to replace lime with waste materials in the acidic drainage treatment.

Calcium oxide or lime is a white crystalline solid with a melting point of 2572°C. It is manufactured by heating limestone, coral, sea shells, or chalk, which are mainly CaCO₃, to drive off CO₂. In the calcining process, quicklime (CaO) is formed when limestone dissociates into CaO and CO₂. To produce lime, crushed limestone is burned in a kiln at temperatures ranging from 890° to 1340°C. A dissociation reaction takes place when the limestone is broken down, releasing CO₂ and producing CaO (quicklime) or CaO.MgO.



Lime Neutralization

Acidic drainage, mine water and other acidic metalliferous effluents are commonly treated in the mining and metallurgical industries by using lime neutralization. This is largely due to the high efficiency in removing dissolved metals through neutralization, combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists of bringing the pH of the acidic drainage to a point where the metals of concern are insoluble (Aubé and Zinck, 2003). Upon neutralization, metals precipitate out of the raw water as oxyhydroxides.

Three typical lime treatment processes are used in the industry (basic, conventional and high density sludge) and have been described in detail in the literature (Aubé and Zinck, 1999; Vachon, 1987; Kuit, 1980).

Basic lime treatment involves the addition of lime to the waste stream followed by solid/liquid separation in a settling pond. In conventional treatment systems, mechanically agitated reactors are used and lime addition is controlled by pH. The high density sludge (HDS) process is the standard in the acid rock drainage (ARD) treatment industry today. Instead of contacting lime directly to the ARD as in the previously described processes, this system contacts recycled sludge with the lime slurry for neutralization.

A series of batch experiments were completed to determine the effectiveness of cement kiln dust and various other 'waste' reagents in mine water treatment. Additional tests including screen analysis characterization and neutralization kinetic tests, pilot plant and field tests were also completed and are presented in Zinck et al. (2005).

Waste Characterization

The alternative reagents evaluated in this study included cement kiln dust, lime kiln dust, papermill sludge and calcium magnesium hydrate. The wastes were fully characterized for their physical, chemical and mineralogical properties.

Cement Kiln Dust

Cement kiln dust (CKD) is a by-product of the cement industry and has shown great promise in replacing lime in wastewater treatment (Zinck et al., 2000; Griffith et al., 2001). It is a fine powdery material similar in appearance to Portland cement. Fresh cement kiln dusts can be classified as belonging to one of four categories, depending on the kiln process employed and the degree of separation in the dust collection system. There are two types of cement kiln processes: wet-process kilns, which accept feed materials in a slurry form; and dry-process kilns, which accept feed materials in a dry, ground form. In each type of process, the dust can be collected in two ways: (1) a portion of the dust can be separated and returned to the kiln from the dust collection system (e.g., cyclone) closest to the kiln, or (2) the total quantity of dust produced can be recycled or discarded.

The chemical and physical characteristics of CKD that is collected for use outside of the cement production facility depends largely on the method of dust collection employed at the facility. Free lime can be found in CKD, and its concentration is typically highest in the coarser particles captured closest to the kiln. Finer particles tend to exhibit higher concentrations of sulfates and alkalis. If the coarser particles are not separated out and returned to the kiln, the total dust will be higher in free lime (since it will contain some coarse particles). CKD from wet-process kilns also tends to be lower in calcium content than dust from dry-process kilns.

Approximately 12.9 million metric tonnes (14.2 million tons) of CKD are produced annually in the United States.

Chemical analyses. A sample of cement kiln dust was received from a major cement supplier, Lafarge Canada. Detailed chemical analysis was completed on the sample of CKD and is presented in Table 1. The composition of the CKD received from Lafarge was consistent with published compositions.

CKD is primarily a crystalline composite material containing major portions of carbonate, silicates, SO_4^{-2} and free lime. The neutralization potential (NP) of the CKD samples characterized was 676 kg CaCO_3 equivalent/ tonne material. This suggests the material would be moderately effective in pH neutralization. By comparison, the NP of hydrated lime is 1661 kg CaCO_3 equivalent/ tonne material. With the exception of Al and Fe (2.13% and 1.38% respectively), CKD has a low metal content. Cobalt, Cu, Zn, As and Cd occur at or below 0.01% concentrations.

Mineralogical characterization. X-ray diffraction analysis (XRD) of the sample identified lime, anhydrite and calcite as the major constituents, with lesser amounts of quartz and Ca-rich silicates (larnite and gehlenite) and possibly traces of portlandite and brownmillerite. The examination of the specimen by combination of optical microscopy, scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) revealed great variation in terms of particle size (less than 5 to almost 300 μm) and chemistry, with the presence of major amounts of Ca-rich silicates that are often showing variable levels of Al, Mg and Fe, anhydrite, calcite and lesser amounts of quartz.

Table 1: Chemical analysis of the CKD, LKD and Papermill sludge.

Analyte	CKD CKD - 0402	LKD LKD- 03- 01	Papermill sludge DOM-10- 02
Al	2.1%	1.4%	2.6%
As	<0.014 %	<0.014 %	0.002%
B	<0.11 %	<0.11 %	0.23%
C _{total}	5.2%	4.5%	18.5%
C _(organic)	NA	NA	13.60%
Ca	33.4%	28.7%	15.11
CO ₃	11.2%	14.9%	34%
CaO _{free}	14.0%	35.1%	<0.03%
Cr	0.01%	NA	0.01%
Cu	0.01%	0.003%	0.01%
Fe _{total}	1.4%	0.6%	1.2%
K	2.3%	0.4%	0.8%
LOM	8.4%	4.0%	42.0%
LOI	0.05%	13.2%	NA
Mg	1.00%	0.4%	0.09%
Mn	0.05%	0.01%	0.42%
Na	0.3%	0.01%	0.01%
Ni	<0.005%	<0.002%	0.01%
P	0.04%	NA	0.30%
Pb	0.01%	0.01%	0.02%
S _{total}	5.6%	3.4%	0.5%
Si	6.3%	2.9%	11.0%
SO ₄	NA	NA	0.2%
Zn	0.01%	0.01%	0.07%
NP* (tonnes)	676	936	381

*units are express as -kg CaCO₃equivalence/tonne

NA- not analyzed

Lime Kiln Dust (LKD)

Lime kiln dust (LKD) is physically similar to cement kiln dust, but chemically quite different. LKD can vary chemically depending on whether high-calcium lime (chemical lime, hydrated lime, quicklime) or dolomitic lime is being manufactured.

Fresh LKD can be divided into two categories based on relative reactivity, which is directly related to free lime and free magnesia content. Free lime and magnesia content are most dependent on whether the feedstock employed is calcitic or dolomitic limestone. LKD with a high free lime content is highly reactive, producing an exothermic reaction upon addition of water. This "quick" LKD is of greatest commercial interest as a direct replacement or substitute for hydrated lime.

Approximately 1.8 to 3.6 million metric tonnes (2 to 4 million tons) of LKD are generated each year in the United States.

In addition to fresh CKD and LKD production, it is estimated that the total amount of kiln dust currently stockpiled throughout the United States exceeds close to 90 million metric tonnes (100 million tons). These stockpiles are usually located relatively close to the cement and lime manufacturing plants, and vary in age and composition, with exposure to the elements (moisture in particular) reducing the chemical reactivity of the dusts.

Chemical analyses. A sample of fresh, calcitic lime kiln dust was obtained from Graymont. As its name implies, LKD has much higher lime content than CKD (Table 1), 35.1 % compared to 14.0% for CKD. The Si, S, Al and Fe content are lower in LKD compared to CKD. A comparison of carbonate content, free lime and neutralization potential for LKD, CKD and hydrated lime is presented in Table 2.

Mineralogical characterization. X-ray diffraction analysis (XRD) of the LKD sample identified lime (CaO), anhydrite (CaSO₄) and calcite (CaCO₃) as the major constituents.

Papermill Sludge

A sample of papermill sludge was received from Domtar, Eddy Speciality Division near Espanola, Ontario. Domtar papermill sludge is produced by mixing the final effluent with lime slurry, which is then dumped into a settling basin, where it comes in contact with wood fibre and residual clay particles (Tisch et al., 1999). Analysis of the papermill sludge showed that dioxin and furan concentrations were below detectable limits, suggesting that the material is non-hazardous to the environment. This sludge has been used in agricultural soil amendments and other land reclamation practices in the United States (Tisch et al., 1999), and is considered a non-hazardous waste.

Chemical analyses. The Domtar sludge also contained significant Al. The Al appears to be in a stable crystalline form as a plagioclase (CaAl₂Si₂O₈) (Table 1). The high carbonate content and trace free lime content is responsible for the paste pH 7.12 of Domtar sludge. Visually, papermill sludge appears to contain fibrous material. This is supported by the organic carbon (C_{organic}) content reported (Table 1).

Mineralogical characterization. X-ray diffraction analysis (XRD) of the papermill sludge identified CaCO₃ (Calcite) > SiO₂ (Quartz) > CaAl₂Si₂O₈ (Plagioclase) > CaP₂O₆ (Calcium Phosphate) in declining amount.

Calcium Magnesium Hydrate (CMH)

Calcium magnesium hydrate (CMH) is mineral soil conditioner composed principally of calcium and magnesium hydroxides. CMH is used for pH adjustment of soils as it is non-caustic and helps in adding plant micronutrients (Ca and Mg) to the soil.

CMH has a high acid neutralizing capacity. Its calcium carbonate equivalent (CCE) is 133%, allowing it to react quickly to provide neutralization. CCE is an expression of the acid-neutralizing capacity of a carbonate rock relative to that of pure CaCO₃ (e.g. calcite), which has a CCE of 100%. Its high magnesium content is especially advantageous for areas deficient in this micronutrient. CMH achieves a higher acid neutralizing effect without extremely fine particle sizing than is normally possible with other sources such as limestone and dolomite. Its high neutralization potential makes it a prospective alternative to lime.

Chemical and physical characterization. Table 2 summarizes the carbonate content, free lime concentration, neutralization potential and particle size (95% passing) for the four ‘reagents’ evaluated (CKD, LKD, CMH and papermill sludge) in comparison to hydrated lime.

Mineralogical characterization. CMH was sent for XRD analyses to determine the major crystalline components present in the material. Only brucite ($Mg(OH)_2$) was detected by XRD, though other possible components, such as portlandite and calcite, may also have been present in minor concentrations.

Table 2: Neutralizing characteristics of CKD, LKD, CMH, papermill sludge and hydrated lime.

Reagent	Carbonates CO_3 (%)	Free Lime CaO_{free} (%)	Neutralizing Potential (NP) (kg/t)	Particle Size 95% passing (microns)
CKD (cement kiln dust)	11.2	14	676	73.3
LKD (lime kiln dust)	14.9	35	936	74.9
CMH (calcium magnesium hydrate)	25.4	N.A ¹	1221	93.4
Papermill (Domtar sludge)	33.8	<0.03	381	N.A ²
$Ca(OH)_2$ (hydrated lime)	1.7	70	1661	49.8

¹Mineralogical analysis of calcium magnesium hydrate shows MgO instead of CaO

²Domtar papermill sludge is very fibrous in nature, making it very difficult to obtain an accurate particle size distribution

Batch ARD Treatment Tests

Batch tests were used to compare the effectiveness of various “wastes” reagents with lime. For each batch neutralization test, 2.5-L of the mine water was placed into a 3-L reactor and mixed at an impeller speed of 700 rpm while being sparged with air for Fe^{+2} oxidation. All batch tests were done in triplicate. The reagents used were cement kiln dust (CKD), lime kiln dust (LKD), calcium magnesium hydrate (CMH), pulp and papermill sludge, and hydrated lime. The reagent was added slowly to raise the pH to the desired set point of 9.5 or maximum achievable pH.

Upon completion of the test, total reagent added was recorded to determine reagent consumption. In addition, the % solids of the slurry, the amount of solids produced and the slurry-settling rate were also recorded.

Some of the solids were oven dried at 60°C and sent for chemical analyses, while other solids were sent in wet slurry form for leachate analyses. CANMET's Analytical Services Group chemically analyzed final effluent samples from the batch neutralization tests. In addition, samples that were filtered by Acrodisc syringe filters (- 45 microns) were also analyzed to determine the degree of suspended material in the treated water.

Acid Rock Drainage Feed

Each batch test was conducted in triplicate using acid rock drainage (ARD) from a mine site in northwestern Quebec. This ARD was chosen for testing as it contains a wide range of contaminants at significant concentration. The ARD tested is considered to be "high strength" due to its high acidity and total dissolved solids content. Table 3 presents the chemical composition of the ARD feed. The initial pH of the mine water was 2.4 and it contained significant quantities of Al, Fe, (Fe⁺² and Fe⁺³), Cu, Cd, Cr, Mn, Ni, Se and Zn.

Treatment Results

With the exception of the CMH and the papermill sludge, all of the reagents were successful in reaching the target pH of 9.5. Despite its high NP, CMH only achieved a final pH of ~9.05, while the papermill sludge reached a final pH of ~7.5 (Table 4)

Treated Effluent Quality

Table 3 presents the final effluent quality for batch tests using CKD, LKD, CMH, papermill sludge and hydrated lime. For the most part, the reagents were successful in removing most of the metals from the mine water. In all cases, the cadmium concentration was below the limit of quantification (LOQ < 0.0015 mg/L). Zinc was also consistently removed to levels below the LOQ (<0.016 mg/L). Lead concentrations in the filtered effluent samples from treatment with the four 'waste' reagents were also low, typically less than 0.3 ppb.

Table 3: Final effluent quality for batch tests using CKD, LKD, CMH, papermill sludge and hydrated lime.

	fractions	avg. pH	Acidity (mg/L)	Chemical Analysis																
				Al (ppm)	As (ppm)	Ca (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe _{total} (ppm)	Fe ³⁺ (ppm)	Mg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	Se (ppm)	Si (ppm)	S _{total} (ppm)	SO ₄ (ppm)	Zn (ppm)
Alkali	Feed Acid Mine Drainage	2.4	3,049	110.2	<0.0015	226	0.0048	0.0477	2.59	497.4	321	126.9	12.07	0.39	0.0027	0.008	2.63	946	3,015	1.07
CKD (cement kiln dust)	effluent 1 (filtered)			2.86	<0.0015	832	<0.0001	0.0040	0.075	0.11		109.5	0.161	0.002	<0.0003	0.021	<0.038			<0.061
	effluent 2 (filtered)			1.72	<0.0015	805	<0.0001	0.0046	0.008	0.07		77.8	0.065	0.004	<0.0003	0.022	<0.038			<0.061
	effluent 1			3.61	<0.0015	809	<0.0001	0.0038	0.019	2.23		111.4	0.216	0.014	0.001	0.023	0.067	716	2,155	<0.061
	effluent 2			2.41	<0.0015	808	<0.0001	0.0045	0.019	2.10		77.1	0.117	0.018	0.001	0.020	0.063	714	2,093	<0.061
	effluent 3 (alkalinity)		30																	
LKD (lime kiln dust)	effluent 1 (filtered)			1.61	<0.0015	898	<0.0001	0.0024	0.004	0.06		69.9	0.008	0.003	<0.0003	0.009	<0.038			<0.061
	effluent 2 (filtered)			0.51	<0.0015	919	<0.0001	0.0046	0.005	47.15		47.2	<0.0068	0.004	<0.0003	0.009	0.053			<0.061
	effluent 1			2.39	<0.0015	742	0.0002	0.0023	0.015	2.24		70.2	0.057	0.017	0.0004	0.007	0.049	624	1,773	0.103
	effluent 2			1.13	<0.0015	825	<0.0001	0.0054	0.013	47.93		47.9	0.038	0.016	0.0004	0.007	<0.072	592	1,691	<0.061
	effluent 3 (alkalinity)		32																	
CMH (calcium magnesium hydrate)	effluent 1 (filtered)			0.23	<0.0015	143	<0.0001	0.0026	0.004	0.58		742.4	0.089	<0.001	<0.0003	<0.006	0.123			<0.061
	effluent 2 (filtered)			<0.082	<0.0015	111	<0.0001	0.0029	0.010	0.62		746.0	0.087	0.002	<0.0003	<0.006	0.119			<0.061
	effluent 1			<0.082	<0.0015	110	<0.0001	0.0038	0.013	1.53		724.3	0.232	0.007	0.0011	0.008	0.121	1033	2,974	<0.061
	effluent 2			0.61	<0.0015	117	0.0002	0.0062	0.024	3.31		765.6	0.167	0.005	0.0032	0.009	0.136	1035	2,978	<0.061
	effluent 3 (alkalinity)		156																	
Ca(OH) ₂ (hydrate lime)	effluent 1 (filtered)			0.46	<0.0015	690	<0.0001	0.0022	0.005	0.04		30.1	0.032	0.004	<0.0003	<0.006	<0.038			<0.061
	effluent 2 (filtered)			0.54	<0.0015	659	<0.0001	0.0039	0.003	0.03		30.0	0.012	0.003	<0.0003	<0.006	<0.038			<0.061
	effluent 1			2.14	<0.0015	831	<0.0001	0.0015	0.014	1.23		32.5	0.051	0.014	<0.0003	<0.006	<0.038	500	1,552	<0.061
	effluent 2			1.38	<0.0015	829	0.0003	0.0040	0.014	0.82		32.1	0.046	0.010	<0.0003	<0.006	<0.038	561	1,613	<0.061
	effluent 3 (alkalinity)		33																	
DOM (Donnar papermill sludge)	effluent 1 (filtered)			0.14	<0.0015	888	0.0026	NA	NA	0.15		156.9	18.1	NA	NA	NA	NA			<0.061
	effluent 2 (filtered)			0.09	<0.0015	840	0.0022	<0.001	0.011	0.16		155.4	18.7	0.055	<0.0003	<0.006	0.082			0.063
	effluent 1			0.22	<0.0015	889	NA	<0.001	0.013	0.31		157.9	18.1	0.047	<0.0003	<0.006	0.093	957	2,732	<0.061
	effluent 2			0.21	<0.0015	813	0.0023	<0.001	0.014	0.40		150.1	18.5	0.053	<0.0003	<0.006	0.088	932	3,644	<0.061
	effluent 3 (alkalinity)		21																	

NA - not enough sample
Acidity - Temperature, 22°C

When comparing the dissolved solids concentrations in the hydrated lime treated effluent to the CKD and LKD effluents, the results were very similar. In fact, the concentrations were almost identical in the lime effluent and the LKD effluent. The CKD effluent had slightly elevated concentrations of Al, Cr, Mn and Se but all the concentrations fell below the Canadian Mineral Mining Effluent Regulations (MMER, 2004).

The CMH out performed all other reagents in terms of metal removal even though it was not capable of achieving the target pH. Due to the high Mg content of the CMH, the Mg concentration in the CMH effluent was much higher than that recorded for the other reagents. Similarly, the calcium content in the CMH effluent was much lower than the ‘waste’ reagent effluents due to the low Ca content in the CMH reagent.

Table 4: Batch leaching conditions, reagent consumption and sludge properties.

Alkali	Trials	pH		AMD volume (ml)	Retention (hr)	Reagent Consumption (g/l)	Sludge Production (g/l)	Slurry ¹ Density (%)	Settling Rate (m/h)	Dewatered Sludge	
		initial	final							Volume ² (ml)	Density ³ (%)
CKD (cement kiln dust)	1	2.34	9.49	2,500	22	4.4	4.1	1.0	2.0	40	17.1
	2	2.38	9.54	2,500	23	4.2	4.1	0.9	1.6	40	
	3	2.58	9.48	2,500	5	5.5	5.4				
LKD (lime kiln dust)	1	2.31	9.54	2,500	5	3.2	3.5	0.9	4.4	60	10.8
	2	2.34	9.50	2,500	5	3.3	3.5	0.9	3.5	60	
	3	2.40	9.81	2,500	5	3.6	3.85				
CMH (calcium magnesium hydrate)	1	2.39	9.07	2,500	27	5.9	4.4	1.0	1.7	25	21.4
	2	2.43	9.05	2,500	27	5.2	3.9	1.0	1.7	25	
	3	2.40	8.83	2,500	5	6.0	4.8				
Papermill (Domtar sludge)	1	2.18	7.45	2,500	24	11.3	8.7	1.3	NA*	NA*	45.7
	2	2.25	7.51	2,500	24	10.0	8.5	1.3			
	3	2.13	7.43	2,500	23.9	10.9	9.0				
Ca(OH)₂ (hydrated lime)	1	2.44	9.48	2,500	6	1.9	3.5	0.7	1.5	70	8.3
	2	2.42	9.47	2,500	6	1.9	3.3	0.8	1.1	78	
	3	2.57	9.65	2,500	5	2.0	2.2				

¹ Samples were taken from the tank immediately after testing

² Volume was recorded after 24hours settling of 1L slurry

³ Sludge density was determined after two weeks settling

* Papermill sludge being a fibrous material did not settle

With the exception of a few metal species such as Al, the papermill sludge was the least effective in terms of metal removal. While the papermill sludge is an effective adsorbent for metal removal (Griffith et al., 2005), it was not effective in pH neutralization. As such, some metal species that were not readily adsorbed on the papermill substrate required hydrolytic precipitation for complete removal. The Domtar papermill sludge did not possess the required neutralization potential to raise the pH during treatment to the level necessary for complete metal removal.

Reagent Consumption

A range of treatment efficiencies were recorded for the various reagents and are presented in Table 4. Lime was much more effective in treating the acid rock drainage solution, requiring only ≈ 2 g/L. The consumption for the other reagents was much higher, with LKD at ≈ 3.4 g/L, CKD at ≈ 4.7 g/L, CMH at 5.7 g/L; the highest consumption recorded was for the papermill sludge at 10.7 g/L.

Depending on the cost associated with waste haulage, some of these ‘waste’ reagents may prove to be cost-effective in replacing lime. Economic benefit of lime alternatives will be discussed in more detail later in this paper.

Sludge Properties

The physical and chemical properties of the sludge produced from the various treatment reagents are presented in Tables 4 and 5, respectively.

Sludge production. In this study, all the reagents used for treatment, except papermill sludge, utilize metal hydrolysis to remove the metals from solution. Papermill sludge removes metals from solution principally through metal adsorption. None of the ‘waste’ reagents tested experienced complete dissolution during treatment. As such, unreacted residuals (e.g. silicates) also report to the sludge, increasing its apparent production.

Thus, as expected, the sludge production was lowest for lime (complete dissolution) at ≈ 3.0 g/L and highest for papermill sludge due to the large proportion of non-reactive fibrous material, at 8.7 g/L (Table 4).

Settleability. The ability of a sludge to settle affects not only effluent quality (TSS, turbidity) but also determines the type of solid/liquid (S/L) separation process(es) required for treatment operations. Sludges that settle faster require less retention time in settling/polishing ponds, and this ultimately impacts on S/L separation capital cost requirements. Most basic treatment sludges settle slowly, on the order of 0.5 to 1.5 m/h. By contrast, sludges produced from HDS treatment using lime tend to settle at rates in excess of 10 m/h (Zinck and Griffith, 2000). The settling rate is an indication of particle size, shape and compactness.

With the exception of the papermill sludge, the settling rates recorded for the ‘waste’ reagent sludges were faster than those recorded for the lime treatment sludge. The lime, CKD and LKD sludge settling rates ranged from 1.3 m/h to 1.8 m/h. The CMH sludge settled much faster than the other sludges at an average rate of 4.0 m/h. The faster settling rate appears to be caused to the high Mg content of this sludge. Studies have shown that Mg-based reagents produce sludges with improved dewatering, compactness and greater stability than calcium-based reagents (US EPA, 1987). This trend was also observed in the sludge density measurements.

Sludge Density/Volume. Sludges can vary significantly in the amount of water that they contain. The percent solids in sludge is an important factor, particularly from a sludge management perspective. The type of treatment process directly affects the amount of solids in sludge and, consequently, sludge management options and costs. Typically, basic treatment processes of the sort simulated here through batch testing generate sludges containing ≈ 1 -2% solids where lime is the reagent. Simple reactor-type systems produce sludges with $\approx 5\%$ solids, and more advanced treatment systems can produce sludges with up to 40+% solids (Zinck, 1997). However, in addition to process conditions, the type of reagent can also influence the density of the resultant sludge by forming different precipitates and by altering the surface charge of the precipitating hydroxides, thereby changing the repulsion/attraction forces that govern agglomeration.

The sludge density (% solids) of the CMH sludge was significantly higher than most other sludge samples (21.4 %). The CKD sludge also recorded a high solids density but this is thought to be due to a high proportion of residuals, as was also observed using non-consumable papermill sludge (Table 4).

Another indication of the sludge density is the sludge volume measurement. The more dense and rounded the sludge particles, the better they compact and the lower the sludge volume. The CMH sludge occupied the smallest volume (25 mL per L treated after 24 hours). The lime sludge was more than three times as voluminous (Table 4). The volume difference between the CMH sludge and the lime sludge may be due in part to the lack of gypsum in the CMH sludge. Sludge volume directly impacts sludge management/disposal costs.

Chemical Composition. The chemical composition of the sludge produced during treatment with each of the five reagents is presented in Table 5. The ARD treatment sludge produced by lime neutralization typically contains significant concentrations of Fe, S (as SO_4^{-2}) and Ca (Zinck, 1997). Sometimes CaCO_3 (calcite) forms instead of gypsum if there is significant dissolved CO_2 present in the raw water. Depending on the ARD composition, the concentration of heavy metals such as Al, Cu, Ni and Zn will vary in the sludge.

The lime sludge as the control contained major amounts of gypsum (CaSO_4), ferrihydrite (Fe), some calcite (CaCO_3) and various metals. The metal content ranged from $\approx 0.004\%$ Pb, $\approx 3.5\%$ Al, $\approx 0.77\%$ Cu, $\approx 0.01\%$ Ni and $\approx 0.04\%$ Zn.

The other sludge samples were generally similar in composition. The CaCO_3 content was much higher in the alternative reagent sludge than in the lime sludge. The carbonate is thought to have originated from the ‘waste’ reagent and remained unreacted during treatment rather than being formed through precipitation. The CMH sludge contained very little SO_4^{-2} , since the relatively low Ca levels limited gypsum precipitation.

Metal concentrations were lower for the papermill treatment sludge. This observation can be explained by: 1) dilution of the metal species in the sludge by non-reactive, fibrous material reporting to the treatment sludge, as indicated by the high carbon content in the sludge; and/or 2) lower metal removal due to incomplete hydrolytic precipitation.

Table 5: Chemical composition of various treatment sludges.

Sludge produced	Al (%)	C (%)	Ca (%)	CO_3^{-} (%)	Cu (%)	Fe_{total} (%)	Mg (%)	Mn (%)	Ni (%)	NP ¹ (tonnes)	Pb (%)	S (%)	SO_4 (%)	Zn (%)
CKD (cement kiln dust)	3.7	2.0	17.7	8.6	0.047	9.8	1.6	0.24	0.0076	254	0.010	8.95	24.9	0.04
LKD (lime kiln dust)	3.8	3.0	16.8	9.4	0.056	11.5	2.2	0.26	0.0213	274	0.005	8.34	22.9	0.03
CMH (calcium magnesium hydrate)	2.5	4.1	4.1	18.4	0.051	9.9	17.3	0.25	0.0096	812	0.014	1.40	3.5	0.05
Papermill (Domtar sludge)	3.5	18.7	11.1	30.9	0.034	6.1	0.8	0.41	0.0114	236	0.003	2.24	4.5	0.09
$\text{Ca}(\text{OH})_2$ (hydrated lime)	3.5	0.8	12.4	3.9	0.077	15.3	3.3	0.37	0.0105	180	0.004	10.35	30.2	0.04

¹ NP - kg CaCO_3 equiv. per tonne sludge

Sludge Leachability. Acidic drainage treatment sludges are waste products that may be subject to waste management regulations in some jurisdictions. A leachate extraction test may be used to evaluate if the waste is capable of yielding a leachate that exceeds regulated concentration limits

for selected contaminants. When a waste fails the test relative to the limits specified in a particular jurisdiction, the waste may be classified as hazardous (Zinck et al., 1996).

Sludge samples from each of the different reagent tests were evaluated for metal mobility using the Toxic Characteristic Leaching Procedure (TCLP). The TCLP is the regulatory leach test adopted by the United States Environmental Protection Agency (US EPA, 1990) and uses a buffered acetic acid leaching medium. The results from the TCLP tests are presented in Table 6. For comparison, the Leachate Toxic Criteria for Ontario (Canada) also appear in Table 6.

Table 6: TCLP leach tests results for treatment sludges.

Parameter	CKD Sludge	LKD Sludge	CMH Sludge	Papermill Sludge	Ca(OH) ₂ Sludge	Leachate Criteria ¹
Final pH	8.2	8.2	9.3	6.0	8.4	-
Al (mg/L)	0.527	0.888	0.105	0.286	0.594	-
As (mg/L)	<0.0009	<0.0009	<0.0009	<0.0009	<0.0009	2.5
Cd (mg/L)	0.0002	0.0001	0.0001	0.0651	0.0004	0.5
Cr (mg/L)	0.0169	0.0065	0.0023	0.0011	0.006	5.0
Cu (mg/L)	0.0027	0.0017	0.0066	0.0732	0.004	-
Fe (mg/L)	<0.00003	<0.00003	<0.00003	<0.00003	<0.00003	-
Mn (mg/L)	0.058	0.0119	0.0007	0.0445	0.038	-
Ni (mg/L)	<0.001	<0.001	<0.001	0.513	<0.001	-
Pb (mg/L)	<0.001	<0.001	<0.001	0.0063	0.0003	5.0
Se (mg/L)	0.014	0.0072	0.0052	0.0049	0.0080	1.0
Zn (mg/L)	<0.0008	<0.0008	<0.0008	1.85	0.020	-

1 - Ontario Leachate Toxic Criteria (mg/L)

All the sludges tested had leachate concentrations far below that stipulated in the Ontario Leachate Toxic Criteria. The papermill sludge released the most metals during the TCLP test. Elevated levels of Cd (0.0651 mg/L), Cu (0.0732 mg/L), Ni (0.513 mg/L) and Zn (1.85 mg/L) were observed. The final leachate pH for the papermill sludge TCLP test was considerably lower (pH 6.0) than the other leachate pH values. Leachate pH is one of the major factors affecting sludge leachability (Zinck, 1999). The CMH sludge had the highest leachate pH (9.3), which reflects its high neutralization potential (812 kg/t) (Table 5) and indicates a high degree of unreacted CMH was present in the sludge. As a result, very little metal leaching was observed for the CMH sludge. The results from these TCLP leach tests do not appear to indicate long-term sludge stability issues.

While these tests are aggressive batch-style leach tests designed to simulate waste disposal in a landfill, they do not take into effect the kinetic effects that occur over time. It is always recommended to undertake long-term column leaching tests to better predict the long-term chemical stability of any material.

Potential Climate Change and Cost Benefits

In Canada, an estimated 1,522,451 tonnes of quicklime was produced in 2003, of which 12% was used for water treatment; similarly, 65% of the 148,605 tonnes of hydrated lime produced was used for water treatment (Panagapko, 2003). If 1.16 tonnes of CO₂ emissions can be reduced for every tonne of lime replaced in water treatment, this would represent an annual emission reduction of 323,973 tonnes of CO₂ for Canada. Detailed calculations can be found in Zinck et al. (2005). It should also be noted that in the treatment process small amounts of CO₂ are also consumed in the reaction with calcium, producing bicarbonate and calcite.

In addition to the climate change benefits, the reagent costs savings are also significant. The average reported values (freight on board (FOB) plant) based on producers' shipments were \$101.52/t for quicklime and \$120.68/t for hydrated lime in 2003. Replacing the lime and hydrated lime used in environmental control with alternative waste reagents could generate an annual savings of ~\$30 M in reagent costs alone. These figures do not account for shipping charges for the reagent (CKD, LKD, etc.), any required plant modifications or added sludge handling costs. These values also do not consider potential cost of the material. For example in Canada, Graymont sells their LKD for municipal sludge stabilization at a cost of \$5 CDN/tonne.

Discussion and Conclusions

Cement kiln dust was shown to successfully remove dissolved metal from ARD to below regulated limits. In addition, the sludge produced from mine water treatment with CKD was evaluated using TCLP testing for metal leachability. Metal mobility was very low from the CKD sludge, comparable to lime sludges, with concentration far below the Ontario Leachate Criteria. Overall, the cement kiln dust tested in this study showed no apparent environmental effects and its impact appeared to be equivalent to that experienced using hydrated lime in environmental control processes.

Lime kiln dust, while physically very similar to CKD, is chemically quite different, containing a much higher proportion of free lime and less silicates. In batch testing, lime kiln dust performed as well or better than CKD in most respects. Its properties are quite similar to lime and thus LKD could be easily exchanged for lime in many applications. Due to its obvious benefits, LKD should perhaps be considered more as a marketable product than a waste. And as mentioned earlier, this once 'waste' material is now being sold in some locations for municipal sludge stabilization at a cost far less than lime.

The source of alkalinity in these waste reagents is typically free lime, calcite, portlandite or brucite. Free lime seems to be contained within pockets in the silicate/oxide CKD matrix, causing neutralization with this 'waste' reagent to be slower than with lime. While the reaction times were lengthier than with lime, this was not seen to be a major issue in water treatment applications.

Papermill sludge from Domtar in Espanola was evaluated through batch neutralization tests but was found not to be an effective reagent for active water treatment as it exhibited difficulties with metal removal, metal leaching, sludge settling and densification. Papermill sludge would be better suited for passive treatment or reclamation applications.

Calcium magnesium hydrate is a mineral soil conditioner composed primarily of magnesium hydroxide. CMH performed very effectively in batch treatment of high strength mine water

despite not being able to achieve the target pH of 9.5. TCLP of the CMH sludge generated very low metal levels in the leachate due primarily to the high residual NP in the CMH sludge. The presence of magnesium during treatment produces a very dense sludge and makes CMH an attractive alternative reagent; however, it requires grinding prior to usage.

This study found that various different wastes could be used as replacement reagents for lime in mine water treatment. Significant GHG and reagent cost savings can be realized if lime was replaced with 'waste' reagents. If in theory, every tonne of lime used for water treatment in Canada was replaced an alternative reagent this would represent an annual emission reduction of 323,973 tonnes of CO₂. Furthermore, replacing the lime and hydrated lime used in environmental control with alternative waste reagents could generate a maximum annual savings of ~\$30 M in reagent costs alone (depending upon the alternative reagent selected).

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Literature Cited

- Aubé, B and Zinck, J.M. 2003. Lime Treatment of Acid Mine Drainage in Canada, In: Brazil-Canada Seminar on Mine Rehabilitation Technological Innovations. Eds. Juliano Peres Barbosa, Paulo Sergio Moreira Soares, Brenda Dixon, Bryan Tisch., Desktop Publishing. Desktop Publishing, Rio de Janeiro, Brazil. pp.23-40.
- Aubé B. and Zinck, J.M, 1999. "Comparison of AMD Treatment Processes and their Impact on Sludge Characteristics". Proceedings for Sudbury '99, Mining and the Environment II p. 261-270.
- Griffith, W.F, J. Zinck, C. Black, J.F. Fiset, J. Barnes. 2005. Papermill Sludge As A Suitable Alternative To Lime In The Treatment Of Acid Mine Drainage (AMD): Task I – Batch Tests, Mining And Mineral Sciences Laboratories (MMSL) Report No. MMSL-INT 03-004(TR)
- Griffith, W.F., T. MacKinnon, Zinck, J.M., Black, C., Moore, C, Salley, J, and Chaulk, J. 2001. Effectiveness of Cement Kiln Dust as a Neutralization Reagent in Water Treatment: Phase II B Pilot Plant Testing, Mining and Mineral Sciences Laboratories Report MMSL 01-15 (CR), April 2001.
- Kuit, W.J. 1980. Mine and tailings effluent treatment at Kimberley, B.C. operations of Cominco Ltd. CIM Bulletin, 73, December 1980:105-112.
- MMER, 2004, Metal Mining Effluent Regulations, SOR/2002-222 , Registration 6 June, 2002, <http://laws.justice.gc.ca/en/F-14/SOR-2002-222/119716.html>
- Panagapko, D. 2003. Canadian Minerals Yearbook, Chapter 30 – Lime.

- Tisch Bryan, P. Beckett, N. Belzile, L. Lantigne, 1999. A Laboratory of the Potential Benefit of Papermill Sludge as a Substrate for the Creation of Wetlands on Mine Tailings. Sudbury, Mining and the Environment II Conference, Sudbury, Ontario.
- US EPA. 1987. United States Environmental Protection Agency Technical Resource Document, *Treatment Technologies for Metal/Cyanide-Containing Wastes*. Hazardous Waste Engineering Research Laboratory, NTIS Order Number PB 38-143896.
- US EPA. 1990. United States Environmental Protection Agency, "Toxicity Characteristic Leaching Procedure, Method 1311". In: Test Methods for Evaluating Solid Waste, EPA SW-846.(Also 40CFR261.24 Appendix II Method 1311).
- Vachon, D., Siwik, R.S., Schmidt, J. and Wheeland, K., 1987. Treatment of Acid Mine Water and The Disposal of Lime Neutralization Sludge. In Proceedings of Acid Mine Drainage Seminar/Workshop, Halifax, Nova Scotia, Environment Canada, March 23-26, 1987. p.537-564.
- Zinck, J.M., Chen, T.T., Mikhail, S., Turcotte, A.M., Wilson, L. and Griffith, W.F. 1996, Characterization and Stability of AMD Treatment Sludge. MMSL Report 96-079(CR) for MEND.
- Zinck, J.M., 1997. Acid Mine Drainage Sludges in the Canadian Mineral Industry: Physical, Chemical, Mineralogical and Leaching Characteristics. Paper presented at *the* Fourth International Conference on Acid Rock Drainage, May 31 - June 6, 1997, Vancouver, British Columbia
- Zinck, J.M., 1999. Stability of Lime Treatment Sludges, Paper presented at the CIM Annual General Meeting, Calgary, May 2-5.
- Zinck, J.M., W.F. Griffith and T. MacKinnon. 2000. Effectiveness of Cement Kiln Dust as a Neutralization Reagent in Water Treatment: Phase II B Batch Tests. Mining and Mineral Sciences Laboratories Report MMSL 00-28 (CR), July 2000
- Zinck, J.M. and Griffith, W.F., 2000. An assessment of HDS-type processes - efficiency and environmental impact. ICARD 2000. In: Proceedings of the Fifth International Conference on Acid Rock Drainage. 1027-1034.
- Zinck, J.M., W.F. Griffith, C. Black, J. Chaulk and G. Poirier, 2005. Potential to Utilize Industrial Wastes and By-Products to Replace Lime in Environmental Control, CANMET Report MMSL 05-034(CR)