

# Chemical Stability of Acid Rock Drainage Treatment Sludge and Implications for Sludge Management

DANNY M. MCDONALD\* AND  
JOHN A. WEBB

*Environmental Geoscience, La Trobe University,  
Victoria 3086, Australia*

JEFF TAYLOR

*Earth Systems, Suite 507, 1 Princess Street Kew,  
Victoria 3101, Australia*

To assess the chemical stability of sludges generated by neutralizing acid rock drainage (ARD) with alkaline reagents, synthetic ARD was treated with hydrated lime (batch and high-density sludge process), limestone, and two proprietary reagents (KB-1 and Bauxsol). The amorphous metal hydroxide sludge produced was leached using deionized water, U.S. EPA methods (toxicity characteristic leaching procedure, synthetic precipitation leaching procedure), and the new strong acid leach test (SALT), which leaches the sludge with a series of sulfuric acid extractant solutions; the pH decreases by ~1 pH unit with each test, until the final pH is ~2. Sludges precipitated by all reagents had very similar leachabilities except for KB-1 and Bauxsol, which released more aluminum. SALT showed that lowering the pH of the leaching solution mobilized more metals from the sludges. Iron, aluminum, copper, and zinc began to leach at pH 2.5–3, ~4.5, ~5.5, and 6–6.5, respectively. The leachability of ARD treatment sludges is determined by the final pH of the leachate. A higher neutralization potential (e.g., a greater content of unreacted neutralizing agent) makes sludges inherently more chemically stable. Thus, when ARD or any acidic metalliferous wastewater is treated, a choice must be made between efficient reagent use and resistance to acid attack.

## Introduction

Acid rock drainage (ARD) is one of the most costly and long-lived environmental issues facing metal and coal mines worldwide (1, 2). Oxidation of sulfide minerals (usually pyrite) by exposure to air and water produces acidic waters (pH often <3) which contain large amounts of dissolved iron, along with aluminum, copper, zinc, and other heavy metals, depending on the specific mineral deposit.

ARD may be extremely toxic to the environment, and must be treated before it can be reused or discharged from a site. The most common active treatment method is to increase the pH with an alkaline reagent such as hydrated lime, precipitating a sludge composed of amorphous ferric oxyhydroxide, often with significant concentrations of heavy metals (e.g., copper and zinc) and amorphous aluminum hydroxide. Crystalline gypsum may also be present in the sludge.

The long-term chemical stability of ARD treatment sludges is a significant problem, because they have the potential to release metals back into the environment if they are exposed to low-pH water. As a result, ARD treatment sludges may be classified as hazardous waste, limiting disposal options. Disposal can represent a significant proportion of overall ARD treatment costs (3–5).

The physical properties of ARD treatment sludges can be substantially improved by the high-density sludge (HDS) process (6), which produces a sludge with 15–70 wt % solids, compared to <5 wt % for standard hydrated lime neutralization sludges (5–8). This process is also claimed to enhance the chemical stability of neutralization sludges (8, 9).

In addition, two proprietary products (KB-1 and Bauxsol) claim to precipitate sludges with superior chemical stability. KB-1 (manufactured by KEECO) is designed to encapsulate the metals precipitated from ARD in low-reactivity silica (10, 11). Bauxsol (Virotec Pty Ltd., Australia) is manufactured from a seawater-neutralized bauxite refinery residue, with additives such as MgO or Ca(OH)<sub>2</sub>. Bauxsol removes metals from ARD by a combination of direct precipitation and adsorption (12, 13).

Two leach tests have been commonly employed to quantify the chemical stability of ARD treatment sludges. The most widely used, the toxicity characteristic leaching procedure (TCLP; U.S. EPA method 1311), was designed to simulate codisposal with municipal (putrescible) waste (14), so the leachate is an organic acid (acetic acid). The alternative synthetic precipitation leaching procedure (SPLP; U.S. EPA method 1312) uses a mixture of inorganic acids (nitric and sulfuric) as the leachate (14); because it simulates an acid rain scenario, the leachate is only moderately acidic (pH 4.2).

Neither of these procedures was specifically designed for evaluating ARD treatment sludge leachability, and as a result they do not model common mine site disposal environments, i.e., mixed with tailings or waste rock, backfill within the mine, or collection ponds (5). Sludges in these environments are likely to encounter waters acidified by sulfide oxidation (pH < 3), and neither the TCLP nor the SPLP tests sludge chemical stability under these conditions.

In this paper, we describe the new strong acid leach test (SALT), designed to closely reflect a sulfidic disposal environment where sludges could come in contact with a virtually unlimited supply of acid. From the results of the SALT tests we provide a general overview of the chemical stability of ARD treatment sludges in acid environments, based on the common laboratory approach (see, e.g., ref 4) of using a constant synthetic ARD composition to reduce the number of variables.

## Methods

**Composition of Neutralization Reagents.** The mineralogical and major element chemical composition of treatment reagents was determined by X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectroscopy, respectively. For mineralogical analysis, a ZnO internal standard was used to quantify the proportion of amorphous material. However, accurate mineralogical quantification of ARD treatment sludges is difficult due to preferential orientation of gypsum. Results within ±5 wt % can be obtained using a gypsum orientation factor of 0.7–0.8 in Rietveld analysis (15). Trace metal analysis used a mixed acid digest method adapted from Eaton et al. (16).

**Preparation of Synthetic ARD.** Synthetic ARD was prepared as 150 L batches of dark brown liquid containing

\* Corresponding author phone: +61 (0)3 9479 5641; fax: +61 (0)3 9479 1272; e-mail: d.mcdonald@latrobe.edu.au.

TABLE 1. Details of Neutralization Procedures

	neutralization equipment	neutralization reagent	final treatment pH	pH of supernatant water after settling (24 h)	reagent use (g/L ARD treated)	reaction time <sup>a,b</sup> (min)	air sparging
run 1	170 L reactor	15 wt % hydrated lime slurry	10.04	9.19	4.06	189	started 95 min after neutralization commenced
run 2	170 L reactor	15 wt % hydrated lime slurry	9.57	8.85	3.64	64	continuous
run 3	170 L reactor	15 wt % limestone slurry	5.17	9.09	5.85	53	continuous
		15 wt % hydrated lime slurry	9.55		4.99	92	
run 4	170 L reactor	15 wt % limestone slurry	5.17	7.71 (after 4 days of sparging)	5.88	77	continuous, including for 4 days between adding CaCO <sub>3</sub> and hydrated lime
		15 wt % hydrated lime slurry	9.11	8.85	0.26	5	
run 5	170 L reactor	15 wt % KB-1 slurry	9.41	9.18	5.07	152	continuous
run 6	170 L reactor	Bauxsol powder, added directly to ARD at the Virotech recommended rate of 0.3 (g/L)/4 h	8.22	8.33	11.71	21 days	no sparging as neutralization was conducted over 21 days
run 7	HDS plant; 250 L of ARD was treated to allow time for the sludge density to build up	10 wt % hydrated lime slurry lower concn slurry used to reduce the chance of HDS plant blockage	reagent added as required to keep reactor 2 at a pH of 9	8.37	3.46	133 min (water)/26.7 h (sludge)	continuous into all three reactors

<sup>a</sup> The reaction time for runs 1–6 is the time taken to add reagent. Further reagent dissolution or Fe oxidation may occur after this. <sup>b</sup> Average residence time of water/sludge in the HDS plant after the initial start-up period. The total treatment time for run 7 was 8 days.

1200 mg/L Fe, 110 mg/L Al, 100 mg/L Cu, and 100 mg/L Zn (all  $\pm 10$  mg/L), made up with tap water. The pH was lowered to 2.3 with sulfuric acid, giving a total sulfate concentration of  $\sim 4000$  mg/L.

**Batch Reactor.** Batches (150 L) of ARD were neutralized in a mixed 170 L polyethylene tank. The neutralization reagents hydrated lime, limestone, and KB-1 (Table 1) were added as 15 wt % slurries; Bauxsol powder was added directly to ensure that Virotec's recommended dosing rate of 0.3 (g/L)/4 h was not exceeded. The pH, EC, ORP, and temperature of the ARD were monitored by standard meters installed with appropriate probes. Once neutralization was complete, mixing and aeration (if used, Table 1) continued for 18–20 h to ensure thorough oxidation of the treated water and sludge, as would naturally occur over time during sludge storage/disposal. The sludge was allowed to settle for 24 h and then collected for analysis.

**HDS Reactor.** The laboratory-scale HDS plant consisted of three 1.1 L reactors and a 1 L separation funnel for solid/liquid separation. A total of 250 L of synthetic ARD (pH 2.3) was pumped into reactor 1 at a rate of 25 mL/min; the ARD retention time was approximately 20 min in each reactor. All three reactors were constantly sparged with air. The overflow from the separator (treated water) flowed into a collection container, and the underflow (sludge) was pumped into reactor 1 at a recycle rate of 18–22 after an initial start-up period (i.e., an 18–22 g dry weight of solids was pumped into reactor 1 for each gram of solids precipitated from the ARD neutralization). The recycled sludge raised the pH in reactor 1 to between 6.7 and 7.2. A 10 wt % hydrated lime slurry was pumped into reactor 2 to increase the pH to 9 to complete the treatment.

**Sludge Analysis.** The sludges from all experiments had a high water content, and were effectively slurries. After oven

drying at 40 °C, to ensure that gypsum and other hydrous precipitates were not dehydrated, the weight percent solids determined from the mass loss was 6–40 wt %. Representative subsamples of the dried sludge were analyzed for neutralization potential using the method of Sobek (17), and for mineral and chemical composition using the methods previously described for the neutralizing reagents.

**Leach Testing.** Each sludge slurry was mixed to ensure homogeneity, and then a subsample equivalent to 50 g of dry solids (calculated from the weight percent solids of the slurry) was added to a plastic leach vessel along with 1 L of the appropriate leachate (see below), mixed end-over-end at 30 rpm for 18 h, and allowed to settle for 1–2 h. The extractant fluid was carefully poured off the top and filtered (0.45  $\mu$ m). The period of end-over-end mixing, as used in TCLP, SPLP, and other sludge studies (see, e.g., ref 18), is a more aggressive procedure than the sludge will undergo at a mine site, but effectively simulates the extended leaching time of the disposal environment, and allows the leaching to proceed to completion.

The TCLP uses two extraction fluids, depending on the alkalinity of the sample. Because all sludges in this study contained some alkalinity, it was decided to use only the stronger extraction fluid: 5.7 mL of glacial acetic acid (CH<sub>3</sub>CH<sub>2</sub>COOH), diluted to 1 L with distilled water (pH 2.88  $\pm$  0.05). The SPLP extraction fluid was a 60:40 (wt %) sulfuric/nitric acid mix, diluted with distilled water until a pH of 4.2 ( $\pm$  0.05) was reached. TCLP, SPLP, and water leach tests were run in duplicate to ensure consistency.

To simulate leaching under the low pH conditions often encountered in mine waters, a new leach test was developed: SALT. Each sludge sample was leached by a series of solutions composed of sulfuric acid diluted to 1 L; the pH of the extractant solution decreased by  $\sim 1$  pH unit with each

**TABLE 2. Comparison of Sludges Produced by the Different Neutralization Procedures**

	reagent	reagent use (g/L ARD treated) (A)	weight of sludge (g/L ARD treated) (B)	vol of sludge <sup>a</sup> (mL/L ARD treated)	solids content of sludge <sup>a</sup> (wt %)(C)	neutralization potential of sludge <sup>b</sup>	rel cost of reagent <sup>c</sup> (D)	overall rating <sup>d</sup> (=ABD/C)
run 1	hydrated lime	4.1	10.3	155	6.4	83.4	1	6.6
run 2	hydrated lime	3.6	10.2	160	6.1	67.3	1	6.0
run 3	limestone/hydrated lime	6.0 (CaCO <sub>3</sub> )/ 4.8 (Ca(OH) <sub>2</sub> )	17.6	162	10.2	452	0.2 (CaCO <sub>3</sub> )	10.3
run 4	limestone/hydrated lime	6.0 (CaCO <sub>3</sub> )/ 0.1 (Ca(OH) <sub>2</sub> )	10.8	70	12.2	173	0.2 (CaCO <sub>3</sub> )	1.1
run 5	KB-1	5.1	14.4	140	9.7	46.8	11	83.3
run 6	Bauxsol	11.7	15.1	40	26.3	40.9	4.7	31.6
run 7	hydrated lime (HDS)	3.5	~10 <sup>e</sup>	~25 <sup>e</sup>	38.9	45.1	1	0.9

<sup>a</sup> Determined after 24 h of settling. <sup>b</sup> Units for neutralization potential are kg of CaCO<sub>3</sub> equivalent/t of dry sludge. <sup>c</sup> Relative cost of reagent to neutralize a set volume of acid, as compared to hydrated lime (transport not included and assuming 100% reagent use efficiency) calculated from information provided from Unimin (limestone and hydrated lime), Virotec (Bauxsol), and KEECO (KB-1). <sup>d</sup> Based only on the cost and mass of reagent used as well as the mass and density of sludge produced; rate of reaction and transport/capital costs not considered. <sup>e</sup> Estimate only, due to sludge recycle in HDS setup.

test, such that the pH at the end of the first extraction was ~6 and that at the end of the last test was ~2. The volume of sulfuric acid for each extraction was chosen to achieve the required pH.

The extractant fluid from each leach test was analyzed for Fe, Cu, Zn, Ca, Na, and Mg by AAS, Al and Si by ICP-AES, and Cl and SO<sub>4</sub> by ion chromatography.

The mass of metal leached (mg) was calculated by adjusting the measured concentrations (mg/L) for the volume of pore water (because the sludge was added as a slurry, pore water was added with it) and the mass of soluble metals within the pore water (effectively insignificant). This was converted to a percentage of the metal leached from the sludge using the sludge's original metal content (determined by acid digestion).

Two reagents (Bauxsol and KB-1) contain aluminum (Table S2 in the Supporting Information), which can contribute to the aluminum within the leachate. As a result, the percentage of aluminum leached in the experiments using these reagents can be greater than 100%, but the calculation is retained to allow comparison with the other sludges.

## Results and Discussion

All neutralizations treated the ARD effectively, raising the pH and removing dissolved metals (Table S1 in the Supporting Information). Run 1 was used to develop the analytical methods, and is only briefly discussed.

**Reagent Composition.** The hydrated lime and limestone used in this study contained small amounts of impurities (Table S3 in the Supporting Information). Both KB-1 (obtained from KEECO) and Bauxsol (obtained from Virotec International, Australia, who sourced it from Comalco, Tasmania) contain significant aluminum levels (Table S2). In KB-1, the aluminum is an amorphous phase. In Bauxsol it occurs as the aluminous minerals boehmite and gibbsite (Table S3), but these cannot account for all the Al<sub>2</sub>O<sub>3</sub> present (Table S2), so some must be present as an amorphous phase. The Bauxsol blend contained 10 wt % MgO and 5 wt % hydrated lime, as recommended by Virotec for the synthetic ARD composition used in the present study.

**Sludge Composition.** Chemical and mineralogical analyses (Tables S2 and S3) showed that all sludges consist predominantly of amorphous ferric oxyhydroxide and crystalline gypsum, except for the Bauxsol sludge, which lacks gypsum. Runs 5 and 6 sludges contain aluminous material inherited from the KB-1 and Bauxsol reagents.

The sludge from run 2 contains minor calcite which was inherited from the hydrated lime (Table S3), and has remained in the sludge because calcite reacts more slowly with ARD

than hydrated lime. The run 7 sludge, also produced with hydrated lime but using the HDS process, contains less calcite than the run 2 sludge but more gypsum, probably because calcite partially dissolved during the longer reaction time achieved by the sludge recycle process. Sludge from runs 3 and 4 contains more calcite, which represents unused limestone, due to the slow kinetics of limestone dissolution and/or armoring of limestone grains with precipitated sludge. In addition, during run 3 secondary calcite precipitated, due to the larger amount of hydrated lime added during neutralization, accounting for the increased amount of calcite in this sludge (Tables S2 and S3).

**Sludge Production.** The neutralization reagents and procedures tested produce substantially different amounts of sludge (both mass and density) and use varying amounts of reagents of differing costs (Table 2). An approximate overall rating of the different reagents and procedures based on these criteria ranks HDS and limestone/lime neutralization the highest (Table 2), but does not take into account factors such as rate of reaction and transport and capital costs.

**Comparison of TCLP, SPLP, and Deionized Water Leach Tests.** The SPLP and deionized water leach tests gave very similar results and extracted minimal amounts of metals (often below detection limits) from the sludges (Figures 2–4, Tables S4 and S5 in the Supporting Information), verifying the results of previous studies (see, e.g., refs 19 and 20). The 1 L of SPLP extractant fluid (pH 4.2) contains less than 1 drop of 60:40 (wt %) H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>, and consequently has a very low acidity. After completion of all SPLP and deionized water leach tests the supernatant fluid had circum-neutral pH (Tables S4 and S5), due to the substantial neutralization potential of the sludges (Table 2). Clearly the SPLP and water leach procedures cannot simulate metal release from sludges at the substantially lower pH values likely to be encountered at mine sites.

The TCLP extraction fluid, which is more acidic than that used in SPLP, has an initial pH of 2.88 and was only partly neutralized by the sludges, so that the pH of the supernatant fluid after completion of leach testing was 4.3–6.3 (Table S6 in the Supporting Information). As a result the TCLP tests leached much greater amounts of metals than the SPLP and water leach procedures, consistent with other studies (see, e.g., ref 20).

The proportion of metals leached by the TCLP depends on a sludge's neutralization potential (Figure 1). A sludge with a small neutralization potential is incapable of neutralizing all the acid added, and the resultant low pH will cause a substantial proportion of the metals present to be leached.

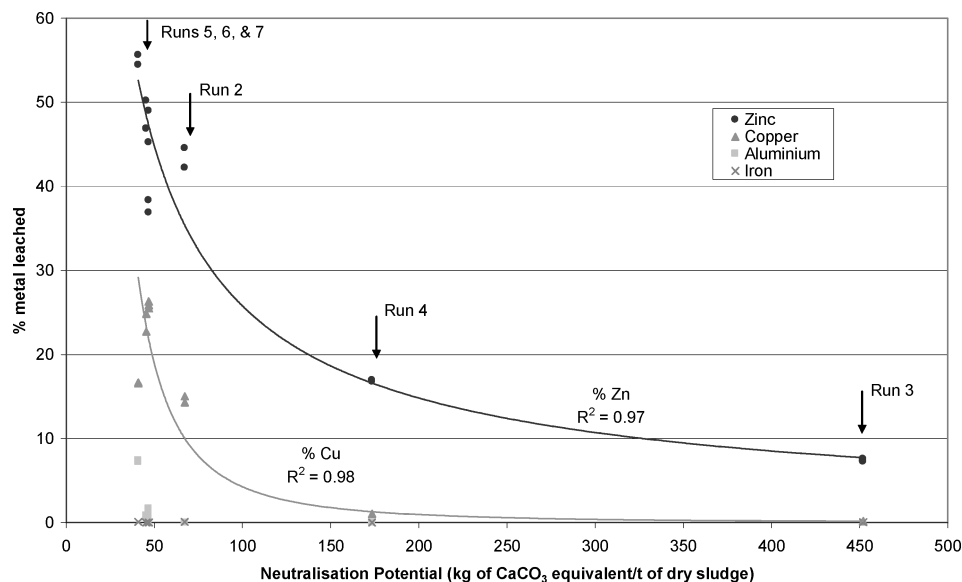


FIGURE 1. Relationship between the percentage of metals extracted by TCLP and the neutralization potential of a sludge.

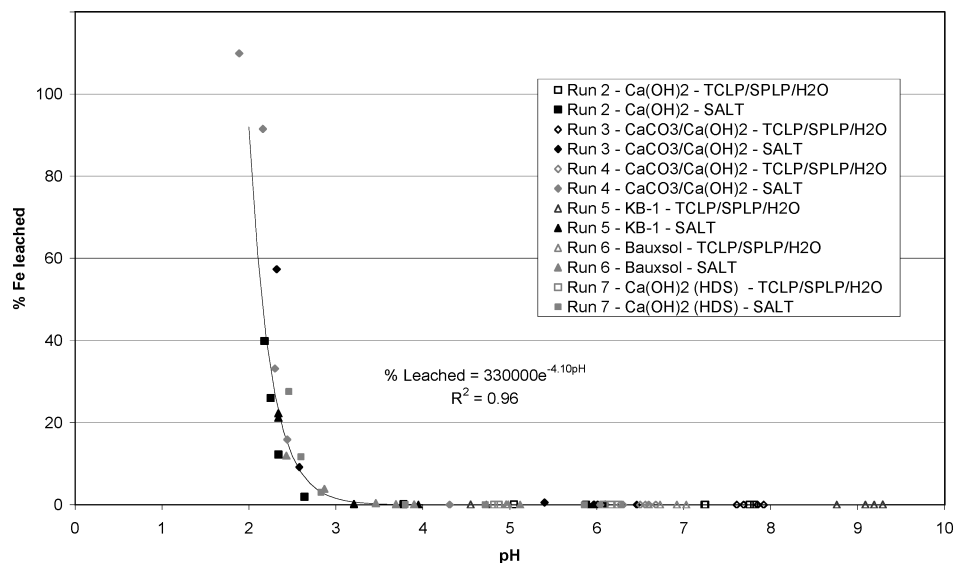


FIGURE 2. Percentage of iron leached from sludge versus the pH of the extractant solution.

Four TCLP extractions were performed on sludge from run 5 (neutralizing reagent KB-1), in sets of two, approximately 2 months apart. The results show large variations (Table S6), probably due to inhomogeneity of the sludge, which consists of two distinct phases: a light brown iron hydroxide (similar to that precipitated by the other neutralizations) and a denser sand-sized fraction of silica particles.

The results of this study for the KB-1 neutralization sludge are closely comparable to those of Mitchell and Wheaton (11), who subjected sludge generated with KB-1 at the Bunker Hill lead-zinc mine to a modified TCLP leach test and recorded significant leaching of Zn.

Sludges produced from the three reagents or treatment methods that have been claimed to have greater chemical stability than that from conventional hydrated lime neutralization (KB-1, run 5; Bauxsol, run 6; HDS, run 7) all had higher concentrations of aluminum, copper, and zinc in the TCLP leachate (Figure 1, Table S6). However, these sludges were not less chemically stable than standard hydrated lime sludge. The larger amounts of metals leached reflect the very low neutralization potentials of these sludges (Table 2), so that the final TCLP pH was lower, resulting in greater metal leaching.

Although TCLP gives a more realistic idea of sludge chemical stability than SPLP and is probably applicable for sludge disposed to municipal waste sites, it does not encompass the range of pH values likely to be encountered at mine sites.

**SALT Results.** To obtain a clear idea of the chemical stability of a sludge, it should be leached under a variety of pH conditions, including low pH values, and SALT was developed for this purpose. In TCLP and SPLP the initial pH of the leachate is fixed (so the final pH of the leachate is determined by the neutralizing potential of the sludge), whereas in SALT the final pH of the leachate is important. Sufficient acid is added to overcome the sludge's neutralizing potential, and hence, much greater amounts of metals are liberated into the extracting fluid. Thus, SALT measures how tightly metals are bound to the sludge, rather than how much alkalinity the sludge contains.

Several conclusions are evident from the SALT tests (Figures 2–5). First, as expected, the lower the pH of the leaching solution, the more metals were leached from all sludges. Second, all the reagents used in this study generated sludges with similar chemical stabilities, except for the Bauxsol and KB-1 sludges, which released more aluminum



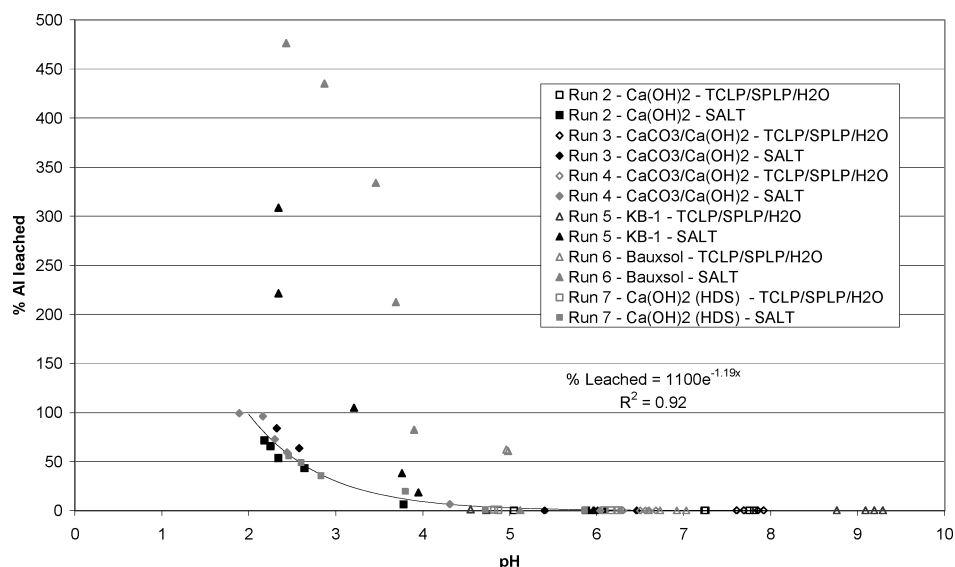


FIGURE 3. Percentage of aluminum leached from sludge versus the pH of the extractant solution.

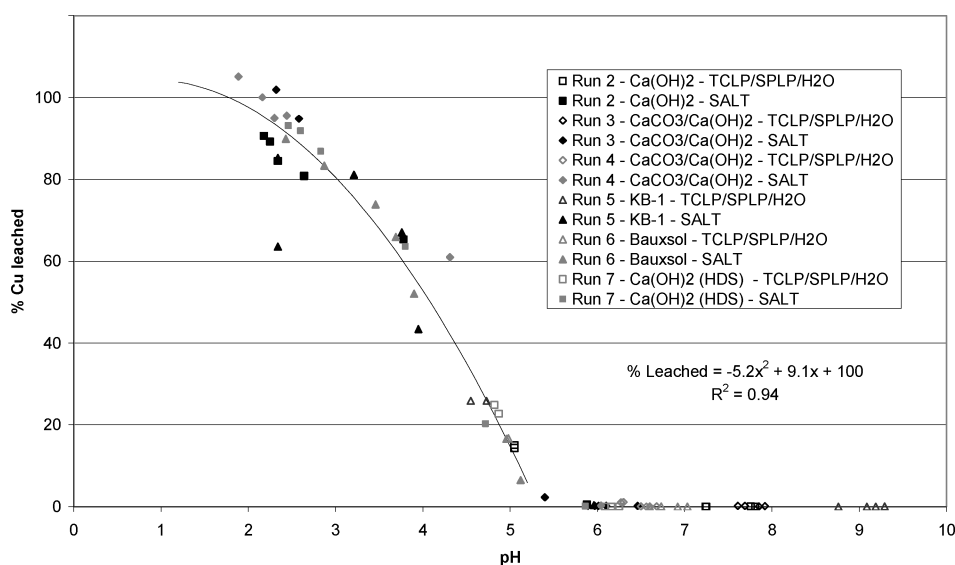


FIGURE 4. Percentage of copper leached from sludge versus the pH of the extractant solution.

because both reagents contain this element (Table S2). The HDS hydrated lime sludge (run 7) has a higher density than normal hydrated lime sludge (run 2), due to its lower water content and coarser gypsum crystals (7), but has the same leachability. Third, different metals leach at very different rates and begin to be liberated at substantially different pH values (Figures 2–5).

Iron begins to dissolve at pH 3; the amount mobilized increases greatly (probably exponentially) at lower pH values, so that ~40% of the iron in the sludge has been liberated at a pH of 2–2.5. These results (Figure 2) reflect the solubility of poorly crystalline ferric oxyhydroxides (ferrihydrite); under very oxidizing Eh conditions, the stability boundary between ferrihydrite and soluble iron (as  $\text{Fe}^{3+}$ ) lies at a pH of 2–3 (21).

Aluminum starts to be released into the leachate at a higher pH (~4.5), and is leached more slowly as the pH drops, such that 60–70% is in solution at pH 2–2.5. This probably reflects the solubility of poorly crystalline aluminum hydroxide.

Copper begins to leach at around pH 5.5, and virtually all of it is in solution at pH 2–2.5. Zinc starts to be mobilized at a pH value of 6.5, and ~100% is soluble by pH 2.5. Copper and zinc are present in ARD treatment sludges as various species adsorbed onto the surface of the poorly crystalline

ferric oxyhydroxide (22, 23). The copper and zinc desorption curves from the present experiments (Figures 4 and 5) are not mirror images of typical adsorption curves for these metals on ferric oxides/hydroxides (22–24), in that desorption is complete at pH values well below those at which adsorption typically commences (2–2.5 compared to 3.5–5).

Trendlines fitted to the data (Figures 2–5) allow prediction of the proportion of metals that will be leached from a sludge at a specific pH. Although there is some spread in the data, the trendlines for Cu and Zn (elements with the most scatter) both have high  $R^2$  values (0.94 and 0.75, respectively). The aluminum data from runs 5 and 6 were not included when the aluminum trendline was calculated, as the reagents KB-1 and Bauxsol contain this element (Table S2). The SALT leach results for the KB-1 sludge contain two points (pH 2.34 and 3.21) that fall below the trend for that sludge, probably due to sludge inhomogeneity (discussed previously).

Similar results have been encountered in other studies. Watzlaf and Casson (25) found that iron and manganese release from sludges increased with a pH decrease in a stirred beaker, and in column leach experiments simulating co-disposal with tailings, Clarke (26) noted that leachate aluminum concentrations rose sharply after the neutralization capacity of the tailings/sludge mixtures had been

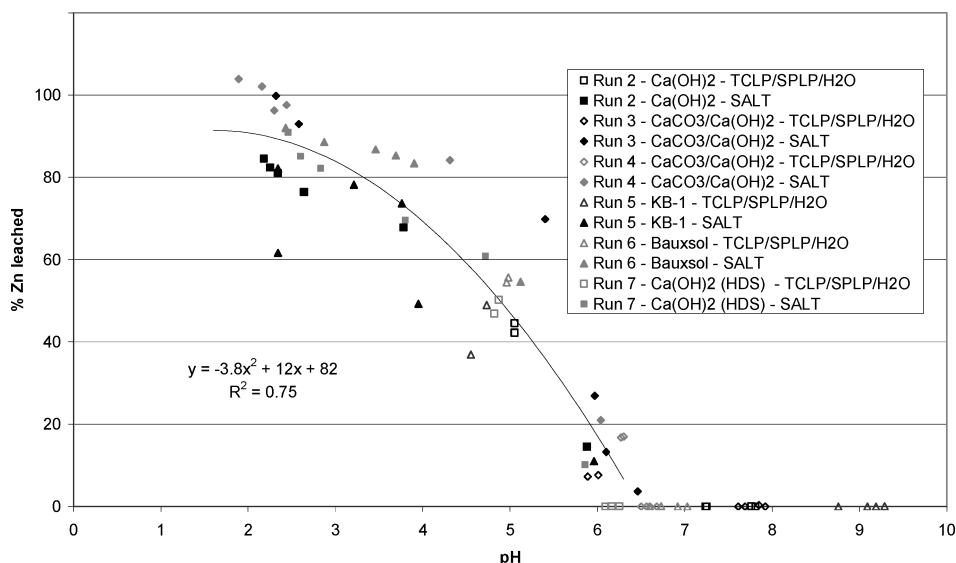


FIGURE 5. Percentage of zinc leached from sludge versus the pH of the extractant solution.

exhausted and the pH of the leachate within the column dropped.

**Neutralization Potential and Reagent Use Efficiency.** A sludge's neutralization potential reflects its composition. Dissolution of the metal hydroxides will neutralize a small amount of acid, and some reagents contain mineral impurities that can be transferred to the sludge and contribute to the neutralization potential, e.g., the limestone often present in hydrated lime (discussed further below). The neutralization potential is also determined by the efficiency of reagent use during ARD treatment. If a treatment process is highly efficient, then most of the reagent will be used in neutralizing the ARD, and there will be little unreacted reagent to contribute to the neutralization potential.

In the present study, the sludges with the lowest neutralization potential were generated by HDS, KB-1, and Bauxsol (Table 2). In the HDS process the greater contact time between the hydrated lime and the ARD, due to the sludge recycle step, allows a higher proportion of the hydrated lime (and limestone impurity) to react, reducing the neutralization potential. The HDS process uses 10–15% less reagent than conventional hydrated lime neutralization (Table 2) (5, 9). The low neutralization potential of the Bauxsol sludge reflected the long reaction time (21 days), whereas that of the KB-1 sludge was due to the lack of any slow-reacting minerals (e.g., calcite) within the reagent (Table S3).

The low neutralization potentials of the HDS, KB-1, and Bauxsol sludges indicate efficient reagent use, but also mean that these are the most readily leached sludges of those tested; a smaller volume of infiltrating acid is required to reduce the pore water pH to levels where metals start to be released. The interrelationship between reagent use efficiency and neutralization potential was concisely stated by Zinck et al. (4): "Higher neutralisation potentials are beneficial to long-term sludge stability, while low neutralisation potentials are attractive as they indicate the efficiency of the treatment process."

Hydrated lime neutralization sludges at 11 Canadian mine sites had neutralization potentials of 108–819 kg of  $\text{CaCO}_3$  equivalent/t of sludge (5). In comparison, the neutralization potentials in the present sludges are very low (45–83 kg of  $\text{CaCO}_3$  equivalent/t of sludge), probably largely reflecting the purity of the analytical grade hydrated lime used (94.5 wt %  $\text{Ca(OH)}_2$ ; Table S3). Commercially available hydrated lime used at mine sites contains less  $\text{Ca(OH)}_2$  (e.g., 82 wt % in hydrated lime supplied by Unimin Australia) and much higher levels of calcium carbonate and magnesium oxide,

carbonate, and hydroxide. These compounds will react slowly with ARD in the presence of hydrated lime, and will therefore be incorporated in the treatment sludge, but can still neutralize acidity infiltrating into the sludge after disposal. As a result, sludges produced by ARD neutralization using impure hydrated lime will intrinsically have higher neutralization potentials.

**Implications for Sludge Stability Leach Tests.** The currently recommended leach tests for assessing the chemical stability of ARD treatment sludges (TCLP, SPLP) are strongly affected by the neutralization potential of the sludge (because both use a fixed initial pH), and they do not subject a sludge to low enough pH values to simulate likely mine disposal options. In addition the leaching medium (acetic acid) will not be encountered in most mine situations. However, TCLP and SPLP may be appropriate tests for the alternative disposal routes where the sludge will not come into contact with significant amounts of acid (e.g., municipal landfill, uncovered sludge dam).

The new procedure SALT overcomes these problems because it is based on the final pH of the leachate and uses the appropriate acid (sulfuric) and pH conditions (as low as 2). The results of the present experiments illustrate clearly that SALT is able to determine the chemical stability of a sludge, i.e., how strongly metals are bound to it, under conditions likely to be encountered at mine sites. The completeness of results obtained by SALT compensates for the number of tests needed (5, 6), and means that the leachability of a sludge in its disposal site can be assessed over a range of pH conditions. In addition SALT provides an excellent test to assess new products claiming greater chemical stability than that from conventional hydrated lime neutralization, as it provides results that are independent of the neutralization potential.

**Implications for Sludge Management.** All neutralization methods produced sludges with similar chemical stabilities at any given pH, except for the Bauxsol and KB-1 sludges, which released more aluminum because these reagents contain this element. As the chemical stabilities of sludges produced with all reagents tested to date are broadly similar, other factors will affect the choice of most appropriate treatment reagent, e.g., the mass and volume of sludge produced (Table 2), the physical stability of the sludge, reagent usage and cost (Table 2), reagent availability and purity, occupational health and safety considerations, and the cost of installing and operating neutralization equipment.

The major factor governing the chemical stability (leachability) of the sludges investigated was the final pH of the leachate solution. Therefore, sludges with a higher neutralization potential are chemically stable for a longer period, not because metals are bound to the sludge more strongly, but because they can neutralize a larger volume of acid leachate before the pH drops to levels where the metals in the sludge are mobilized. This delays the release (and need for retreatment) of metal species. The neutralization potential is most easily increased by decreasing the efficiency of reagent use during ARD neutralization, but this will raise costs by increasing reagent usage. Thus, when ARD is treated, a choice must be made between reagent efficiency and leachability of the sludge generated.

The SALT results in this study show that, once the neutralization potential of an ARD treatment sludge is exhausted, the sludge becomes chemically unstable and begins to leach Fe, Al, Cu, and Zn at pH values of 2.5–3, ~4.5, ~5.5, and ~6.5, respectively. Zinc is of particular concern, as it begins to leach at a near-neutral pH. Therefore, the present results show that ARD treatment sludges should not be disposed of in any environment where they are likely to come into contact with acid; i.e., mine disposal is not generally a wise option. These results are generally applicable to mine sites worldwide; leach testing of sludge produced at an individual mine is advisable to check for any variability related to specific conditions at that site.

### Supporting Information Available

Images of the batch neutralization reactor (Figure S1) and HDS reactor (Figures S2 and S3), chemical composition of the reagents and sludges (Table S2), mineralogy of the reagents and sludges (Table S3), and composition of treated water (Table S1) and leachate from distilled water leach (Table S4), SPLP (Table S5), TCLP (Table S6), and SALT (Table S7). This material is available free of charge via the Internet at <http://pubs.acs.org>.

### Literature Cited

- Lottermoser, B. G. *Mine wastes: characterization, treatment, and environmental impacts*; Springer: Berlin, 2003.
- Taylor, J.; Waters, J. Treating ARD—how, when, where and why. *Min. Environ. Manage.* **2003**, *11* (2), 6–9.
- Mitchell, P.; Warhurst, A.; Noronha, L. Prediction, prevention, control, and treatment of acid rock drainage. In *Environmental policy in mining*; Warhurst, A., Noronha, L., Eds.; Lewis Publishers: New York, 2000; pp 117–143.
- Zinck, J. M.; Hogan, C. M.; Griffith, W. F.; Laflamme, J. H. G. *The effect of process parameters and aging on lime sludge density and stability*; MEND Report 4.42.2b; Natural Resources Canada (CANMET): Ottawa, Ontario, Canada, February 1999; 74 pp.
- Zinck, J. M.; Wilson, J. L.; Chen, T. T.; Griffith, W.; Mikhail, S.; Turcotte, A. M. *Characterization and stability of acid mine drainage treatment sludges*; MEND Report 3.42.2a; Natural Resources Canada (CANMET): Ottawa, Ontario, Canada, May 1997; 73 pp.
- Tremblay, G. A.; Hogan, C. M. *MEND Manual—Volume 5, treatment, active and passive*; MEND Report 5.4.2e; Natural Resources Canada (CANMET): Ottawa, Ontario, Canada, December 2000; 45 pp.
- Brown, M.; Barley, B.; Wood, H. *Minewater treatment: technology, application and policy*; IWA Publishing: London, 2002.
- CEMI. Statement of Qualifications. <http://www.cemi.bc.ca/soq1.html> (accessed April 24, 2004).
- Kuyucak, N. Lime neutralization process for treating acidic waters. U.S. Patent 5,427,691, 1995.
- Anderson, W.; Roma, J. Keeco and silica micro encapsulation. *Water Wastewater Asia* **2003**, January, 18–20.
- Mitchell, P.; Wheaton, A. From environmental burden to natural resource; new reagents for cost-effective treatment of and metal recovery from, acid rock drainage. In *Sudbury '99: mining and the environment II*, Sudbury, ON, Canada, Sept 13–17, 1999; Goldsack, D. E., Belzile, N., Yearwood, P., Hall, G. J., Eds.; Centre in Mining and Mineral Exploration Research CIMMER), Laurentian University: Sudbury, Ontario (see <http://www.e-sga.org/news7/art12.html>), 1999; pp 1231–1240.
- McConchie, D.; Clarke, M.; Hanahan, C.; Davies-McConchie, F. The use of treated bauxite refinery residues in the management of acid sulphate soils, sulphidic mine tailings and acid mine drainage. In *Proceedings of the 3rd Queensland environment conference*, Brisbane, Australia, May 25–26, 2000; Gaul, K., Ed.; 2000; Environmental Engineering Society, Queensland Chapter, The Institution of Engineers, Australia, Queensland Division, and Queensland Chamber of Commerce and Industry: pp 201–208.
- McConchie, D.; Clark, M.; Davies-McConchie, F.; Fergusson, L. The use of Bauxsol technology to treat acid rock drainage. *Min. Environ. Manage.* **2002**, *10* (4), 12–13.
- U.S. EPA. *Applicability of the Toxicity Characteristic Leaching Procedure to mineral processing wastes*; United States Environmental Protection Agency: Washington, DC, April 1998; 28 pp.
- McDonald, D.; Webb, J.; Ruddick, M.; Woollard, J.; Glaisher, R. Quantifying the amorphous content of acid rock drainage (ARD) treatment sludge using XRD and XRF. *Australian X-ray Analytical Association 2005 Schools and Conference*, Fremantle, Western Australia, Feb 14–18, 2005; p 111.
- Eaton, A. D.; Clesceri, L. S.; Greenberg, A. E., Eds. *Standard methods for the examination of water and wastewater*, 19th ed.; APHS-AWWA-WEF: Washington, DC, 1995.
- Sobek, A. A.; Schuller, W. A.; Freeman, J. R.; Smith, R. M. *Field and laboratory methods applicable to overburdens and mines soils*; EPA-600/2-78-054; United States Environmental Protection Agency: Washington, DC, 1978.
- Aube, B. C.; Clyburn, B.; Zinck, J. M. Sludge Disposal in Mine workings at Cape Breton Development Corporation. *Securing The Future: International Conference on Mining and the Environment, Metals and Energy Recovery*; Skelleftea, Sweden, 2005; Vol. 1, pp 37–47.
- Vachon, D.; Siwik, R. S.; Schmidt, J.; Wheeland, K. Treatment of acid mine water and the disposal of lime neutralisation sludge. *Proceedings, acid mine drainage seminar/workshop*, March 23–26, 1987; Environment Canada: Ottawa, 1987; p 617.
- Woollard, J. The composition and stability of mine treatment sludges. Honours Thesis, Department of Earth Sciences, La Trobe University, Melbourne, 2003; 107 pp.
- Drever, J. I. *The geochemistry of natural waters*, 3rd ed.; Prentice Hall Inc.: Upper Saddle River, NJ, 1997.
- Kinniburgh, D. G.; Jackson, M. L.; Syers, J. K. Adsorption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. *Soil Sci. Soc. Am. J.* **1976**, *40* (5), 796–799.
- Webster, J. G.; Swedlund, P. J.; Webster, K. S. Trace metal adsorption onto an acid mine drainage iron(III) oxy hydroxy sulphate. *Environ. Sci. Technol.* **1998**, *32*, 2 (10), 1361–1368.
- Dzombak, D. A.; Morel, F. M. M. *Surface Complexation Modeling: Hydrous Ferric Oxide*; John Wiley & Sons: New York, 1990.
- Watzlaf, G. R.; Casson, L. W. Chemical stability of manganese and iron in mine drainage treatment sludge. In *Mining and Reclamation Conference and Exhibition*, April 23–26, 1990; West Virginia University: Charleston, WV, 1990; Vol. 1, pp 3–9.
- Clarke, N. *Memorandum—potential effects of sludge disposal on the CMT tailings dam*; IMTECH Pty Ltd., July 14, 2000; 20 pp.

Received for review August 2, 2005. Revised manuscript received December 22, 2005. Accepted December 30, 2005.

ES0515194