

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

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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)₂. 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

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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 ^{a,b} (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 |
| run 4 | 170 L reactor | 15 wt % hydrated lime slurry | 9.55 | | 4.99 | 92 | |
| | | 15 wt % limestone slurry | 5.17 | 7.71 (after 4 days of sparging) | 5.88 | 77 | continuous, including for 4 days between adding CaCO ₃ and hydrated lime |
| run 5 | 170 L reactor | 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 |

^a The reaction time for runs 1–6 is the time taken to add reagent. Further reagent dissolution or Fe oxidation may occur after this. ^b 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.

119 1200 mg/L Fe, 110 mg/L Al, 100 mg/L Cu, and 100 mg/L Zn
120 (all ±10 mg/L), made up with tap water. The pH was lowered
121 to 2.3 with sulfuric acid, giving a total sulfate concentration
122 of ~4000 mg/L.

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

136 **HDS Reactor.** The laboratory-scale HDS plant consisted
137 of three 1.1 L reactors and a 1 L separation funnel for solid/
138 liquid separation. A total of 250 L of synthetic ARD (pH 2.3)
139 was pumped into reactor 1 at a rate of 25 mL/min; the ARD
140 retention time was approximately 20 min in each reactor. All
141 three reactors were constantly sparged with air. The overflow
142 from the separator (treated water) flowed into a collection
143 container, and the underflow (sludge) was pumped into
144 reactor 1 at a recycle rate of 18–22 after an initial start-up
145 period (i.e., an 18–22 g dry weight of solids was pumped into
146 reactor 1 for each gram of solids precipitated from the ARD
147 neutralization). The recycled sludge raised the pH in reactor
148 1 to between 6.7 and 7.2. A 10 wt % hydrated lime slurry was
149 pumped into reactor 2 to increase the pH to 9 to complete
150 the treatment.

151 **Sludge Analysis.** The sludges from all experiments had a
152 high water content, and were effectively slurries. After oven
153 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 neutraliza-
tion 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 μm). 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
(CH₃CH₂COOH), diluted to 1 L with distilled water (pH 2.88
±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
(±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 devel-
oped: 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 ~1 pH unit with each
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

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 ^a (mL/L ARD treated) | solids content of sludge ^a (wt %)(C) | neutralization potential of sludge ^b | rel cost of reagent ^c (D) | overall rating ^d (=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 ₃)/ 4.8 (Ca(OH) ₂) | 17.6 | 162 | 10.2 | 452 | 0.2 (CaCO ₃) | 10.3 |
| run 4 | limestone/hydrated lime | 6.0 (CaCO ₃)/ 0.1 (Ca(OH) ₂) | 10.8 | 70 | 12.2 | 173 | 0.2 (CaCO ₃) | 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 ^e | ~25 ^e | 38.9 | 45.1 | 1 | 0.9 |

^a Determined after 24 h of settling. ^b Units for neutralization potential are kg of CaCO₃ equivalent/t of dry sludge. ^c 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). ^d 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 and capital costs not considered. ^e Estimate only, due to sludge recycle in HDS setup.

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 SO₄ 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 Al₂O₃ 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 %) H₂SO₄/HNO₃, 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.

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

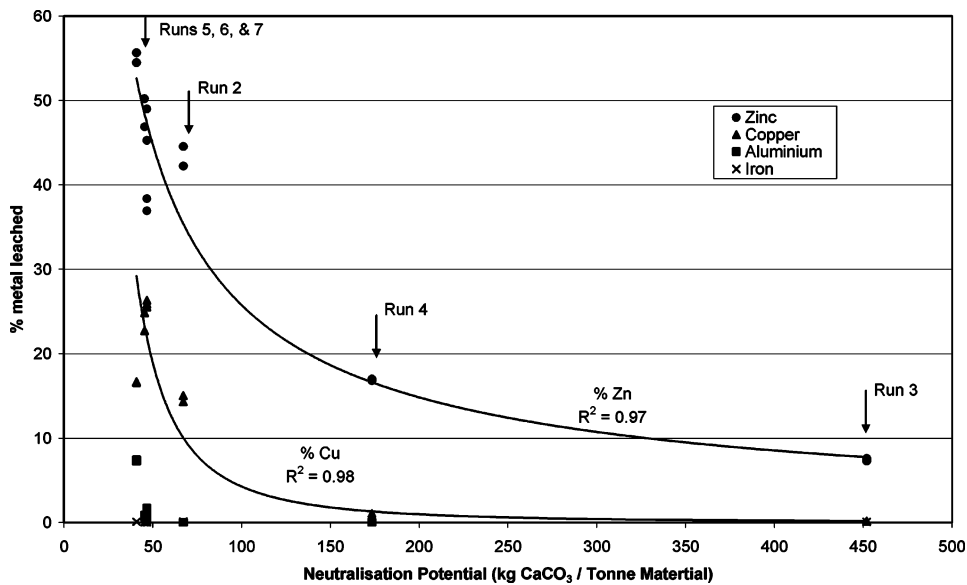


FIGURE 1. Relationship between the percentage of metals extracted by TCLP and the neutralization potential of a sludge.

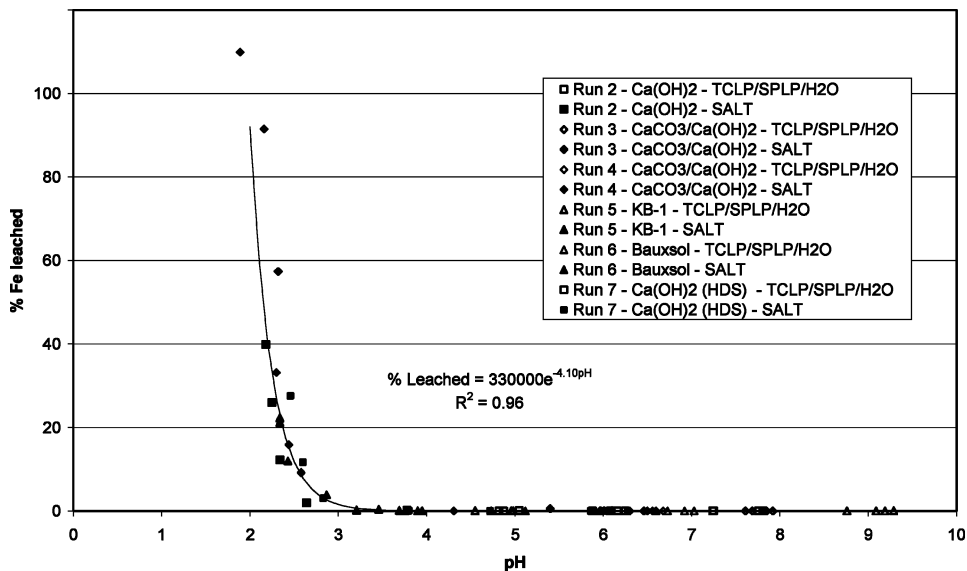


FIGURE 2. Percentage of iron leached from sludge versus the pH of the extractant solution.

286 (Table S6), probably due to inhomogeneity of the sludge, 308
 287 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. 309

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 290 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. 310

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 295 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. 311

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 306 Although TCLP gives a more realistic idea of sludge chemical stability than SPLP and is probably applicable for 312

308 sludge disposed to municipal waste sites, it does not encompass the range of pH values likely to be encountered at mine sites. 309

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 311 **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. 317

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 323 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 because both reagents contain this element (Table S2). The 324
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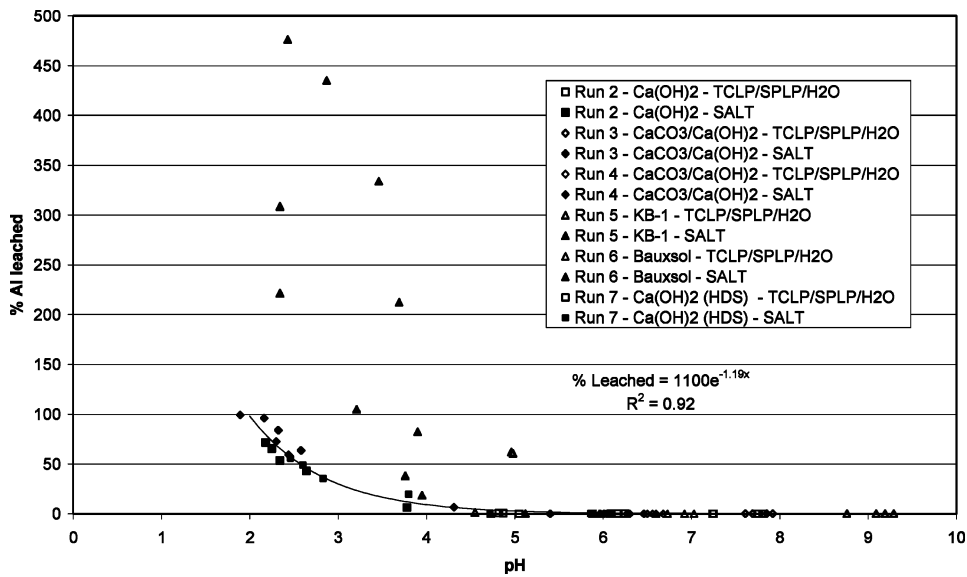


FIGURE 3. Percentage of aluminum leached from sludge versus the pH of the extractant solution.

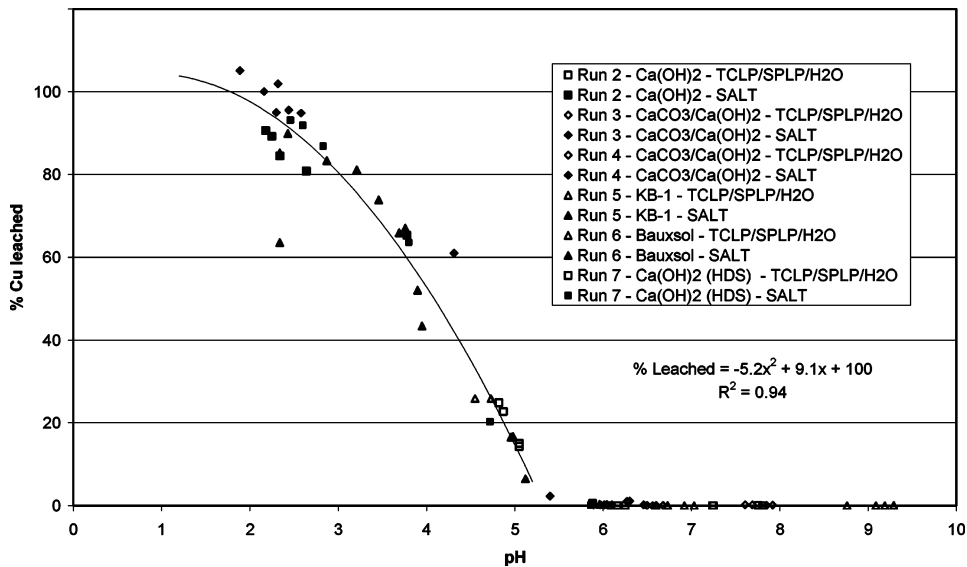


FIGURE 4. Percentage of copper leached from sludge versus the pH of the extractant solution.

330 HDS hydrated lime sludge (run 7) has a higher density than
 331 normal hydrated lime sludge (run 2), due to its lower water
 332 content and coarser gypsum crystals (7), but has the same
 333 leachability. Third, different metals leach at very different
 334 rates and begin to be liberated at substantially different pH
 335 values (Figures 2–5).

336 Iron begins to dissolve at pH 3; the amount mobilized
 337 increases greatly (probably exponentially) at lower pH values,
 338 so that ~40% of the iron in the sludge has been liberated at
 339 a pH of 2–2.5. These results (Figure 2) reflect the solubility
 340 of poorly crystalline ferric oxyhydroxides (ferrihydrite); under
 341 very oxidizing Eh conditions, the stability boundary between
 342 ferrihydrite and soluble iron (as Fe³⁺) lies at a pH of 2.5–3
 343 (21).

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

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

ferric oxyhydroxide (22, 23). The copper and zinc desorption
 353 curves from the present experiments (Figures 4 and 5) are
 354 not mirror images of typical adsorption curves for these
 355 metals on ferric oxides/hydroxides (22–24), in that desorption
 356 is complete at pH values well below those at which adsorption
 357 typically commences (2–2.5 compared to 3.5–5).
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359 Trendlines fitted to the data (Figures 2–5) allow prediction
 360 of the proportion of metals that will be leached from a sludge
 361 at a specific pH. Although there is some spread in the data,
 362 the trendlines for Cu and Zn (elements with the most scatter)
 363 both have high R² values (0.94 and 0.75, respectively). The
 364 aluminum data from runs 5 and 6 were not included when
 365 the aluminum trendline was calculated, as the reagents KB-1
 366 and Bauxsol contain this element (Table S2). The SALT leach
 367 results for the KB-1 sludge contain two points (pH 2.34 and
 368 3.21) that fall below the trend for that sludge, probably due
 369 to sludge inhomogeneity (discussed previously).

370 Similar results have been encountered in other studies.
 371 Watzlaf and Casson (25) found that iron and manganese
 372 release from sludges increased with a pH decrease in a stirred
 373 beaker, and in column leach experiments simulating co-
 374 disposal with tailings, Clarke (26) noted that leachate
 375 aluminum concentrations rose sharply after the neutraliza-

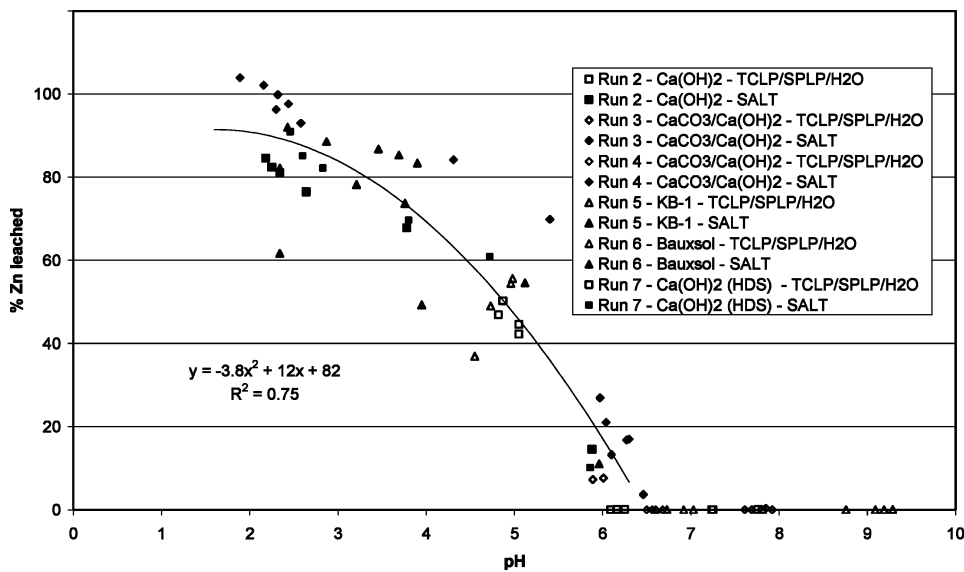


FIGURE 5. Percentage of zinc leached from sludge versus the pH of the extractant solution.

376 tion capacity of the tailings/sludge mixtures had been
 377 exhausted and the pH of the leachate within the column
 378 dropped.

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

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

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

414 Hydrated lime neutralization sludges at 11 Canadian mine
 415 sites had neutralization potentials of 108–819 kg of CaCO₃
 416 equivalent/t of sludge (5). In comparison, the neutralization
 417 potentials in the present sludges are very low (45–83 kg of
 418 CaCO₃ equivalent/t of sludge), probably largely reflecting
 419 the purity of the analytical grade hydrated lime used (94.5
 420 wt % Ca(OH)₂; Table S3). Commercially available hydrated
 421 lime used at mine sites contains less Ca(OH)₂ (e.g., 82 wt %

422 in hydrated lime supplied by Unimin Australia) and much
 423 higher levels of calcium carbonate and magnesium oxide,
 424 carbonate, and hydroxide. These compounds will react slowly
 425 with ARD in the presence of hydrated lime, and will therefore
 426 be incorporated in the treatment sludge, but can still
 427 neutralize acidity infiltrating into the sludge after disposal.
 428 As a result, sludges produced by ARD neutralization using
 429 impure hydrated lime will intrinsically have higher neutral-
 430 ization potentials.

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

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

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

468 occupational health and safety considerations, and the cost
 469 of installing and operating neutralization equipment.

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

484 The SALT results in this study show that, once the neu-
 485 tralization potential of an ARD treatment sludge is exhausted,
 486 the sludge becomes chemically unstable and begins to leach
 487 Fe, Al, Cu, and Zn at pH values of 2.5–3, ~4.5, ~5.5, and
 488 ~6.5, respectively. Zinc is of particular concern, as it begins
 489 to leach at a near-neutral pH. Therefore, the present results
 490 show that ARD treatment sludges should not be disposed of
 491 in any environment where they are likely to come into contact
 492 with acid; i.e., mine disposal is not generally a wise option.
 493 These results are generally applicable to mine sites worldwide,
 494 although leach testing of sludge produced at an individual
 495 mine is advisable to check for any variability related to specific
 496 conditions at that site.

497 **Supporting Information Available**

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

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