

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)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

* 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 ^{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
		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 ₃ 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

^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.

1200 mg/L Fe, 110 mg/L Al, 100 mg/L Cu, and 100 mg/L Zn (all ± 10 mg/L), made up with tap water. The pH was lowered to 2.3 with sulfuric acid, giving a total sulfate concentration of ~ 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 μ 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 (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 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 ~ 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 ^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/capital costs not considered. ^e Estimate only, due to sludge recycle in HDS setup.

187 test, such that the pH at the end of the first extraction was
188 ~6 and that at the end of the last test was ~2. The volume
189 of sulfuric acid for each extraction was chosen to achieve the
190 required pH.

191 The extractant fluid from each leach test was analyzed for
192 Fe, Cu, Zn, Ca, Na, and Mg by AAS, Al and Si by ICP-AES, and
193 Cl and SO₄ by ion chromatography.

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

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

208 Results and Discussion

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

213 **Reagent Composition.** The hydrated lime and limestone
214 used in this study contained small amounts of impurities
215 (Table S3 in the Supporting Information). Both KB-1 (ob-
216 tained from KEECO) and Bauxsol (obtained from Virotec
217 International, Australia, who sourced it from Comalco,
218 Tasmania) contain significant aluminum levels (Table S2).
219 In KB-1, the aluminum is an amorphous phase. In Bauxsol
220 it occurs as the aluminous minerals boehmite and gibbsite
221 (Table S3), but these cannot account for all the Al₂O₃ present
222 (Table S2), so some must be present as an amorphous phase.
223 The Bauxsol blend contained 10 wt % MgO and 5 wt %
224 hydrated lime, as recommended by Virotec for the synthetic
225 ARD composition used in the present study.

226 **Sludge Composition.** Chemical and mineralogical analy-
227 ses (Tables S2 and S3) showed that all sludges consist
228 predominantly of amorphous ferric oxyhydroxide and crys-
229 talline gypsum, except for the Bauxsol sludge, which lacks
230 gypsum. Runs 5 and 6 sludges contain aluminous material
231 inherited from the KB-1 and Bauxsol reagents.

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

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

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

255 **Comparison of TCLP, SPLP, and Deionized Water Leach**
256 **Tests.** The SPLP and deionized water leach tests gave very
257 similar results and extracted minimal amounts of metals
258 (often below detection limits) from the sludges (Figures 2–4,
259 Tables S4 and S5 in the Supporting Information), verifying
260 the results of previous studies (see, e.g., refs 19 and 20). The
261 1 L of SPLP extractant fluid (pH 4.2) contains less than 1 drop
262 of 60:40 (wt %) H₂SO₄/HNO₃, and consequently has a very
263 low acidity. After completion of all SPLP and deionized water
264 leach tests the supernatant fluid had circum-neutral pH
265 (Tables S4 and S5), due to the substantial neutralization
266 potential of the sludges (Table 2). Clearly the SPLP and water
267 leach procedures cannot simulate metal release from sludges
268 at the substantially lower pH values likely to be encountered
269 at mine sites.

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

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

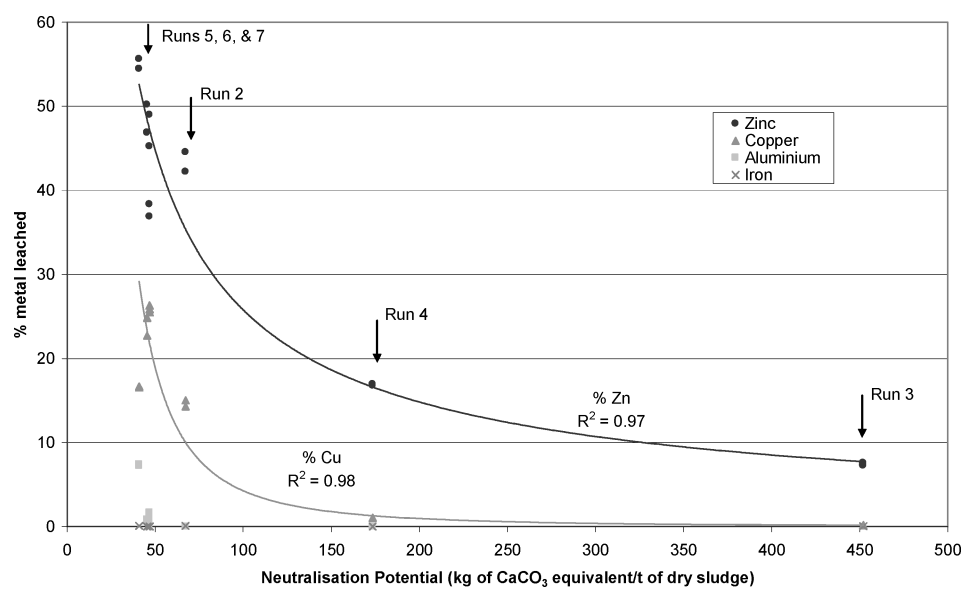


FIGURE 1. Relationship between the percentage of metals extracted by TCLP and the neutralization potential of a sludge.

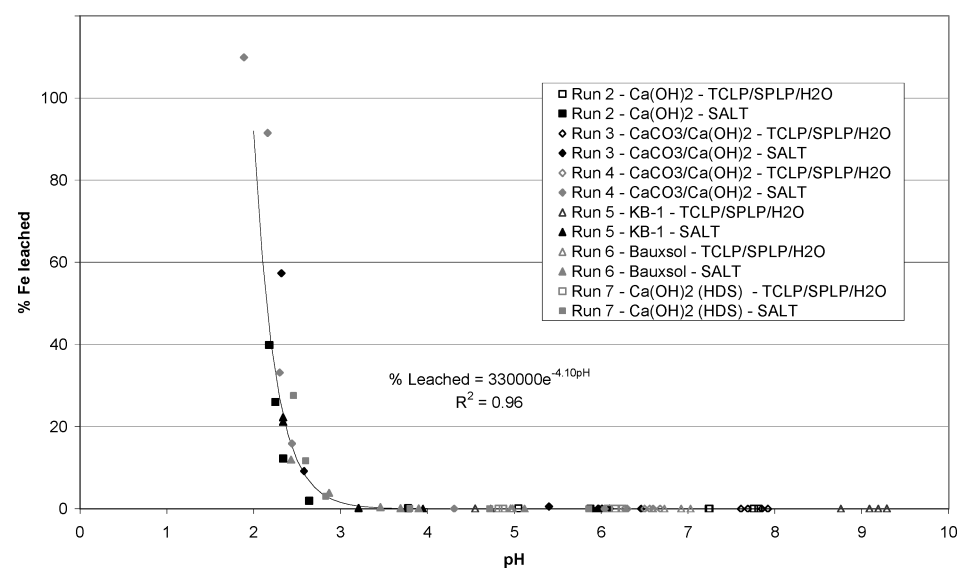


FIGURE 2. Percentage of iron leached from sludge versus the pH of the extractant solution.

283 Four TCLP extractions were performed on sludge from
 284 run 5 (neutralizing reagent KB-1), in sets of two, approxi-
 285 mately 2 months apart. The results show large variations
 286 (Table S6), probably due to inhomogeneity of the sludge,
 287 which consists of two distinct phases: a light brown iron hy-
 288 droxide (similar to that precipitated by the other neutraliza-
 289 tions) and a denser sand-sized fraction of silica particles.
 290 The results of this study for the KB-1 neutralization sludge
 291 are closely comparable to those of Mitchell and Wheaton
 292 (11), who subjected sludge generated with KB-1 at the Bunker
 293 Hill lead–zinc mine to a modified TCLP leach test and
 294 recorded significant leaching of Zn.
 295 Sludges produced from the three reagents or treatment
 296 methods that have been claimed to have greater chemical
 297 stability than that from conventional hydrated lime neu-
 298 tralization (KB-1, run 5; Bauxsol, run 6; HDS, run 7) all had
 299 higher concentrations of aluminum, copper, and zinc in the
 300 TCLP leachate (Figure 1, Table S6). However, these sludges
 301 were not less chemically stable than standard hydrated lime
 302 sludge. The larger amounts of metals leached reflect the very
 303 low neutralization potentials of these sludges (Table 2), so
 304 that the final TCLP pH was lower, resulting in greater metal
 305 leaching.

306 Although TCLP gives a more realistic idea of sludge
 307 chemical stability than SPLP and is probably applicable for
 308 sludge disposed to municipal waste sites, it does not
 309 encompass the range of pH values likely to be encountered
 310 at mine sites.
 311 **SALT Results.** To obtain a clear idea of the chemical
 312 stability of a sludge, it should be leached under a variety of
 313 pH conditions, including low pH values, and SALT was
 314 developed for this purpose. In TCLP and SPLP the initial pH
 315 of the leachate is fixed (so the final pH of the leachate is
 316 determined by the neutralizing potential of the sludge),
 317 whereas in SALT the final pH of the leachate is important.
 318 Sufficient acid is added to overcome the sludge’s neutralizing
 319 potential, and hence, much greater amounts of metals are
 320 liberated into the extracting fluid. Thus, SALT measures how
 321 tightly metals are bound to the sludge, rather than how much
 322 alkalinity the sludge contains.
 323 Several conclusions are evident from the SALT tests
 324 (Figures 2–5). First, as expected, the lower the pH of the
 325 leaching solution, the more metals were leached from all
 326 sludges. Second, all the reagents used in this study generated
 327 sludges with similar chemical stabilities, except for the
 328 Bauxsol and KB-1 sludges, which released more aluminum

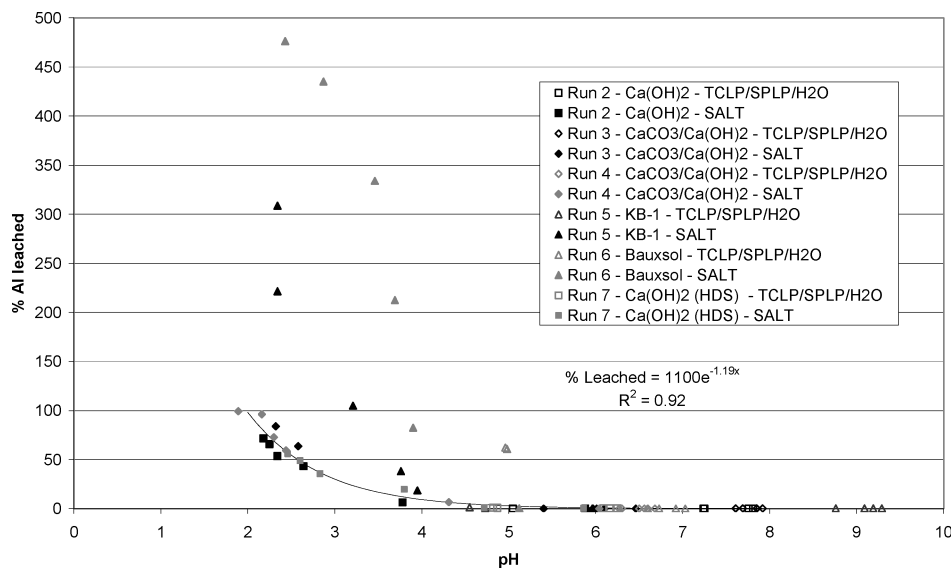


FIGURE 3. Percentage of aluminum leached from sludge versus the pH of the extractant solution.

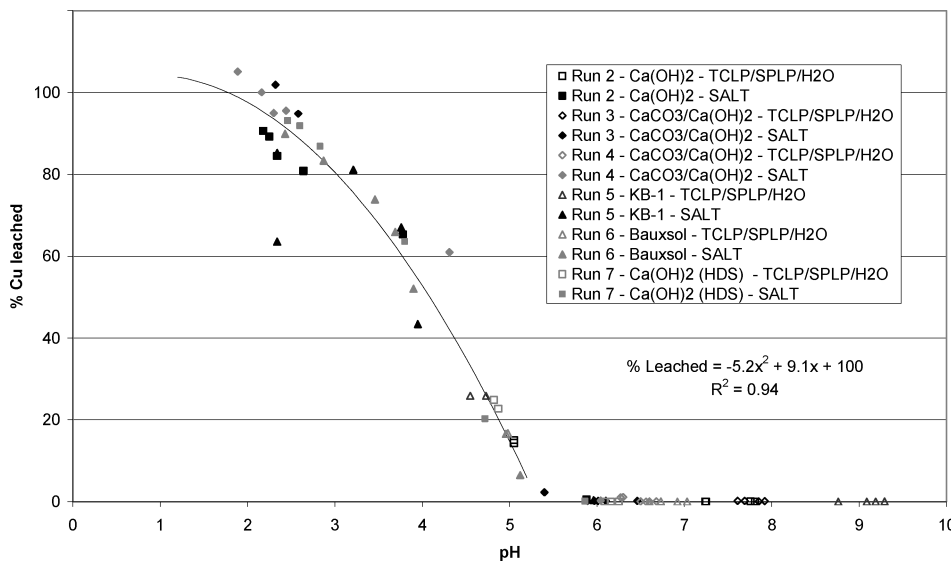


FIGURE 4. Percentage of copper leached from sludge versus the pH of the extractant solution.

329 because both reagents contain this element (Table S2). The
 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 Fe^{3+}) lies at a pH of
 343 2–3 (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).
 358

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 R^2 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-
 376 tion capacity of the tailings/sludge mixtures had been

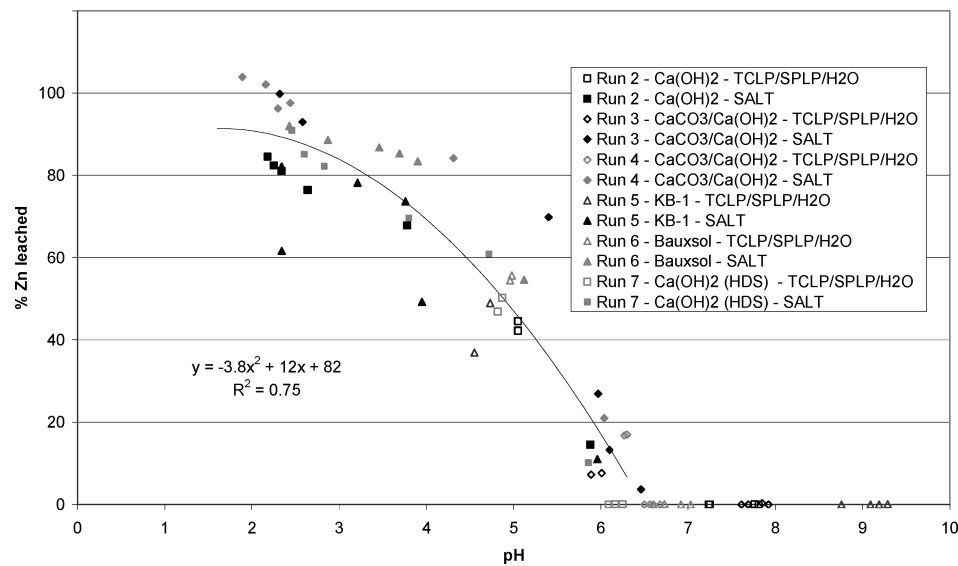


FIGURE 5. Percentage of zinc leached from sludge versus the pH of the extractant solution.

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 neu-
392 tralization 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 neu-
397 tralization 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 neutraliza-
459 tion methods produced sludges with similar chemical
460 stabilities at any given pH, except for the Bauxsol and KB-1
461 sludges, which released more aluminum because these
462 reagents contain this element. As the chemical stabilities of
463 sludges produced with all reagents tested to date are
464 broadly similar, other factors will affect the choice of most
465 appropriate treatment reagent, e.g., the mass and volume
466 of sludge produced (Table 2), the physical stability of the
467 sludge, reagent usage and cost (Table 2), reagent availability
468 and purity, occupational health and safety considerations,
469 and the cost of installing and operating neutralization
470 equipment.

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

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

498 **Supporting Information Available**

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

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