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Conversion of mine drainage treatment sludges to sulfides using biogenic hydrogen sulfide

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Abstract

This study evaluated the potential benefits of converting mixed metal hydroxide sludges to sulfide and carbonate forms by contacting the sludges with hydrogen sulfide and carbon dioxide gas streams. The sulfide and carbonate forms of many metals have higher densities than the corresponding hydroxide forms. Increasing the density of metal sludges has the potential of reducing sludge handling and disposal costs. Sludges were generated from the lime treatment of a metal mine drainage. Aliquots of the supernatant and metal hydroxide sludge were contacted with (1) hydrogen sulfide; (2) carbon dioxide; and (3) a mixture of hydrogen sulfide and carbon dioxide. All sludges were evaluated for (1) density; (2) settling rate; (3) volume; and (4) leaching characteristics. The metal sulfide and carbonate sludges had higher densities and lower volumes than the metal hydroxide sludges. The settling rates were similar for all sludge forms.

Keywords: Sludge; Metal hydroxide; Metal sulfide; Metal carbonate; Sludge density; Sludge volume; Sludge handling; Sludge disposal

1. Introduction

Waste waters containing high concentrations of dissolved metals are generated by the mining industry. The most common treatment method for these waste streams is chemical neutralization. In the chemical neutralization process, metals are precipitated in hydroxide form (Reaction A):

$$M^{2+}_{(aq)} + 2OH^- \longrightarrow M(OH)_{2(s)} \qquad (A)$$

where M^{2+} = metal cation.

There are a number of problems associated with the handling and disposal of metal hydroxide sludges. Typically, these sludges are low density, gelatinous materials having a percent solids composition of 0.5–7% [1,2]. Solids separation can be difficult and dewatering operations are often required for economic reasons prior to disposal [3,4]. Sludge dewatering can be as expensive as the primary treatment of the waste stream [5].

The base metal and metal finishing industries also generate waste streams with elevated levels of dissolved metals. Sulfide precipitation is an alternative treatment method sometimes used in these industries. In this treatment method, metals are precipitated in a sulfide form (Reaction B):

$$M^{2+}_{(aq)} + S^{2-} \longrightarrow MS_{2(s)} \tag{B}$$

The precipitation of a sulfide sludge can reduce or eliminate many of the problems associated with metal hydroxide sludges. Metal sulfides generally have higher densities, lower volumes, and are reported to have better settling characteristics than the corresponding metal hydroxides [6]. Historically, sulfide precipitation has had limited usage in the mining industry due to the high reagent costs.

Recently, hydrogen sulfide produced by sulfate-reducing bacteria (SRB) has been used to treat metal contaminated waste waters [7–9]. These bacteria can be grown in anaerobic bioreactors using waste organics as the carbon source. In addition to producing H_2S, these bioreactors typically produce methane, CH_4, and carbon dioxide, CO_2. The CO_2 in the bioreactor gas stream is a source of carbonate that can also be used to remove metals (Reaction C):

$$M^{2+}_{(aq)} + 2(CO_3^-) \longrightarrow M(CO_3)_{2(s)} \tag{C}$$

Anaerobic digesters at municipal wastewater treatment plants also produce H_2S and CO_2 as waste products. Digester gas can be an inexpensive reagent source for the treatment of metal contaminated waste waters and the conversion of metal hydroxide sludges.

The hypothesis of this study was that the physical properties of a mixed metal hydroxide sludge can be improved by contacting it with H_2S and/or CO_2. In this study, a metal mine drainage was treated using the chemical neutralization process to generate a metal hydroxide sludge. The sludge was subsequently contacted with bottled H_2S and CO_2 gases. The concentrations of H_2S and CO_2 used were based on the waste gas composition of a pilot-scale anaerobic bioreactor.

2. Experimental plan

2.1. Materials and equipment

- Mine drainage (Table 1).
- Hydrated lime, $Ca(OH)_2$. Commercial grade lime slurried with deionized water.
- Hydrogen sulfide, H_2S. Bottled gas containing 4% H_2S and 96% N_2, by volume.
- Carbon dioxide, CO_2. Bottled gas containing 100% CO_2.

Table 1

Chemical composition of the mine drainage and primary and secondary treatment supernatants, expressed in mg/l

	Untreated	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Secondary treatment with H_2S/CO_2
pH*	3.1	9.5	7.7	6.7	7.1
Cu	90	0.14	0.22	0.22	<0.02
Zn	429	<0.02	<0.02	9.2	0.31
Fe	109	<0.05	<0.05	<0.05	<0.05
Mn	41	1.2	0.42	6.2	1.6
SO_4	12,479	9,706	9,449	4,125	4,000

*Standard units.

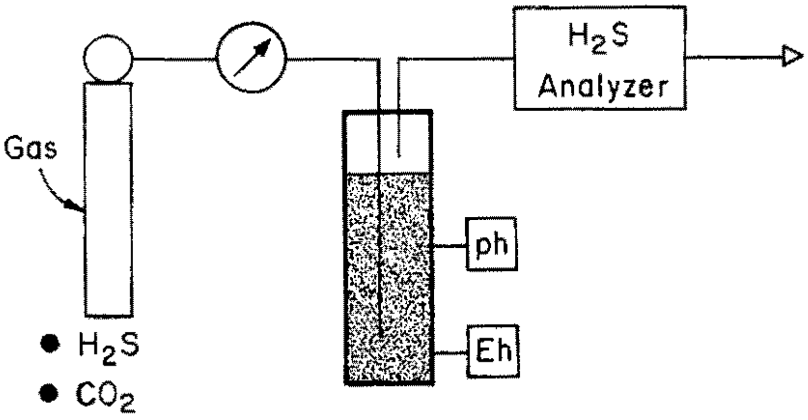

Fig. 1. Schematic of the second stage treatment.

– Nitrogen, N_2. Bottled gas containing 100% N_2.
– Gas–liquid contactor. A clear polyvinyl chloride (PVC) pipe, nominal 6.4 cm diameter × 0.6 m long (Fig. 1). The pipe was fitted with threaded PVC caps. The top cap was fitted with a 1.9 cm PVC pipe for introducing the gas and a discharge port for the spent gas. Side ports were installed for cycling the solid/liquid slurry through pH and Eh electrode wells. The contactor was mounted on top of a magnetic stir plate and a stir bar was placed in the bottom of the contactor.

2.2. *Procedure*

Twelve 1-l aliquots of mine drainage were treated with a $Ca(OH)_2$ slurry. In each treatment, the pH of the mine drainage was increased from 2.9 to approximately 9.5 by the addition of 18.5 g of $Ca(OH)_2$. The first three aliquots served as the experimental control. The second set of three aliquots was subsequently contacted with a 4% H_2S gas stream until the H_2S concentration in the discharge gas stream reached 3%. The third set of three aliquots was contacted with a 9% CO_2 gas stream until buffering occurred at a pH in the mid-6's. The fourth set of three aliquots was contacted with a mixed gas stream of approximately 3.5% H_2S and 9% CO_2 for a period of 10 min. Nitrogen was used as the balance for all gas streams.

After treatment, each of the 12 aliquots were placed in 1-l Imhoff cones. The head space of the cone was sparged with N_2 and the cone sealed with Parafilm. The sludge volume was recorded every 5 min during the first hour, every 15 min during the second hour, and after 24 hours of settling.

All sludges were dried in a vacuum oven, pulverized, and then placed in centrifuge tubes sparged with N_2. Each sludge type was evaluated for (1) density; (2) settling rate; (3) volume; and (4) leaching characteristics [10–13]. The Toxicity Characteristic Leaching Procedure (TCLP); and the Sequential Extraction Procedure (SEP) were used to evaluate the leaching characteristics of the sludges. The metal hydroxide sludge served as the experimental control against which the performances of the other sludges were measured.

Water samples were filtered with a 0.4 micron syringe filter, acidified with hydrochloric acid, and then analyzed for dissolved metals and sulfate by the Inductively-coupled plasma, (ICP), spectroscopy method [14,15]

3. Results

Secondary treatment of sludge and supernatant with CO_2 produced a supernatant with a pH of 6.7 (Table 1). This pH value was consistent with a carbonate buffered chemical system. The sludge and supernatant contacted with H_2S and CO_2 had a supernatant pH of 7.1, a value that was intermediate for the supernatants generated from H_2S and CO_2 treatments. Generally, secondary treatment resulted in low supernatant metal concentrations. However, the supernatant generated from CO_2 treatment showed increased levels of zinc and manganese.

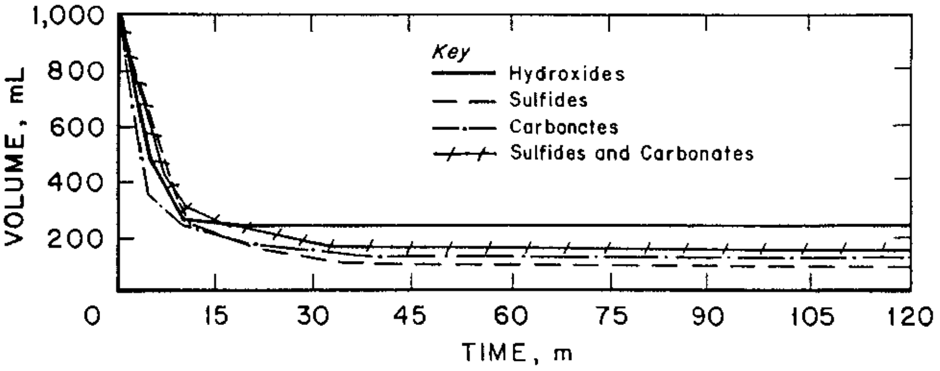

Fig. 2. Sludge settling curves.

After 2 hours of settling, the mean sludge volume of the control hydroxide sludge was 338 ml. For the sulfide, sulfide/carbonate, and carbonate sludges the mean volumes were 182 ml, 148 ml, and 132 ml, respectively (Fig. 2). The percent solids of the hydroxide sludge was 9.8%. The percent solids of sulfide/carbonate and carbonate sludges were 23% and 19%, respectively. The sulfide sludge had a percent solids of 13%.

Metal leachate concentrations from the TCLP are presented in Table 2. The leaching profiles from the SEP are presented in Tables 3–6.

Table 2

Leachate concentrations generated in the Toxicity Characteristic Leaching Procedure, expressed in mg/l

	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Treatment with H_2S/CO_2
Cu	0.03	0.34	0.05	0.62
Zn	0.14	4.8	0.41	1.5
Fe	0.06	0.04	<0.02	<0.02
Mn	<0.006	11	<0.006	9.7

Table 3

Leachate concentrations of copper generated in the Sequential Extraction Procedure, expressed in mg/l

Fraction	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Treatment with H_2S/CO_2
1 Water soluble metals	0.02	0.25	0.05	0.05
2 Ion exchangeable metals	0.37	1.3	0.38	0.91
3 Metals bound to carbonates and hydroxides	33	32	42	34
4 Metals bound to iron and manganese oxides	1.1	2.4	17	1.2
5 Metals bound to sulfides and organics	0.03	10	0	9

Table 4

Leachate concentrations of zinc generated in the Sequential Extraction Procedure, expressed in mg/l

Fraction	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Treatment with H_2S/CO_2
1 Water soluble metals	0.03	0.05	0.32	1.1
2 Ion exchangeable metals	0.01	0.1	0.02	0.009
3 Metals bound to carbonates and hydroxides	160	202	187	171
4 Metals bound to iron and manganese oxides	2.5	5	62	39
5 Metals bound to sulfides and organics	0.08	0.05	0	<0.05

Table 5

Leachate concentrations of iron generated in the Sequential Extraction Procedure, expressed in mg/l

Fraction	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Treatment with H_2S/CO_2
1 Water soluble metals	<0.02	<0.02	<0.02	<.02
2 Ion exchangeable metals	<0.02	<0.02	<0.02	<0.02
3 Metals bound to carbonates and hydroxides	21	25	60	49
4 Metals bound to iron and manganese oxides	7	5.7	39	28
5 Metals bound to sulfides and organics	0.05	<0.05	0	<0.1

Table 6

Leachate concentrations of manganese generated in the Sequential Extraction Procedure, expressed in mg/l

Fraction	Primary treatment	Secondary treatment with H_2S	Secondary treatment with CO_2	Treatment with H_2S/CO_2
1 Water soluble metals	<0.006	0.05	<0.006	<9.006
2 Ion exchangeable metals	<0.006	0.32	<0.006	<0.006
3 Metals bound to carbonates and hydroxides	11	19	13	16
4 Metals bound to iron and manganese oxides	3.6	0.91	7	4
5 Metals bound to sulfides and organics	<0.1	0.04	0	<0.03

4. Discussion

All sludges receiving secondary treatment had increased densities relative to the control sludge (no secondary treatment). The density of the sulfide sludge was 146% of the density of the control sludge. The carbonate and sulfide/carbonate sludges had densities of 213% and 258% of the control sludge density, respectively. Increased densities for metal sulfides and metal carbonates are consistent with reported density values of many metal sulfides and carbonates relative to the corresponding metal hydroxides [6]. The sulfide/carbonate sludge had the highest percent solids, followed by the carbonate, sulfide and hydroxide sludges. Higher sludge densities often reduce or eliminate the need for sludge dewatering.

All sludges that received secondary treatment had reduced volumes after 2 hours of settling relative to the control sludge (Fig. 2). The volume of the sulfide sludge was 54% of the control sludge,, while the volumes of the sulfide/carbonate sludge and carbonate sludge were 44%, and 39% of the control sludge volume, respectively.

An experiment was conducted to determine if improvements in the physical properties of the hydroxide sludge could be attributed to mixing alone. In this experiment, three aliquots of mine drainage were treated with $Ca(OH)_2$. The first aliquot was placed in an Imhoff cone 10 min after the $Ca(OH)_2$ was added. The second aliquot was mixed for 40 min using a magnetic stir bar and then placed in an Imhoff cone. The third aliquot was mixed for 10 min with a magnetic stir bar and then placed in the gas/liquid contactor. N_2 was bubbled through the sludge for 30 min. This sludge was then also placed in an Imhoff cone. After 2 hours of settling, the sludge receiving 10 min of stirring with no N_2 agitation had the greatest volume. The sludge agitated for 40 min with N_2 agitation had 60% the volume of the first aliquot. The sludge receiving 40 min of stirring without N_2 agitation had an intermediate volume at 76% of the first aliquot. From these data it is concluded that improved mixing without chemical transformation has some beneficial impact on sludge properties, probably by encouraging further dissolution of excess lime.

Although we hypothesized that secondary treatment would improve the physical properties of the sludge, it was unclear how the treatments would affect the chemical properties of the sludge. Results from the TCLP indicated that the secondary treatments produced no significant changes in metal mobility for most metals (Table 2). Moderate concentrations of zinc were found in the leachate from the sulfide sludge, however, and moderate to high concentrations of manganese were found in the sulfide and sulfide/carbonate sludge leachates.

The SEP was used to evaluate the changes in the leachability of metal compounds following secondary treatment. The SEP showed a similar leaching pattern for all four sludge types, with two exceptions (Table 3). The leaching pattern showed very little metal mobilization in Fraction 1 (water soluble) and there was a slight increase in metal mobilization in Fraction 2 (ion exchangeable). The greatest metal mobilization occurred in Fraction 3, where the acidic extraction fluid was expected to mobilize metals that were in hydroxide and carbonate forms. There was a substantial decrease in leachate metal concentrations for all metals in Fraction 4, relative to their respective concentrations in Fraction 3. Finally, there was very little metal mobilization in Fraction 5, except for the release of copper in the sulfide and sulfide/carbonate sludges. Copper concentrations were relatively high compared to the hydroxide and carbonate sludges for this fraction,, consistent with the extreme insolubility of copper sulfide minerals.

The SEP used could not distinguish between hydroxides and carbonates. Therefore, it was impossible to determine what the hydroxide-carbonate distribution was in the Fraction 3 leachates for any sludge type. However, most metals in the sulfide sludge were mobilized in Fraction 3, which suggests that, for the H_2S-treated sludge, the bulk of the sludge remained in hydroxide form. This suggests that relatively small changes in the chemical composition of the sludge floc resulted in significant changes in the physical properties of the sulfide sludge. This observation can probably also be extended to the carbonate and sulfide/carbonate sludges as well.

The initial mine drainage was highly acidic and contained elevated levels of dissolved metals. First stage treatment of the drainage resulted in moderately alkaline pH water and substantial metal removal. Secondary treatment of sludge and supernatant with H_2S resulted in a circumneutral pH, which was expected because the sulfide precipitation reaction is net acid-producing (Reaction D):

$$M(OH)_2 + 2H_2S \longrightarrow MS_2 + 2H_2O + 2H^+ \qquad (D)$$

5. Conclusions

(1) Contacting a metal hydroxide sludge generated from acid mine drainage with H_2S and/or CO_2 resulted in significantly greater sludge densities and decreased volumes.

(2) The TCLP results indicated that secondary treatment did not result in any significant changes in iron and copper mobility, although some increased mobilization of zinc and manganese was observed in sludges treated with H_2S and H_2S/CO_2.

(3) The SEP data indicated that for all metals, in all sludge types, the largest sludge fraction was observed to be present in the hydroxide or carbonate form. Copper sulfides were formed in the sludges treated with H_2S and H_2S/CO_2.

(4) Generally, the secondary gas treatments did not adversely affect the final water quality. However, the supernatant of the sludge treated with carbon dioxide had elevated levels of zinc and manganese, presumably due to the formation of soluble metal complexes.

(5) Data suggest that improved mixing alone improves the physical characteristics of hydroxide sludges to some extent, especially in the area of sludge reductions. Further study is needed to delineate the effects of mixing and chemical transformations in the improvement of sludge properties.

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