Use of Recycled Concrete and Magnetite for Mine Water Treatment and Metal Recovery

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Abstract Magnetite and iron ferrites are effective for the removal of radioactive and heavy metals from wastewater. Ferrite is typically prepared in situ using batch methods to utilize the existing iron in the water, whereas magnetite is utilized in a column mode. This paper reviews previous work on the use of these materials for wastewater treatment and presents results on using them for the treatment of mine water. Recent experiments using recycled concrete for pH adjustment and a magnetite/sand column to treat mine water is discussed in detail; the magnetite/sand column can be regenerated and the metals recovered in the eluate.

Key Words Iron ferrites, magnetite, metal recovery, mine water treatment, recycled concrete

Introduction

Iron oxides are widely used for the treatment of liquid wastes containing radioactive and hazardous metals. These processes include adsorption, precipitation, and other chemical and physical techniques (King and Navratil 1986, Driscoll 1986, Macasek and Navratil 1992). For example, a radioactive wastewater precipitation process utilizes ferric hydroxide to remove radioactive contaminants such as americium, plutonium, and uranium (Boyd et al. 1983). However, the metal hydroxide solids can form gelatinous, high-volume precipitates, which are difficult to filter, and sometimes filter aids must be used.

Some adsorption processes for wastewater treatment have utilized ferrites and a variety of iron-containing minerals, such as magnetite (Schwertmann and Cornell 1991). Ferrite is a generic term for a class of magnetic iron oxide compounds (Reynolds 1980). Iron atoms in iron ferrite ($FeO \cdot Fe_2O_3$) can be replaced by many other metal ions without seriously altering its spinel structure (Boyd et al. 1986). Various ferrites and natural magnetite were used in batch modes for actinide and heavy metal removal from wastewater (Boyd et al. 1986, Kochen and Navratil 1987). The use of iron ferrite and magnetite for wastewater treatment has a number of advantages over conventional flocculent precipitation techniques for metal ion removal (Boyd et al. 1986). Ferrite solids are crystalline materials, unlike hydroscopic metal hydroxide sludges, and can be more readily filtered; their ferromagnetic character permits the use of magnetic separation of the high-density solids from solution. A wide variety of metal ion impurities can be effectively removed in one treatment step, and their removal is not seriously affected by high salt concentrations (Boyd et al. 1986). The ferrite method does not require expensive chemicals, and because iron is usually a constituent of waste solutions, its oxidation states can be adjusted by chemical or electrolytic means to form ferrite. In situ and preformed ferrite methods have been used in wastewater treatment applications (Boyd et al. 1986). Powdered magnetite was also used in a column mode, and in the presence of an external magnetic field, enhanced capacity was found for removal of plutonium and americium from wastewater (Kochen and Navratil 1997, Navratil et al. 1995, Ebner et al. 1999). These observations were explained by a nanolevel high-gradient magnetic separation effect, as americium, plutonium, and other hydrolytic metals are known to form colloidal particles at elevated pH levels (Ebner 1999). Recent modeling work supports this assumption and shows that the smaller the magnetite particle, the larger the induced magnetic field around the particle from the external field (Ebner et al. 1997). Other recent studies have demonstrated the magnetic-enhanced removal of arsenic, chromium, cobalt, iron, and uranium from simulated groundwater and wastewater (Cotten et al. 1999a, Cotten et al. 1999b, Navratil 2001, Navratil 2008).

Results of Using Iron Ferrites and Magnetite for Mine Water Treatment

Room-temperature batch equilibrium experiments were performed with five different mine water samples at pH values of 6, 8, and 10 to remove the major metal contaminants, copper, iron, manganese, and zinc, using 0.5 g magnetite (Alfa Aesar 97% powder, minus 325 mesh) per 50 mL water. Complete removal of copper, iron, and zinc occurred at pH 6–8, and manganese was effectively

Table 1 *Summary of metal removal in mine waters with magnetite at minimum pH values*

	Mine Water				
	A	**B**	**C**	**D**	**E**
Original pH	3.7	3.2	3.4	6.8	3.9
Cu, % removed (pH)	>93 (6.0)	>92 (6.0)	81 (6.0)		>92 (8.5)
Fe, % removed (pH)	>96 (6.0)	>99 (10)	>99 (6.0)		>99 (8.5)
Mn, % removed (pH)	>99 (10)	>99 (10)	>99 (10)	>97 (10)	99 (10)
Zn, % removed (pH)	>99 (7.9)	99 (7.9)	>99 (8.0)	96 (8.0)	99 (8.5)

removed at pH 10 (Table 1). Magnetite sorption was also performed on Mine Water A samples at the natural mine water pH (3.7) and at a pH of 1. The results show that there was insignificant metal sorption occurring on the magnetite and actual leaching of iron from the magnetite at pH 1, confirming the ability to strip the loaded sorbent with pH 2–3 water to recover the metals and reuse the sorbent.

In situ ferrite was also tested on Mine Water A; all the primary metals of concern were effectively precipitated at a pH greater than 9. Because magnetite was effective in selectively removing copper and zinc at pH 6–8, one proposed remediation scheme for the mine water would be to use a magnetite/sand column operation with the mine water adjusted to pH 7, followed by batch treatment of the column effluent using in situ ferrite for precipitation of other contaminants at pH 9. Another simpler remediation scheme would be to treat mine water adjusted to pH 10 with the magnetite/sand column.

A sixth mine water sample was obtained, Mine Water F, which is a low-volume stream containing mainly zinc as the contaminant of concern. Most of the experiments for this water were performed on two separate samples to show reproducibility of the results. A third sample was obtained at a later date. The natural pH of the water samples was 7.3, and the main contaminant found was 0.26 mg/L Zn, with minor amounts of silver (0.04 mg/L), cadmium (0.02 mg/L), copper (0.04 mg/L), and lead (0.26 mg/L). After treatment of the mine water samples (25- and 50-mL batches) at various pH values using 0.5 g magnetite, approximately 90% of the zinc was removed above pH 8 in most cases. These results are similar to those of the other mine waters tested.

Results with Recycled Concrete and Magnetite/Sand Column

We were interested in comparing recycled concrete powder with lime as a pH-adjustment reagent since the respective costs are US$4–5/ton versus US$175/ton. Concrete crusher fines were obtained from Allied Recycled Aggregates, Commerce City, Colorado (Source A), and from Recycled Materials Co., Stapleton Recycle Center, Denver, Colorado (Source B). Table 2 shows the results of screening the two sources of recycled concrete powder and their neutralization potentials (NP). Although the minus 100-mesh fraction is only 3–5% of the material, it has the highest NP. The optimum material appears to be Source A, minus 30 mesh.

Results from Table 3 are from 1 L of mine water treated with either recycled concrete or lime to a pH of nominally 8. Iron, manganese, and zinc were tracked as contaminants of concern. Lime removed at least 99% of the specified containments and recycled concrete removed at least 98%. Reagent usage was significantly higher for recycled concrete, with 4.5 g of -100 mesh and 5 g of -30 to +100 mesh, as opposed to 1 g of lime. The sludge volume and behaviour of the recycled con-

Table 2 *Recycled concrete particulate screen analysis and NP*

Tyler Screen Fraction	Source A, %	Source A, NP[a]	Source B, %	Source B, NP[a]
+10 mesh	42.6		37.6	
-10 mesh to +30 mesh	33.3		37.9	
-30 mesh to +100 mesh	18.8	>0.25	21.4	0.09
-100 mesh	5.3	>0.29	3.0	0.24

[a]Neutralization potential as H_2SO_4 g to recycled concrete g

Table 3 *Mine Water E treatment with Source A recycled concrete or lime*

Analysis	-100 mesh	-30 mesh to +100 mesh	$Ca(OH)_2$
Liquor			
Final pH	7.86	8.05	9.00
Fe, mg/L	<0.1	<0.1	<0.1
Mn, mg/L	5.5	8.5	<0.2
Zn, mg/L	<0.2	<0.2	<0.2
Solid			
Final dry mass, g	4.2	8.1	1.3
Settled sludge volume, mL	10	15	55
Al, %	5.24	5.12	0.29
Cu, %	0.01	0.01	0.3
Fe, %	6.25	5.03	15.3
Mn, %	0.68	0.55	2.64
Zn, %	0.16	0.13	0.54

crete system differed significantly from the lime precipitate. Concrete fines appear to settle faster and create a less gelatinous sludge with a 70—80% reduction in volume. This may indicate that localized precipitation is occurring on the recycled concrete particles rather than forming hydroxide complexes, however mineralogical analysis has not been performed to confirm this.

Column experiments utilized 10-mL glass columns (0.5-inch inside diameter) surrounded by four 1.5-inch-diameter NdFeB ring magnets supplied by Amazing Magnets of Irvine, California. A mixed magnetite/sand ratio of 4:1 by weight was utilized using Oglebay Norton silica sand wet-screened to minus 10 by 14 mesh. Results of a column breakthrough experiment are shown in Figure 1; zinc breakthrough occurred on the sand/magnetite column after passing about 8 L, or 420 bed volumes, of Mine Water F at pH 8. The zinc was recovered from the loaded sorbent by treatment with less than 200 mL of pH 2–3 water. Thus one proposed remediation scheme for this water, provided the zinc could be economically recovered and sold, would be to use a magnetite/sand column for the water with minimal pH adjustment for removal of zinc followed by recovery of the zinc from the magnetite using pH 2–3 water.

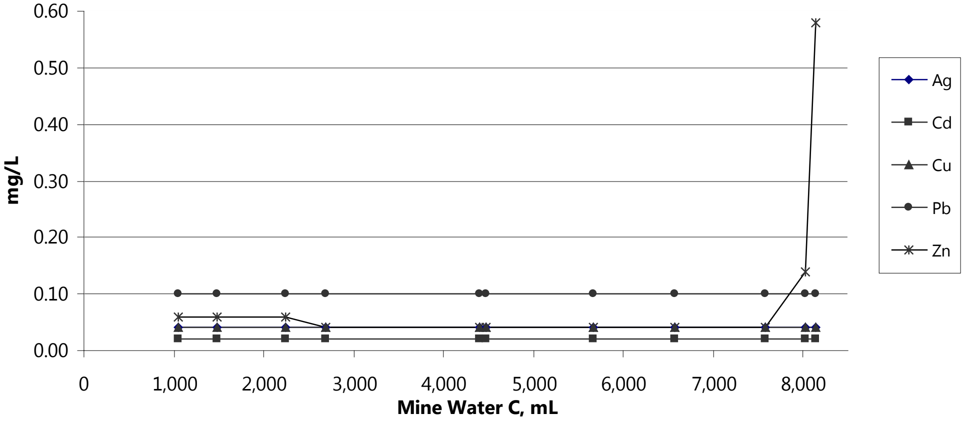

Figure 1 *Mine Water F breakthrough curve on a magnetite/sand column*

Conclusions

Experiments with magnetite treatment of several different mine waters showed complete removal of copper, iron, and zinc occurred at pH 6–8, and manganese was effectively removed at pH 10. Experiments at pH 1–3 showed that there was insignificant metal sorption occurring on the magnetite, confirming the ability to strip the loaded sorbent with pH 2–3 water to recover the metals and reuse the sorbent. In situ ferrite was also tested on some of the mine waters, and all the primary metals of concern were effectively precipitated at a pH greater than 9. Because magnetite was effective in selectively removing copper and zinc at pH 6–8, one proposed remediation scheme for a contaminated mine water would be to utilize a magnetite/sand column operation with the mine water adjusted to a pH of approximately 8 to capture the commodity. If needed, this would be followed by a batch treatment of the column effluent for precipitation of the other contaminants at a pH greater than 9 using in situ ferrite. A simpler process would be to use the magnetite/sand column to remove all the contaminants at pH 9–10, using recycled concrete fines as a pH-adjustment reagent because it costs only US$ 3–4/tonne compared with lime at approximately US$175/ton; this simpler process would require less chemicals, equipment, and operations compared with conventional lime precipitation. However, pilot plant studies are needed to further evaluate the process.

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