PERGAMON

Applied Geochemistry 17 (2002) 569–581

Applied Geochemistry

www.elsevier.com/locate/apgeochem

Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee

Giehyeon Lee[a,]*, Jerry M. Bigham[b], Gunter Faure[a]

[a]*Department of Geological Sciences, Ohio State University, Columbus, OH 43210, USA*
[b]*School of Natural Resources, Ohio State University, Columbus, OH 43210, USA*

Received 1 September 2000; accepted 1 September 2001
Editorial handling by J. Herman

Abstract

This study examined the sorption of trace metals to precipitates formed by neutralization of 3 natural waters contaminated with acid mine drainage (AMD) in the former Ducktown Mining District, Tennessee. The 3 water samples were strongly acidic (pH 2.2 to 3.4) but had distinctively different chemical signatures based on the mole fractions of dissolved Fe, Al and Mn. One sample was Fe-rich (Fe = 87.5%, Al = 11.3%, and Mn = 1.3%), another was Al-rich (Al = 79.4%, Mn = 18.0%, and Fe = 2.5%), and the other was Mn-rich (Mn = 51.4%, Al = 25.7%, and Fe = 22.9%). In addition, these waters had high concentrations of trace metals including Zn (37,700 to 17,400 μg/l), Cu (13,000 to 270 μg/l), Co (1,500 to 520 μg/l), Ni (360 to 75 μg/l), Pb (30 to 8 μg/l), and Cd (30 to 6 μg/l). Neutralization of the AMD-contaminated waters in the laboratory caused the formation of either schwertmannite at pH <4 or ferrihydrite at pH >4. Both phases were identified by XRD analyses of precipitates from the most Fe-rich water. At higher pH values ($\sim$5) Al-rich precipitates were formed. Manganese compounds were precipitated at pH $\sim$8. The removal of trace metals depended on the precipitation of these compounds, which acted as sorbents. Accordingly, the pH for 50% sorption (pH$_{50}$) ranged from 5.6 to 7.5 for Zn, 4.6 to 6.1 for Cu, 5.4 to 7.7 for Ni, 5.9 to 7.9 for Co, 3.1 to 4.3 for Pb, and 5.5 to 7.7 for Cd. The pH dependence of sorption arose not only because of changes in the sorption coefficients of the trace metals but also because the formation and composition of the sorbent was controlled by the pH, the chemical composition of the water, and the solubilities of the oxyhydroxide-sulfate complexes of Fe, Al, and Mn. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The concentrations of trace metals in most natural waters are controlled by adsorption or coprecipitation processes. In theory, the former is the two-dimensional accumulation of an ion at the interface between a preformed solid and the aqueous phase, whereas the latter is the simultaneous removal of a foreign ion during the formation of primary metal precipitates such as Fe, Al, and Mn oxides. Coprecipitation may include adsorption, cluster formation, homogeneous solid solution, heterogeneous solid solution, or a combination of these processes (Karthikeyan et al., 1997; Martinez and McBride, 1998).

Most adsorption and coprecipitation experiments have been constrained to well defined systems, and the applicability of the results may be limited because of the complexity of natural environments. For example, waters contaminated with acid mine drainage (AMD) have a wide range of chemical composition and contain non-conservative elements such as Fe, Al, and Mn, that rapidly form precipitates when AMD is neutralized. The solubility minimum varies for each element, causing a different efficiency of precipitation depending upon the

---

* Corresponding author. Fax.: +1-626-395-2940.
E-mail address: ghlee@caltech.edu (G. Lee).

PII: S0883-2927(01)00125-1

https://doi.org/10.1016/S0883-2927(01)00125-1

pH (Theobald et al., 1963; Jenne, 1968; Rampe and Runnells, 1989; Nordstrom and Alpers, 1999). The precipitates formed by metal hydrolysis may include both oxyhydroxides and hydroxysulfates depending on local geochemical conditions (Bigham et al., 1996a; Nordstrom and Alpers, 1999).

Numerous workers have investigated the retention of trace metals on suspended particulate matter and/or bottom sediments in streams and lakes receiving AMD (Johnson, 1986; Karlsson et al., 1988a,b). These studies have documented the removal of trace metals and the partitioning of metals between solid and aqueous phases by adsorption/coprecipitaton processes. However, there have been few attempts to examine variations in trace-metal behavior in mine drainage systems where the geochemistry is dominated by different non-conservative species. A knowledge of such variations is important to fully understand trace-metal retention and mobility in aquatic systems impacted by mine drainage.

The Ducktown area in SE Tennessee has been highly disturbed by mining operations, and surface waters are seriously degraded by AMD of variable composition (Lee, 2001). The objectives of the present study were to (1) examine the coprecipitation of trace metals with Fe, Al, and Mn compounds obtained by neutralization of these waters in the laboratory, and (2) identify, where possible, the solid phases of Fe, Al, and Mn formed by neutralization. The results of these experiments with complex AMD-contaminated solutions should provide a better understanding of the removal of trace metals from natural waters in response to changes in pH.

2. Methodology

2.1. Description of the study area

Massive sulfide ore deposits in the former Ducktown Mining District of SE Tennessee (Fig. 1) were mined for 140 years beginning in 1847 (Magee, 1968). The ore deposits in the area have been well characterized (e.g. Emmons and Laney, 1926; Magee, 1968) and include: (1) a gossan ore with kaolinite, quartz, and other minerals that extends to a maximum depth of about 30 m; (2) about 1 m of chalcocite ore below the gossan; and (3) the primary sulfide ore from which the overlying chalcocite and gossan ores were derived. The primary ore consists of 65% sulfides and 35% silicate minerals. The primary sulfide minerals are pyrrhotite ($Fe_{1-x}S$), pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and sphalerite (ZnS), and the silicate minerals include quartz, actinolite, hornblende, diopside, garnet, and zoisite. In addition, magnetite, other metallic oxide minerals, carbonates (calcite and dolomite), and traces of native Ag and Au are present.

Past mining and present industrial activities near Copperhill, Tennessee, have contaminated several tributaries of the Ocoee River (Fig. 1) causing increased acidity and high concentrations of trace metals and suspended sediments (Paulson et al., 1993). North Potato Creek, Burra Burra Creek, and Davis Mill Creek (Fig. 1) are the most heavily contaminated tributaries. These creeks flow southwestward across the Copper Basin, where the major mines of the Ducktown Mining District were located.

2.2. Water samples

AMD-contaminated surface waters were collected from 3 different localities in the watersheds of North Potato and Davis Mill Creeks (Fig. 1). Sample BBC was collected before it entered Burra Burra Creek, which is a tributary of North Potato Creek. Sample DMC was collected from the mouth of Davis Mill Creek before the water entered the Ocoee River. Sample ML was taken from the water of a small lake formed in a collapsed stope of the abandoned Isabella Mine.

All samples were collected using large, new, polyethylene bottles (1–7.6 l). The bottles were rinsed 3 times with the water being collected and were then completely filled to eliminate headspace. During the collection of water samples, care was taken to avoid disturbing the streambed in order to prevent streambed sediment from mixing with sediment suspended in the water. The pH was measured at each site with a pHep®3 Microprocessor pH meter, which was calibrated with two buffer solutions at pH 4 and 7. The samples were stored in a dark room at room temperature until analyzed.

2.3. Neutralization

Samples BBC, DMC, and ML were filtered in the laboratory through 0.45-μm membrane filters. Six 200-ml aliquots of the filtrates from each sample were transferred directly to 250-ml plastic centrifuge bottles and graded amounts of a saturated NaOH solution were added to increase the pH and thereby precipitate Fe, Al, and Mn. After adding the base, each aliquot was stirred and the pH was measured daily until it stabilized. Aliquots of the solutions whose pH was raised above 9 required up to 8 days to stabilize. In order to determine the maximum amount of precipitate that could form by neutralization of these solutions, one additional aliquot of each of the 3 solutions was treated with NaOH until the pH reached 12 or higher.

After equilibration, the aliquots were centrifuged at 3000 rpm for 20 min using a Beckman Model J-6M centrifuge, and the supernatant solutions were filtered through 0.45-μm filters. The filtrates were acidified to $pH<2$ with reagent grade HNO_3 and were analyzed by inductively coupled plasma (ICP) spectrometry. Elements in high concentration (Na, Mg, Ca, K, Fe, Al, Mn and Zn) were analyzed by ICP optical emission-spectrometry (OES), whereas trace metals (Cu, Ni, Co,

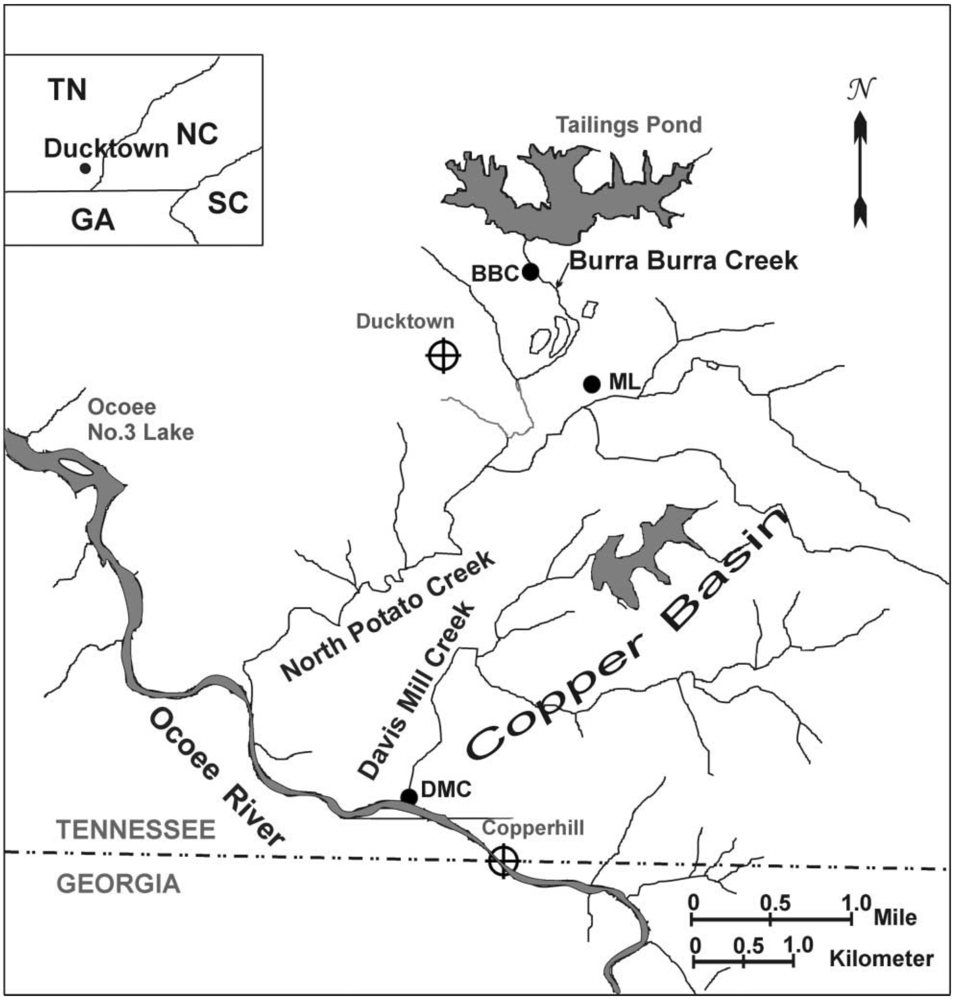

Fig. 1. Map of the watersheds of North Potato and Davis Mill Creeks, which are tributaries of the Ocoee River. Three AMD samples (samples BBC, DMC and ML) were collected in July 1998 (samples BBC and DMC) and March 1999 (sample ML). Circles represent the sample collection sites.

Cd and Pb) were determined by ICP mass-spectrometry (MS). The instruments used were a Perkin-Elmer Optima 3000 (ICP-OES) and a Perkin-Elmer Sciex Elan 6000 (ICP-MS). The detection limits of the ICP-OES and the ICP-MS were 50 and 0.5 μg/l, respectively. Sulfate concentrations were determined gravimetrically by adding saturated $BaCl_2$ solution to form $BaSO_4$ precipitate. The activities of aqueous species and saturation indices of the solid phases were calculated using the computer program PHREEQCI (Parkhurst, 1995).

The effect of filter pore size on the recovery of suspended sediment was examined by sequentially filtering an aliquot of sample BBC through 0.45 (Supor®-450), 0.2 (Supor®-200), 0.1 (Supor®-100), and 0.02 (Whatman Anodisc™ 47) μm membrane filters. The sequential filtration demonstrated that the 0.45-μm filter recovered 97.8% of the total suspended sediment. In addition, the concentrations of Fe, Al and Mn in the 4 filtrates were found to be constant.

The precipitates that formed by neutralization of the solutions were freeze-dried in a Labconco lyophilizer, weighed, and stored in glass vials. Previous studies of AMD precipitates (e.g. Brady et al., 1986; Winland et al., 1991) showed no detectable mineralogical alterations with freeze drying. X-ray diffraction (XRD) analyses of the dried samples were conducted using topfill powder mounts and Cu$K\alpha$ radiation on a vertical, wide-range goniometer (Philips PW 3020/00) equipped with a 1° divergence slit, a 0.2-mm receiving slit, and a diffracted-beam monochromator. Specimens were scanned from 10 to 70° 2θ in increments of 0.05° 2θ with a 4-s step time. Peak positions were determined by using the Jade 3.0 software of Materials Data Inc.

3. Results

3.1. Chemistry of water samples

The 3 water samples collected for this study (BBC, DMC, and ML) (Fig. 1, Table 1) were all strongly acidic (pH 2.2 to 3.4) but had distinctively different chemical signatures based on the mole fractions of dissolved Fe, Al and Mn. Sample ML was Fe-rich (Fe = 87.5%, Al = 11.3%, and Mn = 1.3%); BBC was Al-rich (Al = 79.4%, Mn = 18.0%, and Fe = 2.5%), and DMC was Mn-rich (Mn = 51.4%, Al = 25.7%, and Fe = 22.9%). Calcium was the dominant conservative constituent (followed by Na and K), as would be expected from the mineralogy of the primary ore body (see Section 2.1). Zinc, Cu, Co and Ni were the most abundant trace metal contaminants. Sulfate was the only anion measured, but electroneutrality calculations using PHREEQCI indicated that SO_4^{2-} accounted for most of the negative charge. These calculations produced a small deficit of positive charge in BBC (0.1%) and DMC (0.05%) and an excess of positive charge in sample ML (2.3%).

3.2. Titration of sample ML, Isabella Mine

The Fe concentration in sample ML was more than one order of magnitude higher than the concentrations of all other dissolved metals (Table 1). As expected, most of the Fe was rapidly precipitated with the addition of NaOH (Fig. 2A); the residual Fe concentration in solution was at or below the detection limit (0.05 mg/l) at pH > 4 (Fig. 2B). By contrast, Al and Mn were depleted from this water at pH≈5 and at pH≈8, respectively (Fig. 2C and D). The concentrations of dissolved Mg and Ca did not decrease significantly until the pH exceeded 8 (Fig. 2E). The precipitates formed from sample ML were identified by XRD as either schwertmannite [$Fe_8O_8(OH)_6SO_4$] or 2-line ferrihydrite ($\sim Fe_5HO_8{\cdot}4H_2O$)) depending on the pH of the solution (Fig. 3). Schwertmannite precipitated at pH < 4.0, whereas ferrihydrite formed at higher pH values.

Table 1
Chemical composition of AMD solutions used for neutralization experiments

	Sample I.D.	ML	BBC	DMC
pH	On-site	2.2	3.4	3.1
	Filtrate	2.0	2.6	2.5
Analyte	Units			
Na	mg/l	21.0	13.2	11.2
Mg	mg/l	49.2	50.2	35.0
Ca	mg/l	86.0	96.4	44.9
K	mg/l	2.20	25.0	7.80
SO_4	mg/l	2040	1400	605
Fe	mg/l	677	6.42	6.26
Al	mg/l	42.3	97.4	3.39
Mn	mg/l	9.77	45.0	13.8
Zn	mg/l	17,400	37,700	21,200
Cu	μg/l	13,000	270	980
Co	μg/l	520	1500	530
Cd	μg/l	30	25	6
Ni	μg/l	75	360	48
Pb	μg/l	8	30	7

Sorption edges (used collectively for adsorption-coprecipitation edges in this study) for Pb, Cu, Zn, Cd, and Co were obtained with respect to the precipitate formed by titration of sample ML (Fig. 2F). The fraction of each metal removed was determined by the difference between its concentration in the NaOH-amended aliquots and that of the initial solution. Lead was removed first, and its sorption edge coincided closely with the loss of Fe from solution. No Pb-compounds, including $PbSO_4$, could form in the aliquots according to saturation index (SI) calculations using PHREEQCI. The other trace metals were removed at higher pH's. In all cases, however, the fraction of trace metal remaining in solution became insignificant as the pH increased above 7.5 indicating little, if any, association with precipitates of Ca, Mg or Mn hydroxides.

3.3. Titration of sample BBC, Burra Burra Creek

When drainage waters represented by sample BBC entered Burra Burra Creek (Fig. 1), whitish precipitates formed downstream of the confluence. Accordingly, sample BBC had the highest Al concentration of the 3 drainage waters (Table 1), and titration with NaOH caused precipitates to form in a stepwise manner (Fig. 4A). The first precipitation event occurred at pH≈4 and coincided with the removal of Fe (Fig. 4B). The second event, between pH 4 and 6, correlated with a decrease in dissolved Al (Fig. 4C) and accounted for more than 50% of the total solids precipitated from sample BBC. These Al-rich precipitates were X-ray amorphous; however, SI calculations indicated that jurbanite [$AlOHSO_4$] and basaluminite [$Al_4(OH)_{10}SO_4$] could form in most of the aliquots (Table 2). In addition, the aliquots were undersaturated with respect to $Al(OH)_{3(s)}$ at pH < 5.0 but became supersaturated with respect to this compound at higher pH's. The last precipitation event occurred between pH 6 and 9 and can be attributed to the formation of Mn- and, possibly, Mg-hydroxides (Fig. 4D and E).

Sorption edges (Fig. 4F) show that more than 90% of all trace metals were removed with an increase of the solution pH from 4 to 6 in the range primarily associated with the formation of Al-rich precipitates. Lead

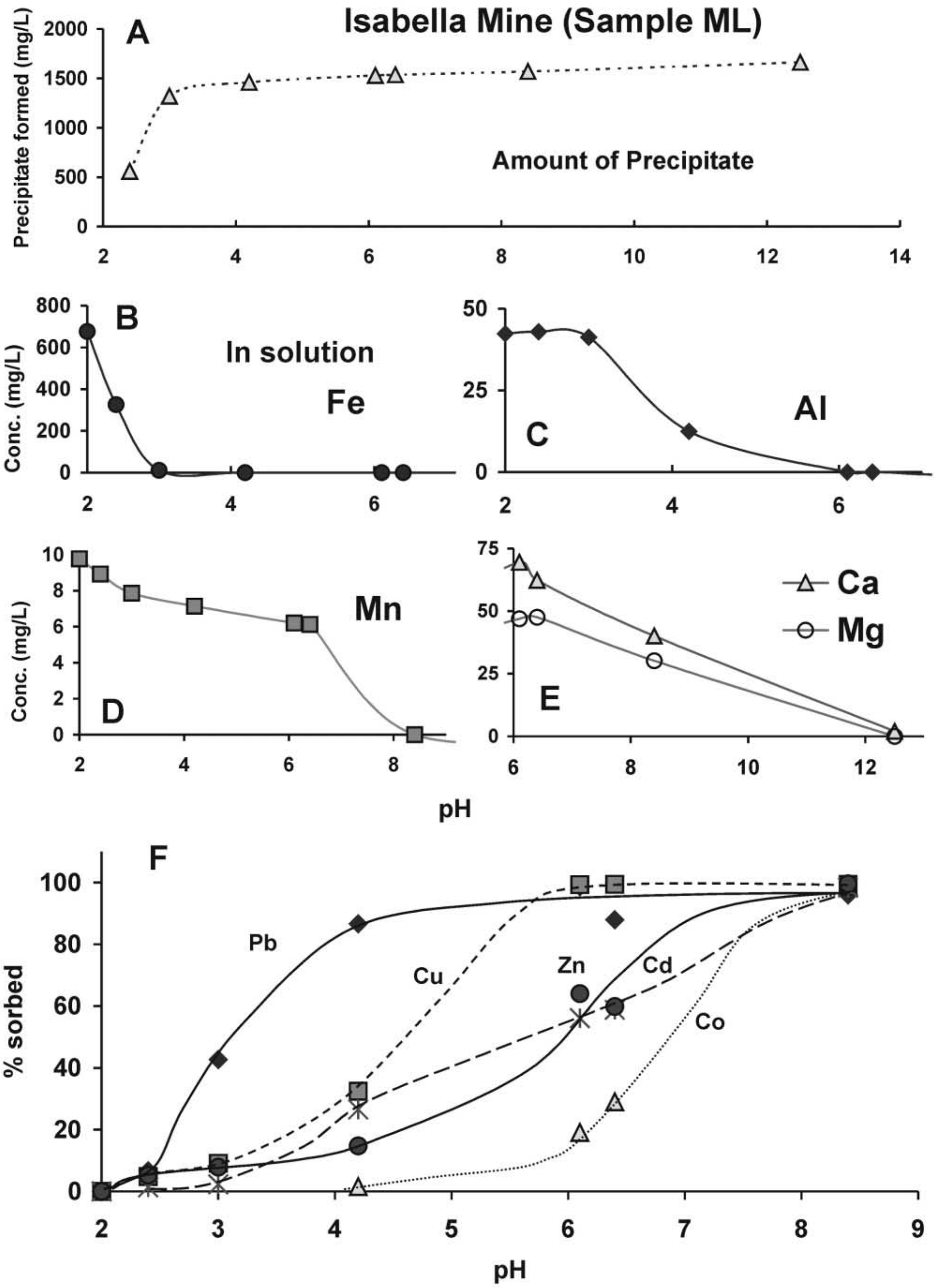

Fig. 2. Chemical analyses of batch solutions from sample ML, which was collected from a lake formed in a collapsed stope of the abandoned Isabella Mine. A. Plot of the amount of precipitate formed in the batch solutions as a function of pH. B–E. Concentrations of dissolved Fe (B), Al (C), Mn (D) and Ca and Mg (E) remaining in the solutions. F. Sorption edges of trace metals to the precipitates formed by neutralization of solutions.

was eliminated first, but removal occurred at a higher pH than with the Fe-rich Isabella Mine sample. In fact, the sorption of all trace metals to the BBC precipitates occurred over a much narrower pH range (4–8) than was observed with sample ML.

3.4. Titration of sample DMC, Davis Mill Creek

The concentration of Mn in sample DMC was greater than that of either Fe or Al but less than Mg and Ca (Table 1). Because of low Fe and Al concentrations, the

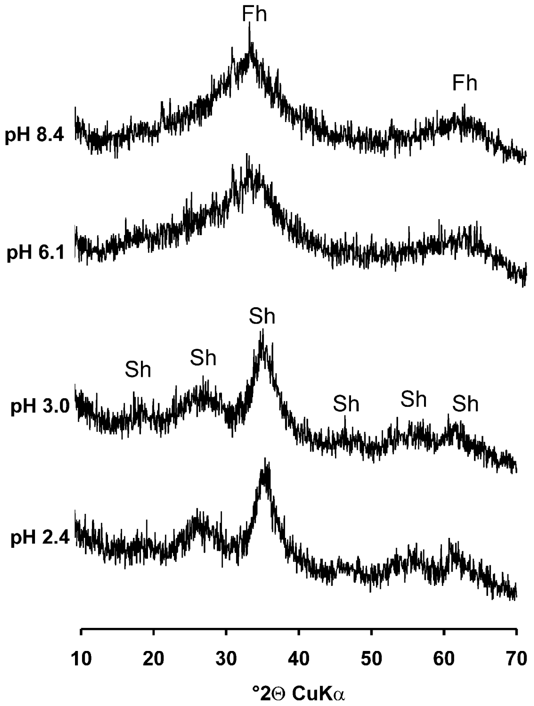

Fig. 3. X-ray diffractograms of precipitates recovered from sample ML at pH 2.4, 3.0, 6.1 and 8.0.

Table 2
Saturation indices (SI) of Al-compounds in the aliquots of sample BBC calculcated by PHREEQCI program

Aliquots	pH	$Al_4(OH)_{10}SO_4$	$Al(OH)_{3(a)}$	$AlOHSO_4$
1	3.3	−4.63	−5.95	0.72
2	4.2	−1.62	2.99	1.61
3	4.3	−1.32	3.97	1.71
4	5.0	0.69	10.65	2.34
5	6.3	2.64	15.93	1.78
6	8.7	1.59	6.94	−4.07

amount of precipitate formed with titration of the sample to pH 7.5 was less than 10% of the total (Fig. 5A). Iron and Al removal (Fig. 5B and C) followed the same pH trends as observed previously for samples ML and BBC, but the most significant precipitation event occurred at pH 8 and coincided with the removal of Mn from solution (Fig. 5D). Additional quantities of precipitate were contributed by the formation of Ca and Mg hydroxides at still higher pH (Fig. 5E). Although Mn accounted for at least 50% of the total precipitate formed from sample DMC, no crystalline phases were detected by XRD analysis of the precipitates.

More than 80% of the Pb in aliquots of sample DMC was scavenged at pH < 3.5 (Fig. 5F). The only sorbent in this pH range consisted of Fe compounds because other major elements remained in solution (Fig. 5B–E). Sorption of Cu began at pH > 5 and was completed at pH ~7.5 when all the Fe and Al had been lost from solution. Removal of the remaining trace metals was minimal at that pH. As pH increased, trace metals were sorbed in the same sequence as in sample ML; however, the sorption edges for Ni, Cd, and Co occurred abruptly at pH 7 to 8 (Fig. 5A, D and F) indicating that Mn hydroxide(s) was the primary sorbent. Consequently, their sorption edges were shifted toward higher pH compared to those obtained from samples ML and BBC. Because the Zn concentration of DMC was higher than the concentrations of Mn, Fe, and Al (Table 1), a portion of the Zn was possibly removed by precipitation of Zn hydroxide in agreement with the SI of $Zn(OH)_2$ calculated by PHREEQCI.

4. Discussion

4.1. Formation of sorbents

Samples ML, BBC and DMC provide an opportunity to examine the behavior of different sorbents that are likely to form when AMD is neutralized by mixing with higher pH waters in the field. The order in which the removal of Fe, Al and Mn occurred by titration of these samples was consistent with the negative logarithms of the first hydrolysis constants for Fe^{3+} ($pK_1 = 2.2$), Al^{3+} ($pK_1 = 5.0$) and Mn^{2+} ($pK_1 = 10.9$). As noted by Dzombek and Morel (1990), the sorption or precipitation of hydrolysable metal ions generally occurs at pHs near their pK_1 values.

4.1.1. Fe precipitates

The X-ray identification of schwertmannite and ferrihydrite as titration products of sample ML are consistent with the results of Bigham et al. (1996a,b) who reported that schwertmannite is the dominant Fe phase precipitated from mine waters having pH values between 2.8 and 4.5. All titration aliquots plot in the stability regions for either schwertmannite or ferrihydrite (Fig. 6).

Recently, Yu et al. (1999) reported the apparent solubilities of schwertmannite [$Fe_8O_8(OH)_{8-2x}(SO_4)_x$] and ferrihydrite [$Fe_2O_3{\cdot}1.8H_2O$] formed in mine drainage in Korea and Ohio, USA, using the activities of H^+, OH^-, Fe^{3+}, and SO_4^{2-} of the waters in contact with these minerals. They estimated the logarithms of the solubility product of schwertmannite ($\log K_s = 10.5$) and ferrihydrite ($\log K_f = 4.3$) using the plot of (pFe + 3pOH) versus (pSO_4 + 2pH). The solubility line of schwertmannite in Fig. 6 is defined by the dissolution reaction of this mineral (Yu et al., 1999) as:

$$Fe_8O_8(OH)_{8-2x}(SO_4)_x + (8+2x)H_2O = 8Fe^{3+} + 24OH^- + xSO_4^{2-} + 2xH^+ \tag{1}$$

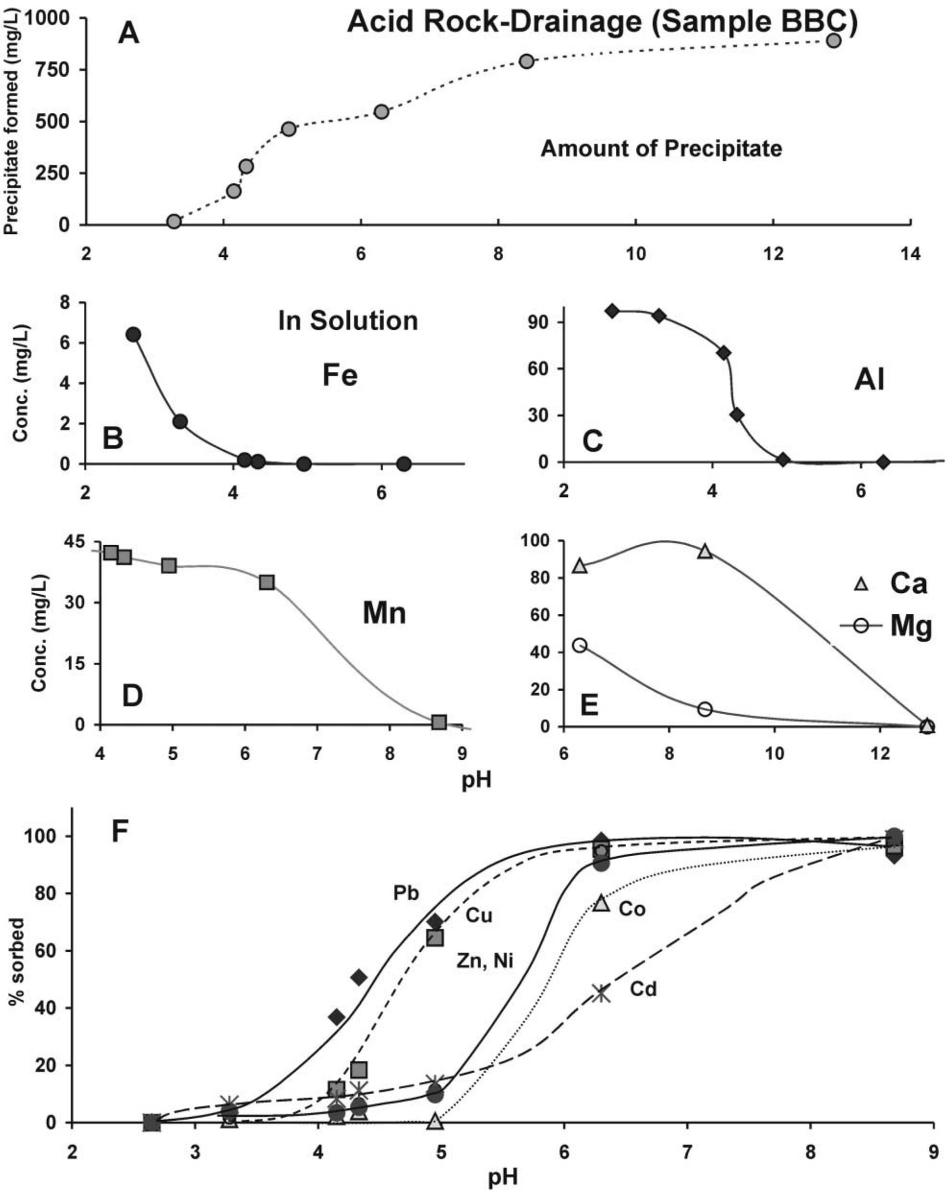

Fig. 4. Chemical analyses of the batch solutions of sample BBC, which was acidic rock-drainage flowing into Burra Burra Creek. A. Amount of precipitate formed in the batch solutions at different pH. B–E. Concentrations of dissolved Fe (B), Al (C), Mn (D) and Ca and Mg (E) remaining in the solutions. F. Sorption edges of trace metals to the precipitates formed by neutralization of solutions.

Bigham et al. (1996b) suggested that the stoichiometry of SO_4 (x) in the formula of schwertmannite varied from 1.0 to 1.75, whereas Yu et al. (1999) reported slightly higher SO_4 contents ($1.74 \leqslant x \leqslant 1.86$). The stoichiometry of SO_4 constrains the boundary between the stability regions of schwertmannite and ferrihydrite as follows:

$$pSO_4 + 2pH = \frac{pK_s - 8pK_f}{x} \quad (2)$$

Eq. (2) can be derived from the transformation reaction of schwertmannite to ferrihydrite as suggested by Yu et al. (1999). This boundary in Fig. 6 was adjusted to $pSO_4 + 2pH = 10.5$, where $pK_s = -10.5$ and $pK_f = -4.3$, for consistency with the XRD results obtained in the present study. The corresponding SO_4 stoichiometric coefficient of schwertmannite (x) is 2.28, which is higher than those suggested by Bigham et al. (1996b) and Yu et al. (1999). No chemical data are available to confirm this stoichiometry; however, Nordstrom (1991) and

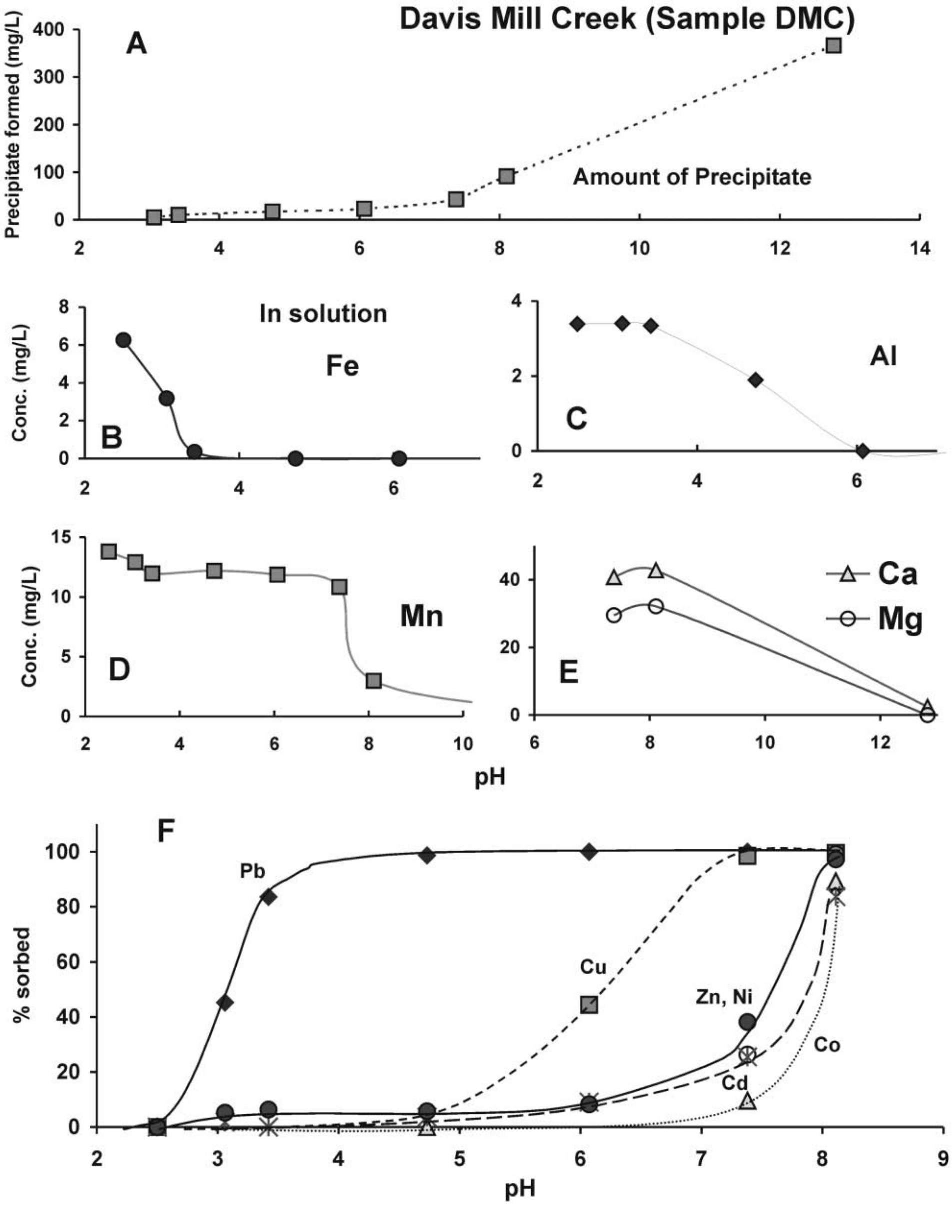

Fig. 5. Chemical analyses of the batch solutions of sample DMC collected at the mouth of Davis Mill Creek before it entered the Ocoee River. A. Amount of precipitate formed in the batch solutions at different pH. B–E. Concentrations of dissolved Fe (B), Al (C), Mn (D) and Ca and Mg (E) remaining in the solutions. F. Sorption edges of trace metals to the precipitates formed by neutralization of solutions.

Kimball et al. (1994) found that the stoichiometric ratio of the activities between dissolved Fe^{3+} and OH^- in equilibrium with colloidal mine drainage precipitates was 2.4 as compared to that of 3.0 where solubility control is provided by pure ferric hydroxide. If the stoichiometric coefficient of SO_4 is 2.28, Eq. (1) becomes

$$\begin{aligned} &Fe_8O_8(OH)_{3.44}(SO_4)_{2.28} + 12.56H_2O = 8Fe^{3+} \\ &\quad + 24OH^- + 2.28SO_4^{2-} + 4.56H^+ \end{aligned} \tag{3}$$

Eq. (3) can be rearranged as

$$\begin{aligned} &Fe_8O_8(OH)_{3.44}(SO_4)_{2.28} + 8H_2O = 8Fe^{3+} \\ &\quad + 19.44OH^- + 2.28SO_4^{2-} \end{aligned} \tag{4}$$

where the stoichiometric ratio between dissolved Fe^{3+} and OH^- is 2.43. Therefore, if the SO_4 in schwertmannite is responsible for the deviation of the stoichiometric ratio from pure ferric hydroxide, then the stoichiometry

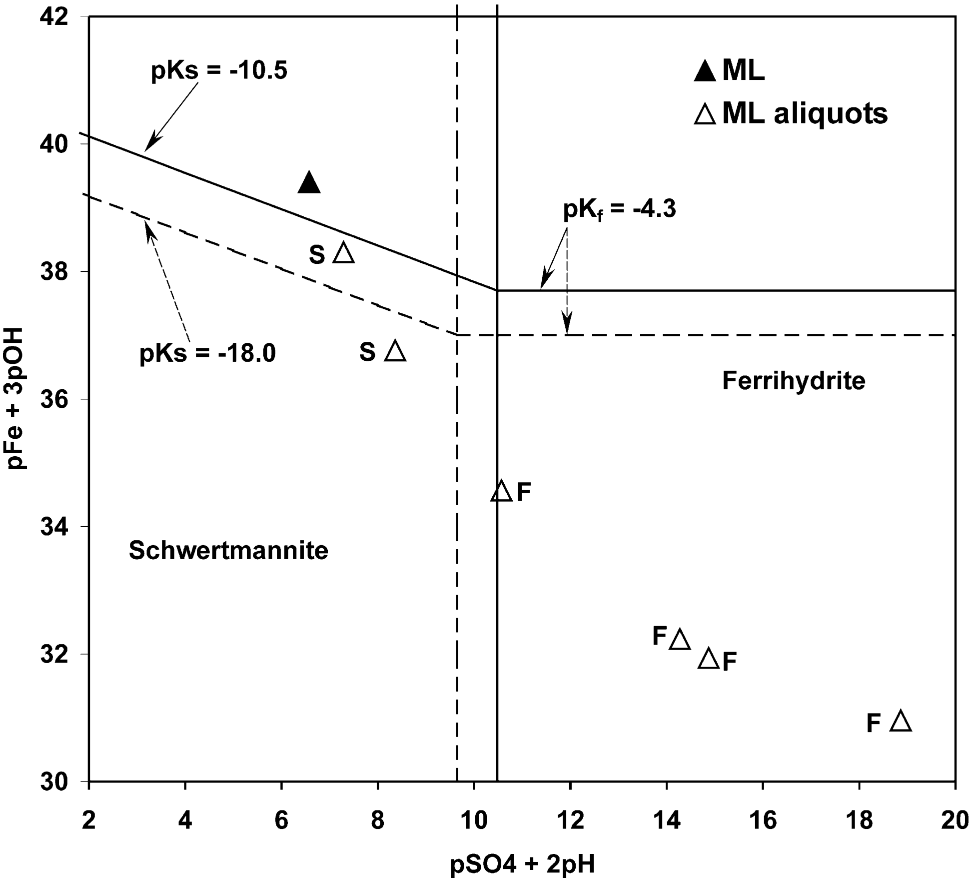

Fig. 6. Plot of pFe + 3pOH versus $pSO_4 + 2pH$ for sample ML and its batch solutions against solubility lines of schwertmannite and ferrihydrite, where pi indicates the negative logarithms of the activity of an aqueous species, i. Solid lines are defined by log $K_s = 10.5$ for schwertmannite (Yu et al., 1999) and dashed lines by log $K_s = 18.0$ for the same mineral (Bigham et al., 1996a,b). Both lines are defined by log $K_f = 4.3$ for ferrihydrite after Yu et al. (1999). S and F represent schwertmannite and ferrihydrite, respectively, as identified by XRD analyses.

would be similar to that reported by Nordstrom (1991) and Kimball et al. (1994).

4.1.2. *Al precipitates*

The Al-rich precipitates produced by titration of sample BBC were X-ray amorphous; however, a plot of log Al^{3+} activities versus pH shows that the decreased Al^{3+} activities at pH > 5 are consistent with the formation of solid $Al(OH)_{3(am)}$ (Fig. 7). Previous studies have shown similar results (e.g. Nordstrom and Alpers, 1999; Nordstrom and Ball, 1986). Because sample BBC contains a high SO_4^{2-} concentration (1400 mg/l), $Al–SO_4$ compounds may influence Al activities at pH < 5 (Table 2). Several previous studies (Karathanasis et al., 1988; Sullivan et al., 1988; van Breeman, 1973) have reported that a jurbanite-like mineral, having a stoichiometry of $Al:OH:SO_4 = 1:1:1$, might control the activity of Al^{3+} in acidic, SO_4-rich waters. Adams and Rawajfih (1977) found that amorphous basaluminite $[Al_4(SO_4)(OH)_{10}{\cdot}5H_2O]$ was precipitated during titrations of aluminum sulfate with Na-, K- and Ca-hydroxides, and Nordstrom et al. (1984) have also suggested that the most common phase in mine-drainage systems seems to be an amorphous Al hydroxysulfate with basaluminite stoichiometry.

4.1.3. *Mn precipitates*

Birnessite is one of the most common Mn minerals identified in soil environments (McKenzie, 1989), and manganite (γ-MnOOH) is the most stable and abundant mineral among those in the MnOOH group (Post, 1999). Saturation indices calculated by PHREEQCI indicated that these two minerals could form from sample DMC with increasing pH, but no crystalline phases were detected by XRD analysis of the precipitates recovered from the aliquots of sample DMC. Post (1999) noted that it is difficult to identify Mn minerals in fresh precipitates because these materials are typically

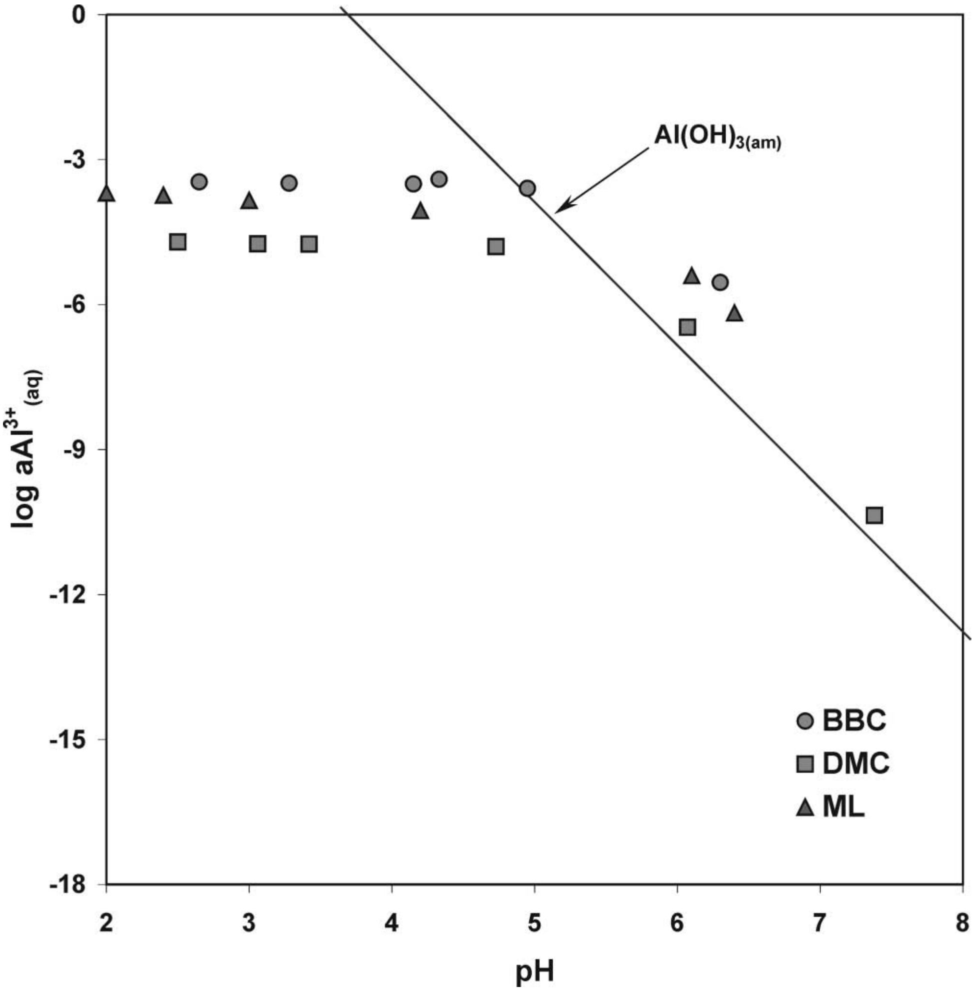

Fig. 7. Plot of log Al^{3+} activities versus pH for the 3 AMD waters and their batch solutions against the solubility lines of amorphous $Al(OH)_3$, whose solubility product was calculated using free energy of formations listed in Faure (1998).

fine-grained, poorly crystalline, and contain multiple valence states of Mn.

4.1.4. Ca and Mg

The removal of dissolved Ca and Mg from solution at high pH (Figs. 2E, 4E and 5E) could be due to the formation of insoluble hydroxides or to sorption of these ions on other precipitates. The pH values of their removal from solution are in agreement with previous studies of the adsorption/coprecipitation of Ca and Mg on ferrihydrite [$Fe_5HO_8{\cdot}4H_2O$] (Baltpurvins et al., 1997; Kinniburgh et al., 1976). Baltpurvins et al. (1997) reported that significant sorption of Ca^{2+} to ferrihydrite occurred only at pH values higher than the point of zero charge (PZC) (pH ~ 8), but that Mg^{2+} was sorbed over the pH range 3 to 6 depending on the molar ratio of Mg^{2+} to Fe^{3+}. These authors suggested that Ca^{2+} was adsorbed rather than coprecipitated owing to its larger ionic radius, whereas some Mg^{2+} could coprecipitate with Fe^{3+} during the formation of ferrihydrite because of the similarities in their ionic radii. Saturation indices calculated using PHREEQCI indicated that Ca or Mg hydroxides should not form from any of the samples.

4.2. Trace metal sorption

Trace metals in the aliquots of sample ML were scavenged by two different sorbents because the precipitates that formed were composed of either schwertmannite ($pH < 4$) or ferrihydrite ($pH > 4$). Webster et al. (1998) reported that schwertmannite was a more effective sorbent of Pb, Cu and Zn than ferrihydrite, but that there was no difference in the sorption of Cd. The pH-dependent sequence of sorption edges from sample ML is $Pb > Cu > Zn \approx Cd > Co$, which is in agreement with previous sorption studies of trace metals on hydrous ferric oxides (e.g. Dzombak and Morel, 1990; Kinniburgh et al., 1976). In addition, the sequence from sample BBC (Pb > Cu > Zn≈Ni > Co > Cd) is generally in accord with previous adsorption studies of trace metals on hydrous oxide gels of Al by Kinniburgh et al. (1976) except that the order of Pb and Cu sorption are switched. Since sample BBC contained a small amount of Fe, the sorption of Pb was probably affected by the presence of Fe precipitate.

Numerous workers have studied the pH-dependent sorption of trace metals on different types of Mn oxides and oxyhydroxides. The results have been variable, presumably due to a wide range in the point of zero charge (PZC) for these minerals ($pH_{pzc} = 1.8$ to 7.5) (Kinniburgh and Jackson, 1981 and references therein). The sorption edges of Zn, Ni, Cd, and Co from sample DMC (Fig. 5F) were shifted toward higher pH compared to those from samples ML and BBC. By contrast, previous studies have shown that hydrous Mn oxide has a stronger adsorption affinity for alkali metals and trace metals such as Zn and Cd than do hydrous oxides of Fe and Al due to (1) a greater electronegativity of the Mn ions (Tamura et al., 1996) and (2) a higher adsorption enthalpy/bonding energy (Trivedi and Axe, 2000). According to the results of this study, however, Mn oxide does not form at $pH < 7$ and, thus, should not play a role as a scavenger of trace metals in most acid mine waters.

The pH values at 50% sorption (pH_{50}) were determined from sorption edges of the trace metals (Table 3). The pH_{50} values ranged from 5.6 to 7.5 for Zn, 5.4 to 7.7 for Ni, 5.9 to 7.9 for Co, and 5.5 to 7.7 for Cd and were about two pH units higher for sample DMC as compared to samples BBC and ML. This result is attributable to the absence of sufficient amounts of sorbent in sample DMC compared to the other two samples at $pH < 7$. By contrast, Pb and Cu were more than 95% sorbed at $pH < 7$ in all 3 samples (ML, BBC, and DMC) indicating their strong affinity to Fe and Al hydroxides and hydroxysulfates. Because Pb and Cu were removed from solution before (i.e. at a lower pH) Mn oxides had formed, the pH_{50} values covered a narrower range (pH 3.1 to 4.3 for Pb and 4.6 to 6.1 for Cu). It is interesting that the pH_{50} of Pb for DMC (3.1) was lower than that for BBC (4.3) in spite of a smaller amount of sorbent in DMC. This behavior is presumably attributable to the fact that the mole fraction of Fe is higher in DMC (22.9%) than in BBC (2.5%). These results indicate that the primary factors governing the removal of trace metals in AMD-contaminated waters are: (1) the pH range of the drainage system, (2) the relative abundance of dissolved Fe, Al, and Mn, and (3) the solubilities of various Fe-, Al- and Mn-hydroxides/hydroxysulfates.

Table 3
pH_{50} of trace metals in the AMD waters

	BBC	DMC	ML
Pb^{2+}	4.3	3.1	3.1
CU^{2+}	4.7	6.1	4.6
Zn^{2+}	5.6	7.5	5.7
Ni^{2+}	5.4	7.7	[a]
Co^{2+}	5.9	7.9	6.8
Cd^{2+}	6.4	7.7	5.5

[a] Not determined.

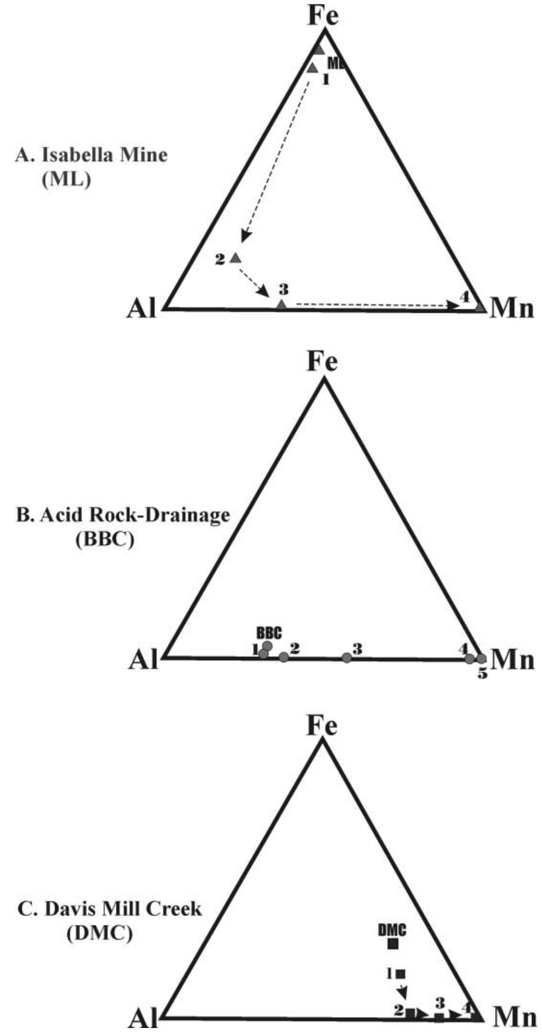

Fig. 8. Evolution of natural AMD waters with increasing pH: A. Relative abundances of dissolved Fe, Al and Mn in the aliquots of sample ML. The pH's of the aliquots 1, 2, 3 and 4 were 2.4, 3.0, 4.2 and 6.1, respectively; B. Those in the aliquots of sample BBC. The pHs were 3.3 (1), 4.2 (2), 4.3 (3), 5.0 (4) and 6.3 (5); C. Those in the aliquots of sample DMC. The pH's of the aliquots were 3.1 (1), 3.4 (2), 4.7 (3) and 6.1 (4).

4.3. Evolution of AMD-contaminated water

Even though the chemical compositions of the 3 waters (samples ML, BBC and DMC) were significantly different, the relative abundance of Fe, Al and Mn in solution changed systematically in all 3 as the pH increased. During neutralization, Fe was removed from solution at pH$<$4, Al at pH$\approx$5 and Mn at pH$\sim$8. For example, sample ML, which was originally Fe-dominant, became Al-rich due to the removal of Fe and finally Mn-rich as a result of the precipitation of Al-compounds as shown in Fig. 8A. In the same manner, samples BBC and DMC evolved to become Mn-rich at circumneutral pH (Fig. 8B and C). The sequential precipitation of Fe-, Al- and Mn-compounds has been observed by Theobald et al. (1963) along several cross-sections above and below the confluence between Deer Creek and the Snake River, Colorado. They noted that Fe-, Al- and Mn-hydroxides sequentially precipitated on the stream bed as the pH of acidic water from the Snake River increased as a result of mixing with the water of Deer Creek (pH 8). Rampe and Runnells (1989) reported a similar observation on a desert stream channel as the pH increased from 2.9 to 7.5 about 40 m downstream.

The original chemical compositions of the 3 samples presumably resulted from the chemical evolution by neutralization in natural environments. Sample ML was Fe-rich AMD from a lake formed in a collapsed stope of the old Isabella Mine. Because sample BBC was Fe-poor and Al-rich, a portion of the Fe had apparently been removed before it was collected. In the case of sample DMC, Fe and Al were sequentially removed from solution as the water flowed downstream to the mouth of Davis Mill Creek, thus making this sample Mn-rich. The evolution of AMD water is an important geochemical process governing the transport of trace metals under natural conditions because Fe, Al and Mn form precipitates that play a dominant role in scavenging trace metals.

5. Conclusions

Three surface waters severely contaminated with AMD were collected from watersheds in the former Ducktown Mining District, Tennessee. These waters had significantly different chemical compositions, which enabled the authors to study the removal of trace metals as a function of pH from a range of aqueous environments commonly encountered in mine effluents. The results of this study emphasize several phenomena regarding the scavenging of trace metals.

Iron, Al and Mn become non-conservative and form precipitates over different pH ranges. Schwertmannite and ferrihydrite form at pH values higher and lower than 4, respectively. Aluminum and Mn compounds form at pH$\sim$5 and at pH$\sim$8, respectively. Consequently, the relative abundance of Fe, Al and Mn in solution determines the pH range for the removal of trace metals from natural waters. The results of this study show that the sorption of trace metals generally coincides with the precipitation of the most abundant of these 3 elements. Therefore, the pH dependence of sorption is caused not only by changes in the sorption coefficients of the trace metals but also by the fact that the formation and composition of the sorbent is controlled by the pH and chemistry of the water. If insufficient amounts of sorbent are formed, trace metals will remain in solution even at pH values >7.

Acknowledgements

The authors gratefully acknowledge the analytical support of Dr. J. Olesik for ICP analyses, of Mr. U. Soto for XRD analyses and of Mr. S. Jones for fig. preparation. This study was supported by the Friends of Orton Hall and the Geochemistry Support Funds of the Department of Geological Sciences and by the Graduate Student Alumni Research Award of the Graduate School of The Ohio State University. The authors appreciate Dr. J. Herman's comments and suggestions which greatly helped to improve the manuscript.

References

Adams, F., Rawajfih, Z., 1977. Basaluminite and alunite: a possible cause of sulfate retention by acid soils. Soil Sci. Soc. Am. J. 41, 686–692.

Baltpurvins, K.A., Burns, R.C., Lawrance, G.A., Stuart, A.D., 1997. Effect of Ca^{2+}, Mg^{2+}, and anion type on the aging of iron(III) hydroxide precipitates. Environ. Sci. Technol. 31, 1024–1032.

Bigham, J.M., Schwertmann, U., Pfab, G., 1996a. Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. Appl. Geochem. 11, 845–849.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winlnd, R.L., Wolf, M., 1996b. Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochim. Cosmochim. Acta 60, 2111–2121.

Brady, K.S., Bigham, J.M., Jaynes, W.F., Logan, T.J., 1986. Influence of sulfate on Fe-oxide formation: comparisions with a stream receiving acid mine drainage. Clays and Clay Minerals 34 (3), 266–274.

Dzombak, D.A., Morel, F.M.M., 1990. Surface Complexation Modeling: Hydrous Ferric Oxide. John Wiley and Sons.

Emmons, W.H., Laney, F.B., 1926. Geology and ore deposits of the Ducktown Mining District, Tennessee. USGS Prof. Paper 139, 1–114.

Faure, G., 1998. Principles and Applications of Geochemistry. Prentice Hall, New Jersey.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. Adv. Chem. Ser. 73, 337–387.

Johnson, C.A., 1986. The regulation of trace element concentrations in river and estuarine waters contaminated with acid mine drainage: the adsorption of Cu and Zn on amorphous Fe oxyhydroxides. Geochim. Cosmochim. Acta 50, 2433–2438.

Karathanasis, A.D., Evangelou, V.P., Thompson, Y.L., 1988. Aluminum and iron equilibria in soil solutions and surface waters of acid mine watersheds. J. Environ. Qual. 17, 534–543.

Karlsson, S., Allard, B., Håkansson, K., 1988a. Chemical characterization of stream-bed sediments receiving high loadings of acid mine effluents. Chem. Geol. 67, 1–15.

Karlsson, S., Allard, B., Håkansson, K., 1988b. Characterization of suspended solids in a stream receiving acid mine effluents, Bersbo, Sweden. Appl. Geochem. 3, 345–356.

Karthikeyan, K.G., Elliott, H.A., Cannon, F.S., 1997. Adsorption and coprecipitation of copper with the hydrous oxides of iron and aluminum. Environ. Sci. Technol. 31, 2721–2725.

Kimball, B.A., Broshears, R.E., McKnight, D.M., Bencala, K.E., 1994. Effects of instream pH modification on transport of sulfide-oxidation products, Chapter 16. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation, 1994. ACS Symposium Series 550. Am. Chem. Soc, Washington, DC, pp. 224–243.

Kinniburgh, D.G., Jackson, M.L., 1981. Cation adsorption by hydrous metal oxides and clay, Chapter 3. In: Anderson, M.A., Rubin, A.J. (Eds.), Adsorption of Inorganics at Solid-Liquid Interfaces. Ann Arbor Sci. Pub. Inc, Michigan, pp. 91–160.

Kinniburgh, D.G., Jackson, M.L., Syers, J.K., 1976. Adsroption of alkaline earth, transition, and heavy metal cations by hydrous oxide gels of iron and aluminum. Soil Sci. Soc. Am. J. 40, 796–799.

Lee, G., 2001. Transport and Fate of Trace Metals in Streams Contaminated with Acid Mine-drainage in the Ducktown Mining District, Tennessee. PhD thesis, Ohio State University.

Magee, M., 1968. Geology and ore deposits of the Ducktown district, Tennessee. In: Ridge, J.D. (Ed.), Ore deposits of the United States, 1933–1967. Petroleum Engineers, New York, Am. Inst. Mining Metall, pp. 207–241.

Martinez, C.E., Mcbride, M.B., 1998. Solubility of Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} in aged coprecipitates with amorphous iron hydroxides. Environ. Sci. Technol. 32, 743–748.

McKenzie, R.M., 1989. Manganese oxides and hydroxides. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments, 2nd Edition, Chapter 9. Soil Sci. Soc. Amer, pp. 439–466.

Nordstrom, D.K., 1991. Chemical modeling of acid mine waters in the western United States USGS Toxic Substance Hydrology Program, Meeting Proceedings. USGS Water Res. Invest. Rep. 91-4034, 534–538.

Nordstrom, D.K., Alpers, C.N., 1999. Geochemistry of acid mine waters Chapter 6. In: Plumlee, G.S., Logsdon, M.J. (Eds.), The Environmental Geochemistry of Mineral Deposits, 1999. Rev. Econ. Geol., Vol. 6A. Soc. Econ. Geol. Inc, Littleton, Colorado, pp. 133–160.

Nordstrom, D.K., Ball, J.W., 1986. The geochemical behavior of aluminum in acidified surface waters. Science 232, 54–56.

Nordstrom, D.K., Ball, J.W., Robertson, C.E., Hanshaw, B.B., 1984. The effect of sulfate on aluminum concentrations in natural waters: II. Field occurrences and identification of aluminum hydroxysulfate precipitates. Geol. Soc. Am. Program Abstr. 16 (6), 611.

Parkhurst, D.L., 1995. Users guide to PHREEQC—a computer program for speciation, reaction-path, advective transport, and inverse geochemical calculations. Water-Res. Invest. Rep. 95–4227.

Paulson, R.W., Chase, E.B., Williams, J.S., Moody, D.W., 1993. National water summary 1990–91. Hydrologic events and stream water quality. USGS Water Supply Paper 2400, 499–506.

Post, J.E., 1999. Manganese oxide minerals: Crystal structures and economic and environmental significance. Proc. Natl. Acad. Sci. USA 96, 3447–3454.

Rampe, J.J., Runnells, D.D., 1989. Contamination of water and sediment in a desert stream by metals from an abandoned gold mine and mill, Eureka District, Arizona, USA. Appl. Geochem. 4, 445–454.

Sullivan, P.J., Yelton, J.L, Reddy, K.J., 1988. Iron sulfide oxidation and the chemistry of acid generation. Environ. Geol. Water Sci. 11, 289–295.

Tamura, H., Katayama, N., Furuichi, R., 1996. Modeling of ion-exchange reactions on metal oxides with the Frumkin isotherm. 1. Acid-base and charge characteristics of MnO_2, TiO_2, Fe_3O_4, and Al_2O_3 surfaces and adsorption affinity of alkali metal ions. Environ. Sci. Technol. 30, 1198–1204.

Theobald Jr., P.K., Lakin, H.W., Hawkins, D.B., 1963. The precipitation of aluminum, iron and manganese at the junction of Deer Creek with the Snake River in Summit County, Colorado. Geochim. Cosomochim. Acta 27 (2), 121–132.

Trivedi, P., Axe, L., 2000. Modeling Cd and Zn sorption to hydrous metal oxides. Environ. Sci. Technol. 34, 2215–2223.

Van Breemen, N., 1973. Dissolved aluminum in acid sulfate soils and in acid mine waters. Soil Sci. Soc. Am. Proc. 37, 694–697.

Webster, J.G., Swedlung, P.J., Webster, K.S., 1998. Trace metal adsorption onto an acid mine drainage iron(III) oxyhydroxysulfate. Environ. Sci. Technol. 32, 1361–1368.

Winland, R.L., Traina, S.J., Bigham, J.M., 1991. Chemical composition of ochreous precipitates from Ohio coal mine drainage. J. Environ. Qual. 20, 452–460.

Yu, J.-Y., Heo, B., Choi, I.-K., Cho, J.-P., Chang, H.-W., 1999. Apparent solubilities of schwertmannite and ferrihydrite in natural stream waters polluted by mine drainage. Geochim. Cosmochim. Acta 63, 3407–3416.