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Chemical and physical properties of iron hydroxide precipitates associated with passively treated coal mine drainage in the Bituminous Region of Pennsylvania and Maryland

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Abstract

Changes in precipitate mineralogy, morphology, and major and trace element concentrations and associations throughout 5 coal mine drainage (CMD) remediation systems treating discharges of varying chemistries were investigated in order to determine the factors that influence the characteristics of precipitates formed in passive systems. The 5 passive treatment systems sampled in this study are located in the bituminous coal fields of western Pennsylvania and northern Maryland, and treat discharges from Pennsylvanian age coals. The precipitates are dominantly (>70%) goethite. Crystallinity varies throughout an individual system, and lower crystallinity is associated with enhanced sorption of trace metals. Degree of crystallinity (and subsequently morphology and trace metal associations) is a function of the treatment system and how rapidly Fe(II) is oxidized, forms precipitates, aggregates and settles. Precipitates formed earlier in the passive treatment systems tend to have the highest crystallinity and the lowest concentrations of trace metal cations. High surface area and cation vacancies within the goethite structure enable sorption and incorporation of metals from coal mine drainage-polluted waters. Sorption affinities follow the order of Zn > Co ≈ Ni > Mn. Cobalt and Ni are preferentially sorbed to Mn oxide phases when these phases are present. As pH increases in the individual CMD treatment systems toward the pH_{pzc} of goethite, As sorption decreases and transition metal (Co, Mn, Ni and Zn) sorption increases. Sulfate, Na and Fe(II) concentrations may all influence the sorption of trace metals to the Fe hydroxide surface. Results of this study have implications not only for solids disposal and resource recovery but also for the optimization of passive CMD treatment systems.

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1. Introduction

Drainage from abandoned mined lands (AML) remains a widespread problem in the Appalachian coal fields, with about 3900 km of streams affected by coal

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mine drainage (CMD) in Pennsylvania alone (PA Department of Environmental Protection, 1998). Coal mine drainage can contain acidity, sulfates and metals, including Fe, Al and Mn, as well as As, Co, Ni and Zn. Over 100,000 tons of Fe are discharged from coal mines each year in the United States (Hedin, 1996). The oxidation of pyrite exposed during mining and the subsequent oxidation and hydrolysis of Fe produces hydroxide precipitates such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), schwertmannite ($Fe_{16}O_{16}(OH)_y(SO_4)_z \cdot nH_2O$) and ferrihydrite ($Fe_5HO_8 \cdot 4H_2O$), depending on pH conditions. These precipitates can coat the bottoms of streams and smother aquatic life. Schwertmannite is the main mineral formed in acidic mine drainage with pH between 3.0 and 4.5, while ferrihydrite and goethite form at $pH > 5.0$ and 6.0, respectively (Bigham et al., 1992). Both schwertmannite and ferrihydrite are metastable with respect to goethite and will eventually transform to goethite over time (Bigham et al., 1992).

Iron hydroxides generally exist as colloidal particles with high surface to volume ratios; thus they have a high specific surface area, with values up to 348 m^2/g reported in literature (e.g., Borggaard, 1983; Bigham et al., 1990; Cornell and Schwertmann, 1996; Kosmulski et al., 2004). As a result, they tend to be excellent sorbents of trace elements (e.g., As, Co, Ni and Zn) and subsequently control their mobility, fate and transport in polluted and unpolluted waters (Carlson and Schwertmann, 1981; Chapman et al., 1983; Blowes and Jambor, 1990; Kimball et al., 1995; Herbert, 1996; Schemel et al., 2000).

Depending on the chemistry of a discharge, various treatment methods have been developed to remediate CMD-contaminated water. Passive treatment of net-alkaline drainage typically consists of a series of ditches, ponds and aerobic wetlands that aerate and detain water allowing the Fe to oxidize, precipitate and settle (Watzlaf et al., 2000). Net-acidic drainage must first be neutralized, which can be achieved through the use of either an anoxic limestone drain (ALD), if the water is devoid of dissolved O_2, Al and Fe(III), or a reducing and alkalinity producing system (RAPS) (Watzlaf et al., 2000). Over time, the ponds and wetlands used in CMD treatment systems accumulate Fe-rich solids, and their ability to treat contaminated water is reduced. Most passive systems are constructed to hold 10–30 a of precipitates. The pond sludge must eventually be cleaned out in order to maintain treatment effectiveness, resulting in removal and disposal costs. These costs can be offset if the Fe hydroxides can be recovered and used as a resource. However, as physical properties can affect trace element associations, the precipitates must be fully characterized in order to determine an appropriate end use or disposal method.

Properties of Fe hydroxides have been examined in detail, including their formation and occurrence in natural and metal contaminated waters (Herbert, 1996; Childs et al., 1998; Hudson-Edwards et al., 1999) and their mineralogy and morphology (Schwertmann et al., 1985; Gerth, 1990; Bigham et al., 1992). Iron oxide content of precipitates in mine drainage treatment wetlands has also been examined in relation to sediment color (Tarutis and Unz, 1994) and mineralogy/morphology (Karathanasis and Thompson, 1995). Numerous investigations into the sorptive properties of synthetic Fe oxides and hydroxides (e.g., Benjamin and Leckie, 1980; Balistrieri and Murray, 1982; Borggaard, 1983; Schwertmann et al., 1985; Ali and Dzombak, 1996a; Webster et al., 1998), and, to a lesser extent, mine drainage Fe hydroxides (e.g., Smith et al., 1998; Schemel et al., 2000) have also been conducted. Physical parameters (settleability, particle size, viscosity, specific resistance, specific surface area and wet packing density) of mine drainage precipitates have also been examined (Jeon, 1998). However, no study has characterized and compared the chemical and physical properties of the precipitates that form within different CMD passive treatment systems. Here the authors investigate changes in precipitate mineralogy, morphology, and major and trace elemental concentrations and associations throughout 5 CMD systems treating discharges of varying chemistries. The goal is to create a conceptual predictive model for the type of precipitates formed in passive systems with implications for improvement in design of passive systems as well as resource recovery.

2. Treatment systems

The 5 passive treatment systems (Morrison II, Howe Bridge, Elklick, P–A, Scrubgrass) sampled in this study are located in the Bituminous coal fields of western Pennsylvania and northern Maryland (Fig. 1), and treat discharges from Pennsylvanian age coals (Clarion, Kittanning, Pittsburgh, Freeport). Morrison II (Fig. 2A; Clarion coal) treats drainage from a reclaimed surface mine. Water is captured and sent through an anoxic limestone drain (ALD) before traveling through a serpentine ditch. At Howe Bridge (Fig. 2B; Clarion coal), discharge from an abandoned gas well is piped to an ALD, and then sent through two ponds, a wetland and a reducing and alkalinity-producing system (RAPS). At Elklick (Fig. 2C; Kittanning coal), water from an abandoned borehole is collected and sent through an ALD followed by a pond, ditch and wetland. Water at the P–A site (Fig. 2D; Freeport coal) is aerated by a blower and then flows into a pond, down a ditch and into two additional ponds. At the Scrubgrass site (Fig. 2E;

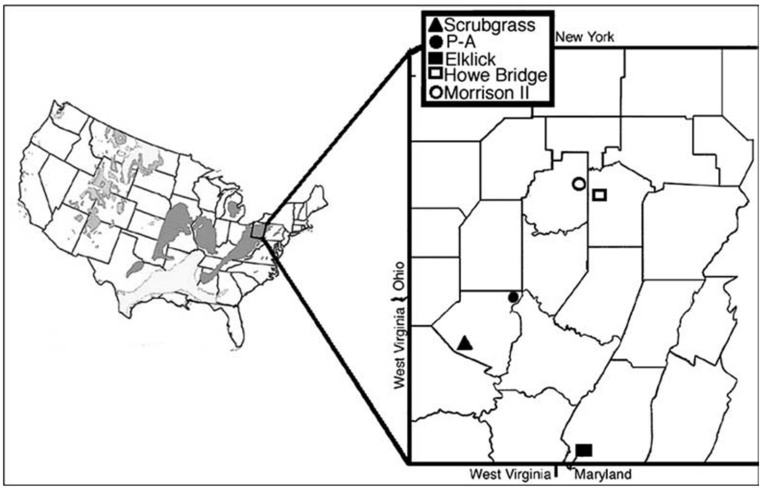

Fig. 1. Location of passive treatment systems sampled in this study.

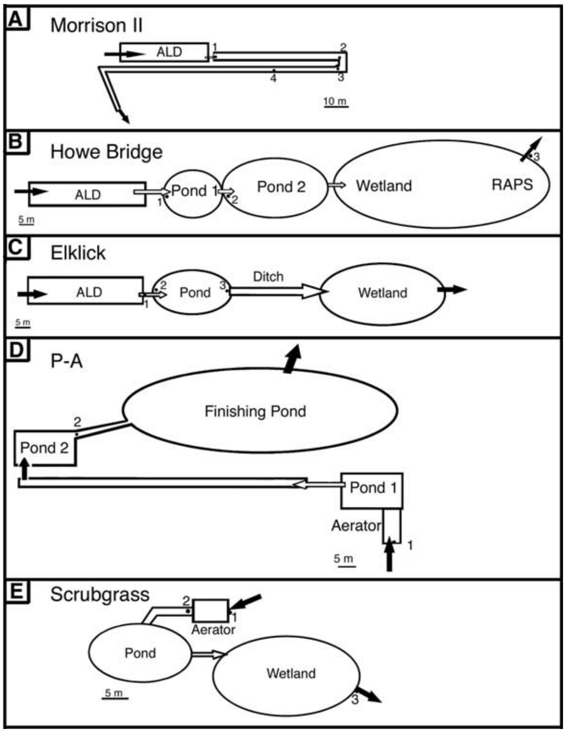

Fig. 2. Schematics of passive treatment systems and sampling points; arrows indicate flow direction: (A) Morrison II; (B) Howe Bridge; (C) Elklick; (D) P–A; (E) Scrubgrass.

Pittsburgh coal), water is aerated with a low-pressure system prior to flowing through a pond and wetland. Both the Scrubgrass and P–A systems treat underground mine discharges.

3. Methodology

3.1. Sampling and sample preparation

Water samples were collected in acid washed HDPE bottles for metals analysis at each sampling location (Fig. 2). Samples were filtered through a 0.2-μm syringe cellulose acetate filter and acidified in the field to pH < 2 with HCl (it is possible colloidal material finer than this was present). Field pH was measured using an Orion 250A pH meter with a temperature compensated probe; field alkalinity was determined using either the Orion® Total Alkalinity Test Kit with a calibrated pH meter, or the Hach® digital titration method.

Grab samples of the precipitates (representing up to several years of accumulation) were collected in 1 L HDPE bottles, bags or glass sampling containers. In the laboratory, visible organic matter was removed by hand and splits of the precipitate samples were dried at <40 °C to prevent volatilization and potential loss of structural water.

3.2. Chemical and physical analysis

Trace and major element concentrations in the water samples were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at the University of Pittsburgh Geochemistry Laboratory and at the U.S. Department of Energy/National Energy Technology Laboratory (U.S. DOE/NETL), using a Spectro-Flame and Perkin–Elmer Optima 3000, respectively. Sulfate concentrations were determined by ion chromatography or from total S measured by ICP-AES. Ferrous iron concentrations were determined in the laboratory by titration with $K_2Cr_2O_7$ (method of Fales and Kenny, 1940). Although this method is older, it is considered very reliable. Given the circumneutral pH values, it is expected that all dissolved Fe is in the Fe(II) form. Ferrous iron concentrations as determined by this method agreed well with total Fe as determined by ICP. It is possible to stabilize the Fe(II)/Fe(III) ratio from field to lab. To et al. (1999) describe a method using selective ligands to stabilize Fe(II) and Fe(III), thereby limiting any changes.

Total metals in the precipitate samples were determined through instrumental neutron activation analysis (INAA) and total acid digestion (using $HClO_4$–HNO_3–HCl–HF), followed by analysis using ICP-AES at Activation Laboratories in Ontario, Canada. In order to determine how trace metals were associated with the precipitates, a sequential extraction procedure was developed. The procedure (described fully in Kairies, 2003) used various extracting solutions to target particular phases. Extracting solutions and their target phases included Milli-Q® water (MQW, 18 MΩ cm; water soluble), 0.1 M acetic acid (exchangeable and carbonates), 0.1 M cold hydroxylamine hydrochloride (Mn oxides and hydroxides), 0.25 M hot hydroxylamine hydrochloride in 0.25 M HCl (Fe oxides and hydroxides) and H_2O_2 followed by 1 M ammonium acetate (metals bound to organics and sulfides). X-ray diffraction (XRD) patterns were obtained at the University of Pittsburgh Materials Science Laboratory using a Phillips X'pert powder diffractometer with Cu Kα radiation. Back-filled powder mounted samples were scanned from 5° to 15° 2θ using a 0.5° divergence slit and from 15° to 75° 2θ using a 1.0° divergence slit. Peak positions (d-spacings) were determined using the Phillips X'pert Organizer software. Morphology was determined using a Phillips XL30 FEG scanning electron microscope (SEM) with EDAX, also at the Materials Science Laboratory.

4. Results

4.1. Water chemistry

Water quality data (Table 1) collected from Howe Bridge and Elklick were averaged with long-term water quality data (6–10 a) from the U.S. DOE NETL in order to obtain representative average water chemistry at these sites. Multi-year data better represents the average condition under which most of these precipitates formed. Iron phases and aqueous species can show seasonal and diel variation (McKnight et al., 1988). However, the precipitates represent 3–10 a of deposition and the majority of the precipitates likely formed under average conditions, as many of the discharges exhibit little variation over time. Depending on the removal rate of Fe (wetlands are usually sized to remove 10–20 g/day/m^2; Hedin et al., 1994), an average of 3–5 cm of precipitate accumulates annually in ponds and wetlands. Waters collected from Scrubgrass, P–A and Morrison II are from one sampling event, as these sites were recently constructed and put into operation at the time of sampling, no long-term data are available. However, data from the other sites suggest there have been no major variations in water chemistry over the 5–10 a period the systems have been in operation.

Raw (influent) water quality data are indicated in the table and are included even though precipitates may not have been formed at this point. Influent water cannot be sampled at the Morrison II site as the water is piped directly into an anoxic limestone drain with no external access. As can be seen in Table 1, the raw (influent) water quality in these systems varies considerably between sites, with Fe ranging from 56 to 270 mg/L; Mn from 0.7 to 41 mg/L; Al from <0.10 to 1.4 mg/L and concentrations of Co, Ni and Zn ranging from <0.005 up to 1.5 mg/L.

4.2. Mineralogy and morphology

Mineralogy of the precipitates is presented in Table 2. For all samples, the main mineral present is goethite, although Howe Bridge (HB-2 and HB-3) and Morrison II (MOR-2 and MOR-3) samples contain minor amounts of lepidocrocite. Quartz, present in many of the precipitates, represents siliciclastic input (from weathering processes) into the treatment system. The ponds and wetlands are open to input from the surrounding area and exogenous material may be washed in during storm events, though such input is likely minimal. Precipitate crystallinity decreases (XRD peaks become broader and less intense) from the beginning to the end of the treatment systems (e.g., Elklick, Fig. 3), with the exception of the Morrison II system, in which crystallinity increases (results not shown).

Three general morphological categories are present: spherical (either spiky or globular), acicular, and platy; the first two of which occur as aggregates ranging in size from 0.5 to 2 μm. Representative SEM micrographs are shown in Fig. 4. The spiky (Fig. 4A), globular (Fig. 4B) and acicular particles (Fig. 4C) are characteristic of goethite (Domingo et al., 1994; Cornell and Schwertmann, 1996; Webster et al., 1998). Platy particles (Fig. 4D) are likely lepidocrocite (Domingo et al., 1994; Cornell and Schwertmann, 1996). Other particles include jagged quartz crystals up to 100 μm in diameter (identified by SEM-EDAX and confirmed by XRD). The size and morphology is consistent with detrital quartz rather than authigenic silica (e.g., Roscoe, 1999). No Al phases were evident in these samples.

Table 1
Water chemistry in mg/L

System and sample location	pH su	Alkalinity (mg/L $CaCO_3$)	Fe^{2+}	Tot Fe	Al	Ca	Co	K	Mg	Mn	Na	Ni	Zn	SO_4^{2-}
Clarion coal														
Morrison II														
1	5.89	149	215.4	215.4	0.5	200.6	0.71	6.2	117.0	40.7	5.2	0.84	1.49	1200
2	5.97	n.d.	217.9	217.9	0.5	193.8	0.71	6.2	116.2	40.8	4.9	0.84	1.51	1204
3	6.34	n.d.	209.2	255.6	1.4	195.2	0.74	6.2	116.0	40.9	5.0	0.86	1.64	1214
4	6.37	n.d.	190.2	194.7	0.3	196.3	0.73	6.4	116.5	41.1	5.2	0.93	1.45	1217
Howe Bridge														
Raw	5.72	33	270.2	269.7	0.1	154.2	0.44	6.1	106.2	41.1	10.5	0.49	0.58	1294
1	6.37	121	246.5	245.8	0.1	200.0	0.44	6.1	102.5	39.7	10.0	0.51	0.57	1261
2	6.38	115	237.9	238.0	0.1	201.6	0.39	5.9	101.9	38.9	12.5	0.43	0.43	1238
3	5.94	62	69.9	71.1	0.3	234.7	0.13	6.1	95.9	34.7	11.9	0.12	0.17	1083
Kittanning coal														
Elklick														
Raw	6.01	35	54.7	56.0	<0.10	79.3	0.07	2.1	22.1	4.7	1.8	0.10	0.14	336
1	6.64	156	51.0	54.6	<0.10	129.4	0.07	2.1	22.2	4.8	1.6	0.08	0.08	332
2	6.74	n.d.	41.1	42.4	<0.10	126.0	0.07	2.1	22.5	4.6	1.7	0.08	0.09	344
3	6.93	83	6.5	8.5	<0.10	129.0	0.05	2.1	22.2	4.4	1.8	0.07	0.05	333
Freeport coal														
P–A														
1 (Raw)	6.79	444	n.d.	80.6	<0.10	178.9	0.028	8.71	38.7	1.6	781.6	0.04	0.135	1849
2	7.42	n.d.	n.d.	11.3	<0.10	179.4	0.027	8.88	39.5	1.6	789.5	0.04	0.015	1881
Pittsburgh coal														
Scrubgrass														
1 (Raw)	6.11	190	n.d.	66.3	<0.10	94.5	<0.015	5.4	32.9	0.6	296.0	<0.015	0.17	544
2	6.63	184	n.d.	42.4	<0.10	96.8	<0.015	5.5	33.2	0.6	293.0	<0.015	0.03	544
3	6.66	190	n.d.	32.8	<0.10	98.6	<0.015	5.6	33.6	0.6	295.0	<0.015	0.02	543

As < DL of 0.2 mg/L for all samples. n.d., not determined.

Table 2
Mineralogy

System	Location	Mineralogy	
		Major	Minor
Morrison	1	Goethite	Quartz
	2	Goethite	Lepidocrocite
	3	Goethite	Lepidocrocite
	4	Goethite, quartz	
Howe Bridge	1	Goethite	Quartz
	2	Goethite	Quartz, lepidocrocite
	3	Goethite	Quartz, lepidocrocite
Elklick	1	Goethite	Quartz
	2	Goethite	
	3	Goethite	
P–A	1	Goethite	
	2	Goethite, quartz	
Scrubgrass	1	Goethite	Quartz
	2	Goethite	
	3	Goethite	

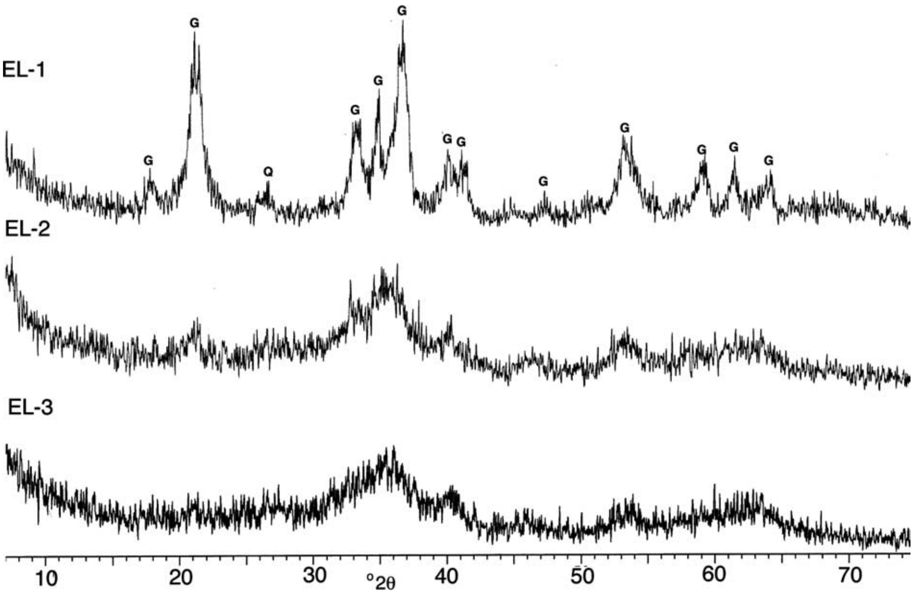

Fig. 3. Diffraction patterns of samples collected at Elklick. Crystallinity decreases from EL-1 (closer to influent) to EL-3 (furthest from influent). G, goethite; Q, quartz.

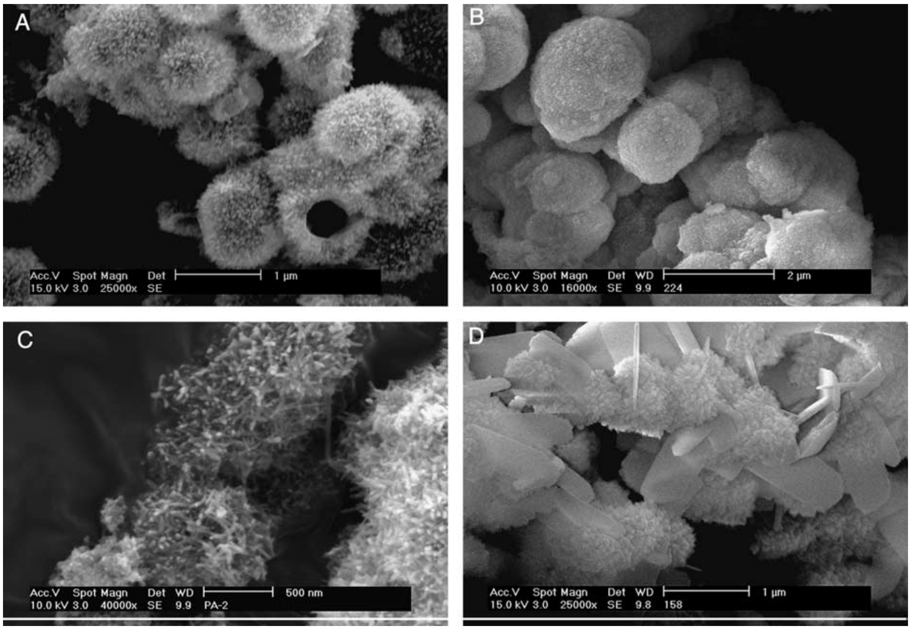

Fig. 4. Morphologies seen in precipitates collected from the passive treatment systems: (A) spiky; (B) globular; (C) acicular; (D) platy and spiky.

4.3. Precipitate chemistry

4.3.1. Trends within an individual treatment system

Trace and major elemental composition of the bulk precipitates are presented in Table 3. Iron content ranges from 42% to 57%, with varying amounts of Al (up to 1.05 wt%), As (up to 3010 mg/kg), Co (up to 936 mg/kg), Mn (up to 3.6 wt%), Ni (698 mg/kg) and Zn (up to 2400 mg/kg). It is known that naturally occurring goethite rarely exists as pure α-FeOOH, as it usually

Table 3
Precipitate chemistry reported in wt% (where noted) or mg/kg

System and sample location	FeOOH%	Fe%[a]	Al%[b]	Ca%[b]	K%[b]	Mg%[b]	Na%[a]	P%[b]	S%[b]	As[a]	Co[a]	Mn[b]	Ni[b]	Pb[b]	Zn[a]
Clarion coal															
Morrison II															
1	77	49	1.05	0.21	0.03	<0.01	0.01	0.003	0.77	119	92	1216	189	40	2400
2	87	55	0.51	0.06	0.04	<0.01	<0.01	<0.001	0.71	34	69	1080	90	31	2240
3	86	54	0.44	0.06	0.05	<0.01	0.01	<0.001	1.29	28	40	645	42	34	1500
4	74	47	1.05	0.07	0.26	<0.01	0.03	0.003	1.59	34	26	440	28	34	1000
Howe Bridge															
1	87	55	0.04	<0.01	<0.01	<0.01	0.03	0.039	0.99	11	34	1550	37	21	303
2	91	57	0.04	<0.01	<0.01	<0.01	0.03	0.036	1.13	19	25	1294	29	29	405
3	80	50	0.19	0.20	<0.01	0.02	0.03	0.802	0.59	0	27	2265	50	27	177
Kittanning coal															
Elklick															
1	85	54	<0.01	0.18	<0.01	<0.01	0.02	0.067	0.35	11	68	1645	70	23	202
2	81	51	0.01	0.19	0.01	<0.01	0.02	0.051	0.34	15	126	4030	128	13	554
3	67	42	0.12	0.64	0.07	0.02	0.03	0.024	0.21	6	936	35928	698	32	757
Freeport coal															
P–A															
1	90	56	0.01	0.64	<0.01	<0.01	0.56	0.022	0.632	327	22	387	37	41	70
2	79	50	0.47	2.14	0.13	0.06	0.47	0.006	0.445	114	56	1040	80	38	140
Pittsburgh coal															
Scrubgrass															
1	80	50	0.37	0.24	0.10	0.04	0.20	0.212	0.43	3010	4	80	10	21	38
2	78	49	0.56	<0.01	0.18	0.02	0.09	0.027	0.29	437	4	84	11	31	39
3	85	53	0.10	<0.01	0.04	<0.01	0.06	0.010	0.25	121	6	312	6	20	94

[a] INAA.

[b] Digestion and ICP.

contains cations such as Al, Co, Ni and Zn that have been incorporated into the structure (Kühnel et al., 1975; Burns and Burns, 1977).

In all 5 systems sampled for this study, As (present as either arsenate or arsenite anions) in the precipitates decreases from the influent to the effluent of each system. The precipitates are enriched in Al, As, Co, Mn, Ni and Zn relative to their associated waters (Tables 1 and 3). Given the pH conditions, Al may be present as a hydroxide (Hem, 1992), though crystalline Al phases were not evident in the XRD patterns. Cobalt, Mn, Ni and Zn concentrations in the precipitates increase as the water flows through the treatment systems with the exception of Morrison II, where the concentrations of these metals decrease.

4.3.2. Comparison between passive treatment systems

Variations in the trace metal content of precipitates are also seen between treatment systems, with certain systems exhibiting greater concentrations than other systems. Precipitates from Elklick contain the highest concentrations of Mn, Co and Ni, while those from Morrison II contain the highest amounts of Al and Zn. Arsenic concentration is greatest in the Scrubgrass and P–A precipitates.

5. Discussion

5.1. Partitioning of trace elements

Distribution coefficients (K_d) are used to quantify equilibrium metal partitioning. However, such calculations are useful only for the specific conditions under which they are measured and cannot be applied to other systems (Honeyman and Leckie, 1986; Rose and Bianchi-Mosquera, 1993). Additionally, in these systems it cannot be assumed there is equilibrium between the water and the precipitate, nor can it be assumed that transport has not occurred. Munk et al. (2002) studied trace element distribution in Al hydroxides precipitated from polluted mine waters. They used a concentration ratio (CR) to explain trace element distribution:

$$CR = [X]_s/[X]_l,$$

where X represents the concentration of a particular element in the solid ($[X]_s$) and aqueous ($[X]_l$) phase. While the formulation is the same as K_d, the use of the term CR does not assume equilibrium between waters and coexisting solids. Following the work of Munk et al. (2002), the CR is presented as a dimensionless quantity, assuming in these dilute solutions that 1 L of solution ~1 kg.

In this study, concentration ratios allow for comparison of precipitate enrichment as well as the distribution of elements between the solid and liquid phase (where trends may not be obvious by looking at precipitate and water chemistry alone) not only within a treatment system, but also between systems. If an element was below the detection limit (DL) in the water (see Table 1), the DL was assumed to be the maximum concentration of this element, and the subsequent ratio is the minimum CR for that sample. Concentration ratios were not determined for elements below DL in the precipitate.

Precipitates from Howe Bridge (Fig. 5A), Elklick (Fig. 5B), Scrubgrass (Fig. 5C) and P–A (Fig. 5D) generally become increasingly enriched through the treatment system in Co, Mn, Ni and Zn relative to the associated mine waters. The exception is the Morrison II system (Fig. 5E), where enrichment in the precipitates generally decreases relative to the water through the treatment system. Arsenic in the precipitates decreases in the P–A (Fig. 5D) and Scrubgrass systems (Fig. 5C).

In this study, metal affinities for the goethite surface (determined by log CR) generally follow the order:

$$\mathrm{Zn} > \mathrm{Co} \approx \mathrm{Ni} > \mathrm{Mn}$$

Although the CR values vary between systems, the order of sorption affinity remains the same. These results are comparable to experimental and modeled K_d values ($\mathrm{Cr} > \mathrm{Pb} > \mathrm{Cu} > \mathrm{Zn} > \mathrm{Ni} > \mathrm{Ca}$) determined by Dzombak and Morel (1990) and work on synthetic goethite ($\mathrm{Cu} > \mathrm{Pb} > \mathrm{Zn} > \mathrm{Co} > \mathrm{Ni} > \mathrm{Mn} > \mathrm{Ca} > \mathrm{Mg}$) by Gerth (1990) and Cornell and Schwertmann (1996).

Given that the log CR values of the CMD precipitates are comparable to log K_d laboratory values, and that Fe hydroxides are excellent sorbents of ions (Balistrieri and Murray, 1982), it is likely that the trace metal associations seen in the passive treatment precipitates are related to sorption of the metals to the surface of the precipitate. Sorption and the influence of the Fe hydroxide surface and structure, the point of zero charge, crystallinity, and other species present in both the water and the precipitates, are examined below.

5.2. Iron hydroxide surfaces and structures and the point of zero charge

Sorption on Fe hydroxide particles is controlled by the surface hydroxyl groups that are singly, doubly or triply coordinated with Fe atoms (Cornell and Schwertmann, 1996). The surface can be positively, negatively or neutrally charged ($\mathrm{FeOH_2^+}$, $\mathrm{FeO^-}$ and $\mathrm{FeOH^0}$) through the adsorption or desorption of protons (pH dependent), making the Fe hydroxides amphoteric (Cornell and Schwertmann, 1996). Specific sites are available for anion and cation sorption, and these sites may be physically and electrically isolated from each other (Coughlin and Stone, 1995). Empty surface sites in the goethite structure are often occupied by additional hydroxyl groups, which are also available for reaction (Cornell and Schwertmann, 1996).

Iron hydroxides are known to have high surface areas (Schwertmann et al., 1985; Bigham et al., 1990; Cornell and Schwertmann, 1996; Kosmulski et al., 2004). Because of this property, numerous sites are available for sorption reactions; the number and type of surface hydroxyl groups available are a function of pH. Sorption of most metals to the Fe hydroxide surface is generally followed by diffusion of the metal into internal bonding sites and subsequent incorporation into the Fe hydroxide crystal structure, potentially freeing up surface sites for continued sorption (Coughlin and Stone, 1995; Cornell and Schwertmann, 1996).

The pH of the point of zero charge ($\mathrm{pH_{pzc}}$) is the pH at which the net surface charge is equal to zero. A net positive charge exists at $\mathrm{pH} < \mathrm{pH_{pzc}}$; this results in increased anion sorption. Correspondingly, the net negative charge at $\mathrm{pH} > \mathrm{pH_{pzc}}$ results in increased cation sorption (Dzombak and Morel, 1990; Cornell and Schwertmann, 1996). Although the $\mathrm{pH_{pzc}}$ of natural goethite is unknown and was not determined for these systems, synthetic goethite has been found to have a $\mathrm{pH_{pzc}}$ between 7.5 and 9.0 (Yates and Healy, 1975; Zeltner and Anderson, 1988; Jeon, 1998). The $\mathrm{pH_{pzc}}$ of natural goethite is likely similar, but would be affected by pH of the water and the presence of other dissolved species in mine drainage polluted waters.

As water flows through the passive treatment systems, the pH generally increases. For example, at Elklick pH increases from 6.6 to 6.9 (Fig. 5B and Table 1), and at Scrubgrass the pH increases from 6.1 to 6.6 (Fig. 5C and Table 1). The increase in pH at these sites is likely due to alkalinity addition and $\mathrm{CO_2}$ sparging (due to agitation/oxidation of the water). As the $\mathrm{pH_{pzc}}$ of goethite (7.5–9.0) is approached, it is expected that positive sorption sites will decrease (resulting in a subsequent decrease in anion sorption), while negative sorption sites will increase (resulting in increased cation sorption). This could account for the decrease in As and increase in metal cations observed in systems in this study. An exception to this is the Howe Bridge site, where pH actually decreases while metal CR values increase (Fig. 5A). At Howe Bridge, CR values are lower than at the other sites, which could be due to the decrease in pH, likely caused by precipitate formation. Unlike the other 4 sites, at Morrison II, Co, Mn and Zn CR values decrease

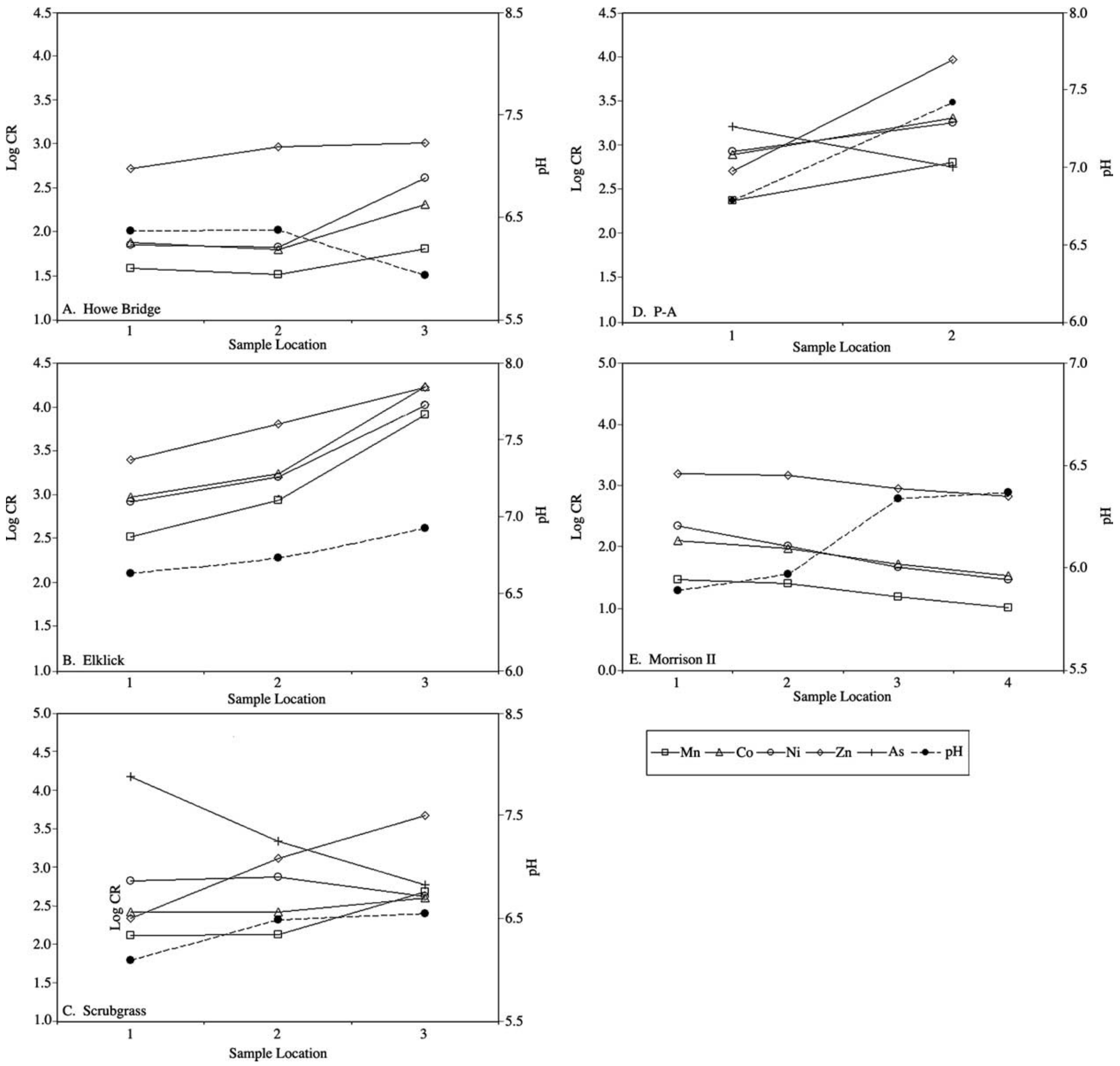

Fig. 5. Concentration ratios: (A) Howe Bridge; (B) Elklick; (C) Scrubgrass; (D) P–A; (E) Morrison II. Flow through each system is from left to right on the graph.

while pH increases. This could be due to changes in crystallinity, as discussed below.

5.3. Sorption and crystallinity

As noted previously, precipitates from the Morrison II system differ from the other treatment systems in that although pH increases from 5.9 to 6.4, crystallinity increases (Fig. 5E and Table 1), and concentration ratios of Co, Mn, Ni and Zn decrease from the influent to the effluent (Fig. 5E). In this system, the increased crystallinity potentially overwhelms the enhanced sorption of trace metal cations associated with rising pH. Low crystallinity and high surface area of minerals such as ferrihydrite make them highly effective at sorbing trace elements from solution (Xu et al., 1997). As the crystals become larger, surface area decreases, which corresponds to fewer surface sorption sites and a lower sorption capacity. It has been found that the crystal structure of goethite may prohibit metal sorption and release due to its small interatomic spacing (Coughlin and Stone, 1995). At the other sites, the decrease in crystallinity throughout the individual systems corresponds to an increase in trace metal sorption, supporting the idea that the degree of crystallinity affects the degree of sorption. Increasing oxidation rates can also increase crystallinity.

At the Morrison II site, sample locations 2, 3 and 4 are areas of enhanced aeration and increased oxidation, as there is a drop in elevation going around a bend to the lower portion of the ditch. As a result, crystallinity is higher and cation sorption decreases. The CR of Al is not discussed here because it could be present as a separate hydroxide phase that precipitated elsewhere and was subsequently transported and deposited. Due to the amorphous nature of the samples, it could not be determined by XRD if Al hydroxide phases are present. However, at the pH values observed in these systems, very low concentrations of Al would be soluble and available for substitution into the goethite structure. Goethite can undergo isomorphic substitution (solid solution) for Fe^{3+} by other trivalent cations, and Al is one of the best known and studied examples of isomorphous substituting constituents (Cornell and Schwertmann, 1996). Aluminum's strong affinity for the goethite surface may lead to the formation of an Al substituted goethite (Cornell and Schwertmann, 1996).

Sorption of anions (As) does not appear to be influenced by precipitate crystallinity. In every system, As concentration in the precipitates decreases from the beginning to the end, regardless of crystallinity.

Transformation from one structure to another (e.g., ferrihydrite to goethite, poorly crystalline goethite to crystalline goethite) could result in the release of sorbed and structurally incorporated metals. Aged Fe oxyhydroxides do not release sorbed metals on laboratory time scales (Jenne, 1968; Rose and Bianchi-Mosquera, 1993), but release could occur if precipitates are dehydrated and become more crystalline. If a poorly crystalline precipitate transforms to more crystalline goethite or even hematite, metals can be excluded from the new structure due to the decreased crystal lattice space and/or decreased in surface area on which sorption reactions can occur (Coughlin and Stone, 1995).

In addition to crystallinity, the aggregation of particles could also control the sorption and desorption of trace metals. Aggregation decreases the surface area available for sorption and can also prevent trace metal release as surfaces once exposed are no longer open to the surrounding solution (Coughlin and Stone, 1995).

5.4. *Influence of dissolved species on metal sorption*

5.4.1. *Sodium*

The presence of elevated concentrations of Na in solution could enhance anion sorption due to the effect of the ionic strength (strength of the electrostatic field caused by ions) of the solution. The electrical aspects of the solid/liquid interface are believed to be influenced by the major ions in solution (Balistrieri and Murray, 1982). If a net positive charge is created by the major cations in solution (e.g., Na), anion sorption (e.g., As) could be enhanced.

Sorption of cations onto the Fe hydroxide surface can be either specific or non-specific. Specific adsorption leads to the formation of inner-sphere complexes in which the element is coordinated to one or two surface Fe atoms. Most heavy metal and alkaline earth cations sorb in this manner (Cornell and Schwertmann, 1996). Non-specific adsorption, exhibited by alkali metals (e.g., Na), involves ion pair formation and the formation of outer-sphere complexes. The ion is surrounded by water molecules and held to the surface by electrostatic conditions (Collins et al., 1999) and the extent of sorption depends on ionic strength of the solution, which in turn influences electrostatic conditions at the surface (Cornell and Schwertmann, 1996).

When present at low levels in the water (<100 mg/L), dissolved Na has minimal effect on the Fe hydroxide surface. Smith et al. (2002) found that Na had a nominal effect on the sorption of As by soils. Although further investigation is necessary to confirm the role of Na in As sorption, the high Na concentrations at the Scrubgrass (293 mg/L) and P–A (790 mg/L) sites could result in a significant increase in the positive surface charge. This in turn could enhance anion sorption and explain the elevated As concentrations seen in the first precipitates forming in the two systems. As the pH_{pzc} is approached, the effect of ionic strength could decrease as competition from other sorbing cations (with higher affinities for the oxide surface) increases.

5.4.2. *Sulfate*

Dissolved SO_4 in the discharges could influence the sorption of Zn, Cu, Pb and Cd onto the precipitates by creating a net negative charge at the Fe hydroxide surface (e.g., Balistrieri and Murray, 1982; Ali and Dzombak, 1996b). Alternatively, SO_4 can form ternary structures with the trace metal cations of Co, Mn, Ni and Zn, creating a mixed metal–ligand surface complex that increases the amount of metal cations associated with the Fe hydroxides (Schindler, 1990; Ali and Dzombak, 1996b; Webster et al., 1998).

Either process (electrostatic alteration or formation of ternary complexes) could be operating in the mine drainage treatment system, as SO_4 is ubiquitous in many discharges. Other anions present in CMD, such as CO_3^{2-} and HCO_3^-, can also act in a manner similar to SO_4^{2-} (Balistrieri and Murray, 1982).

5.4.3. *Manganese and iron*

The presence of a particular trace metal in solution does not necessarily reflect what will sorb and accumulate in the precipitate. The presence of other dissolved constituents may hinder sorption and subsequent incorporation into the goethite structure. The dissolved Mn concentration in water at the Howe Bridge site is an order of magnitude higher than at the Elklick site, but the concentration of Mn in the Elklick precipitates is up to

15 times higher then that at the Howe Bridge site (Fig. 6A). A combination of two processes can be used to explain this. In the first, Fe(II) inhibits Mn^{2+} oxidation, and in the second Fe(III) acts to oxidize Mn^{2+}.

Following sorption, Mn must be oxidized from Mn^{2+} to Mn^{3+} before it can be incorporated into the goethite structure and allow continued surface sorption to occur (Giovanoli and Cornell, 1992). In passive treatment systems Mn^{2+}, the most common form of Mn in natural waters (Hem, 1992), can be oxidized and removed only after the oxidation and removal of Fe^{2+}. This typically does not happen abiotically at pH < 9.0, as the kinetics of this reaction are low; once Mn is oxidized, it is immediately reduced by the Fe^{2+} (Hedin et al., 1994). Fig. 6B shows that the concentration of dissolved Fe is about 4–5 times less at Elklick than at Howe Bridge. The majority of total dissolved Fe throughout Howe Bridge and Elklick is in the Fe^{2+} form, except for location 3 at Elklick, which is mostly Fe^{3+} (Table 1).

It is reasonable to assume that continued sorption of Mn to the precipitates at the Howe Bridge site is limited by the incorporation of Mn into the goethite structure. Incorporation cannot occur until Mn is oxidized, but at Howe Bridge it is inhibited by the presence of high amounts of dissolved Fe^{2+} (up to 247 mg/L) found in most of the system. At Elklick, however, Fe^{2+} concentrations decrease from 51 mg/L to 6.5 mg/L between Locations 1 and 3, and sorption of Mn and subsequent oxidation and incorporation into the goethite structure can occur, accounting for the high Mn in the precipitate at Elklick.

Alternatively, at low concentrations of dissolved Fe, a catalytic mechanism can result in the oxidation of Mn^{2+} by Fe^{3+} (Hem, 1964; Hem, 1977):

$$2\mathrm{Fe(OH)}_2^+ + 3\mathrm{Mn}^{2+} + 2\mathrm{H_2O} \rightarrow \mathrm{Mn_3O_4} + 2\mathrm{FeOH}^+ + 6\mathrm{H}^+$$

The reaction proceeds to the right at a pH > 6.5, when dissolved Fe^{2+} activity is low (concentrations of 10^{-12} molal; Hem, 1977; Cravotta and Trahan, 1999). Cravotta and Trahan (1999) used this mechanism to explain the removal of dissolved Mn in oxic limestone drains built to treat drainage from coal mines. It is feasible that

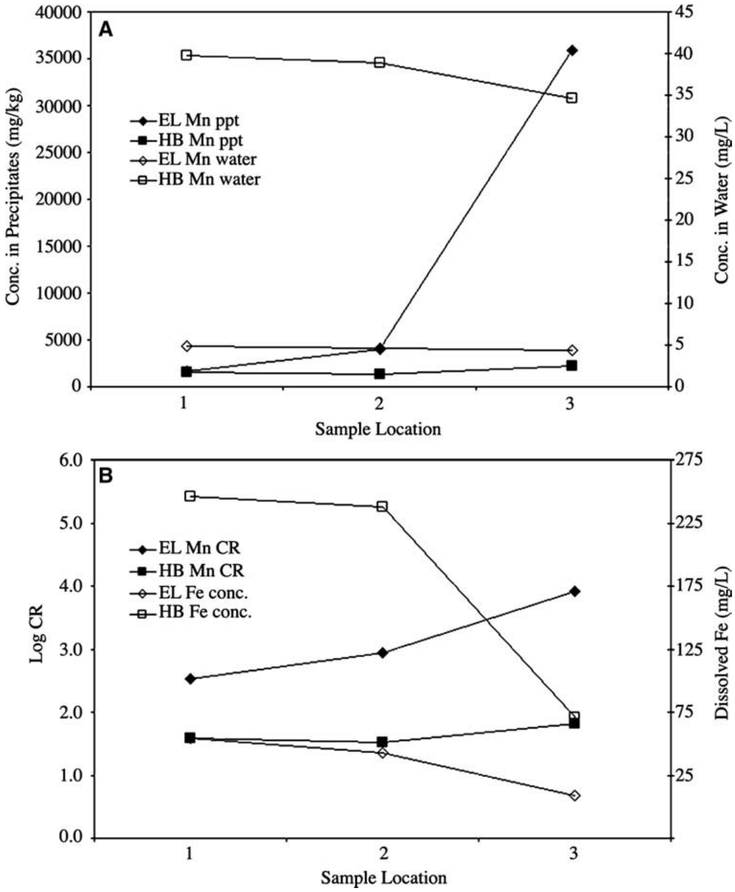

Fig. 6. (A) Manganese concentration in the precipitates and water collected from Howe Bridge and Elklick. (B) Manganese concentration ratios and dissolved Fe for Howe Bridge and Elklick.

this process could also be operating in the Elklick system (Fig. 6).

Regardless of the mechanism by which Mn can oxidize and precipitate on the goethite surface, it is possible that the presence of Mn oxide or hydroxide phases could enhance the sorption of other metals such as Co, Ni and Zn. As stated earlier, these metals have an increased affinity at Elklick (Elklick CR values are ~1.5 times greater than those of the Howe Bridge system). This could be due to the presence of Mn oxide and/or hydroxide phases on the goethite surface at the Elklick site. Hydrous Mn oxides are known to have higher sorption capacities compared to the Fe hydroxides, especially for Co and Ni (Manceau et al., 2000; Trivedi and Axe, 2000; Trivedi et al., 2001). Thus, it is necessary to identify the phases in treatment system precipitates (e.g., goethite, Mn hydroxides and organic matter) that are actually associated with trace metals of interest.

5.5. Sequential extraction and trace element associations

In order to determine how metals are associated with the precipitates, a sequential extraction procedure was developed (Kairies et al., 2002; Kairies, 2003). This 5 step procedure is a modification of a combination of procedures (Tessier et al., 1979; Lovley and Phillips, 1987; Schwertmann and Cornell, 1991; Ure et al., 1993; McCarty et al., 1998), and was used to extract metals loosely sorbed and tightly sorbed to the Fe hydroxide surface, bound to Mn oxides and hydroxides, bound to Fe oxides and hydroxides and bound to organic matter and sulfides.

Results of the extraction method for a sample from the Morrison site are presented in Fig. 7A, and are representative of the results seen in most of the other samples used in that study. This figure shows that the trace metals (including Mn) are released in the step targeting the Fe oxide and hydroxide phase, indicating they are tightly bound or incorporated into the goethite structure. Transition metals are specifically sorbed to the Fe hydroxide surface and reversal of this is difficult (Cornell and Schwertmann, 1996), which is why sorbed metals are not exchanged with the acetic acid step. However, in one sample from the Elklick system (EL-3, Fig. 7B), the majority of the Mn (35,000 mg/kg, about 97% of the total extractable Mn) was released during the 0.1 M hydroxylamine hydrochloride extraction step, indicating the presence of Mn oxide or hydroxide phases. Due to the amorphous nature of this sample, it could not be determined by XRD if such phases were present. Additionally, the majority of Co was released in this step, indicating that it was sorbed or incorporated into the Mn oxide/hydroxide structure, and therefore had a higher affinity for Mn hydroxides than for Fe hydroxides. Nickel was partitioned between the Mn and Fe oxide/hydroxide phases, as was Zn, though Zn was more strongly partitioned into the Fe hydroxide phase while Ni was more strongly partitioned into the Mn oxide/hydroxide phase (if that phase was present). These results indicate that the majority of trace metals are incorporated into the Fe oxide/hydroxide phase (or will partition into a Mn oxide/hydroxide phase if present), and they are not easily desorbed/released. This implies that CMD precipitates could have the ability to continually uptake metals and prevent them from being released back into the aquatic environment. It is important to note that if the sediments are subjected to reducing conditions, metals could be released into the environment.

5.6. Influence of coal seam and overburden on precipitate chemistry

Post-mining water quality depends on the coal seam from which a discharge originates as well as the overburden of that coal seam. Mining exposes minerals in the overburden such as pyrite to weathering processes, which results in the formation of acid mine drainage. Aluminum likely originates through the dissolution of aluminosilicate minerals. A number of tools, such as acid base accounting, can be used for the prediction of post-mining water quality (Brady et al., 1998). In a similar manner, it might be possible to predict the trace metal constituents that could accumulate in the precipitates that form based on the water quality of the discharges.

It is generally believed that coal is deposited in freshwater environments. Deposition of overburden strata can occur in freshwater, transitional (brackish) or marine environments, and the overburden depositional environment partially dictates the authigenic and diagenetic minerals that form in coal and its associated strata (Brady et al., 1998). Strata deposited under marine and brackish conditions are typically high in S due to SO_4 in the seawater. Higher concentrations of Mn are also associated with marine and brackish strata.

These trends are reflected in the water quality data (Table 1) from this study. High SO_4 (up to ~1300 mg/L) and Mn (up to 41 mg/L) are seen in discharges originating from the Clarion seam, which is overlain by marine units. In marginally brackish environments (overburden of Kittanning and Freeport coals, Elklick and P–A discharges), the S and Mn contents are likely a function of the extent of marine influence, and in freshwater environments (Pittsburgh coal, Scrubgrass discharge), the S and Mn contents are considerably lower than coal seams overlain by marine units.

Sulfate, sodium and ferrous iron concentrations can all influence the sorption of trace metals to the Fe hydroxide surface. In order to accurately predict the type of precipitate that will form from a given discharge, factors that can influence discharge geochemistry, such

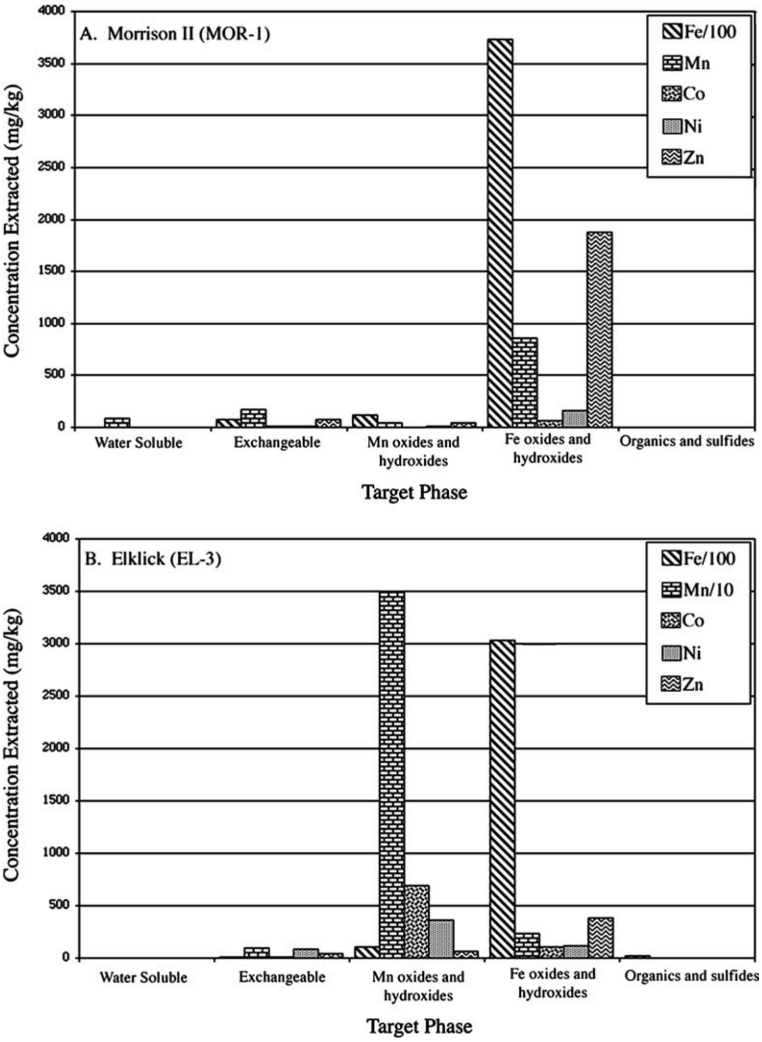

Fig. 7. Results of sequential extraction procedure: (A) Morrison II, sample MOR-1 (note Fe concentration is divided by 100); (B) Elklick, sample EL-3 (note Fe concentration is divided by 100 and Mn concentration is divided by 10).

as overburden geology, should be considered. The pH of the water, which is also a function of the strata it travels through (e.g., shales vs. alkalinity generating limestones), will also influence the type of Fe hydroxide that forms, as well as what trace metals are subsequently sorbed. Even though trace metals may be present at or below detection limits, they can still concentrate in the precipitate, especially if sorption is promoted by the presence of other dissolved constituents.

The type of mine (underground vs. surface) may also influence water quality. The Scrubgrass and P–A discharges both originate from underground coal mines, and the high levels of Na seen in these discharges could be due to subsurface cation exchange reactions or reactions with brines (e.g., Capo et al., 2001; Winters and Capo, 2004).

6. Conclusions

Even though a metal is present in solution, its concentration is not necessarily an accurate predictor of what metals accumulate in the precipitate. This work shows that many variables affect metal sorption to CMD precipitates, including (1) goethite crystallinity, (2) pH of the associated water, (3) trace metal affinities for the goethite surface and (4) the presence of dissolved Na and SO_4, and all should be used in predictive modeling of CMD precipitate formation. As described above, such a model has implications for passive treatment system design and resource recovery efforts.

Precipitates formed in 5 coal mine drainage passive treatment systems in southwestern Pennsylvania and northwestern Maryland are dominantly (>70%)

goethite; crystallinity varies throughout an individual system, and lower crystallinity is associated with enhanced sorption of trace metals. High surface area and cation vacancies within the goethite structure enable sorption and incorporation of metals from CMD polluted waters. Sorption affinities (determined by the log of the concentration ratio) follow the order of Zn > Co $\approx$ Ni > Mn and are consistent with those determined experimentally on synthetic goethite. Cobalt and Ni are preferentially sorbed to Mn oxide phases when these phases are present.

As pH increases in the individual CMD treatment systems toward the goethite pH_{pzc}, As sorption decreases and transition metal (Co, Mn, Ni and Zn) sorption increases. In the Morrison II system, As sorption also decreases with increasing pH, but there is no corresponding increase in transition metal cation sorption as the goethite pH_{pzc} is approached. This could be due in part to higher crystallinity within the Morrison II system relative to the other CMD systems, which inhibits trace metal cation sorption processes. Aluminum enrichment and the high affinity of Al for the goethite surface, particularly at the Morrison II site, could also be a result of isomorphous substitution. It is possible that a separate Al hydroxide phase is present, but this could not be determined from the data.

Discharge water chemistry can have a strong effect on metal sorption. Dissolved Na present at levels >100 mg/L increases the ionic strength of the waters and could increase the positive charge at the surface of the precipitates, resulting in enhanced sorption of anions such as those of As. Further investigation into the influence of Na on the sorption of anions onto the goethite surface is necessary. Dissolved SO_4 could also change electrostatic conditions at the surface by making it more negative and enhancing trace metal cation sorption (e.g., Co, Mn, Ni and Zn). It is also possible that SO_4 could form ternary complexes with these cations.

Even though dissolved Mn concentrations at Howe Bridge are 10 times higher than that at Elklick, the concentrations of Mn in the precipitates at Elklick are about 15 times higher than at Howe Bridge, showing that dissolved elemental concentrations do not necessarily reflect what ultimately accumulates in the precipitate. Sorption and incorporation of Mn are limited by oxidation processes, which are limited by the presence of Fe(II) in solution.

Results of this study have implications not only for disposal of precipitates but also for the optimization of passive treatment systems. Degree of crystallinity (and subsequently morphology and trace metal associations) are a function of the treatment system and how rapidly Fe(II) is oxidized, forms precipitates, aggregates and settles. Precipitates formed earlier in the passive treatment systems tend to have the highest crystallinity and the lowest concentrations of trace metal cations.

In order to optimize passive treatment systems for resource recovery purposes, net-alkaline waters (whether naturally so or made alkaline through the use of an ALD) with low amounts of trace metals should undergo intense oxidation as soon as possible and be allowed to precipitate and settle in large, unvegetated ponds (to minimize organic material in the precipitates) early in the system. Increased oxidation could enhance the crystallinity of the precipitate, as seen in Morrison II. Precipitates formed after this point are likely to be less crystalline and have greater enrichment of Al, Co, Mn, Ni and Zn. Jeon (1998) found that the greater the crystallinity exhibited by the precipitate, the smaller the settling volume of the precipitate. A more crystalline precipitate will not only occupy less space in treatment ponds, potentially extending the life of the system, it will also be cleaner and could potentially be recovered and used in the Fe oxide industry. Iron hydroxide precipitates from several passive treatment systems in western Pennsylvania have been recovered and used in various applications (Kairies, 2003; Hedin, 2002). Resource recovery efforts for waters with high amounts of trace metals are likely not the best option. Passive systems that enhance the formation of a more poorly crystalline Fe hydroxide should be investigated for optimum removal of trace metals.

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