Mineral-water interactions in acid mine drainage environments: A TEM, AEM, and EFTEM study

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Background. Mineral-water interfacial interactions associated with working and abandoned sulphide-bearing mines and mining wastes are among the most complex, dynamic, and environmentally important of all near-surface rock-water systems (e.g. Jambor and Blowes, 1994). These mining sites, numbering approximately 200,000 in the United States alone, typically release large amounts of heavy metals into the environment ranging up to hundreds of kilometers down hydrologic gradients in relatively short times. Contamination occurs when high solute concentrations of iron form during the weathering of pyrite and associated metal sulphides. Acidic effluent flowing from mine adits and waste piles mix with air and oxygenated surface water and precipitate iron oxides, oxyhydroxides, and/or hydroxysulphates. These phases form mineral/rock coatings and iron-rich sediments that may contain very high concentrations of associated metals (up to percent levels of, for example, Cu, Zn, and Pb).

Field and laboratory studies suggest that both the growth/dissolution of discrete metal-bearing precipitates and adsorption/desorption reactions are the most important processes in the attenuation/release of toxic metals. However, despite thermodynamic predictions, as well as mineralogical (e.g. XRD) and geochemical (e.g. extraction) techniques, many of the phases and interfaces which contain metals other than iron have generally not been identified with reliable certainty (e.g. Jambor, 1994). An understanding of the minerals and mineral coatings present, as well as their composition, degree of crystallinity, and microfabric are all critical in understanding toxic metal partitioning (including sorption/desorption reactions) under different Eh/pH environments in these complex natural systems. Further, modelling the formation of AMD environments, and the transport of toxic metals through and away from these sites, would be greatly aided by a much more complete knowledge of the bulk and interface phases that contain these metals.

This study concerns samples from the Mike Horse Mine, located along a section of the headwaters of the Blackfoot River in western Montana, USA. Silver, gold, zinc, and copper were mined from sulphide-bearing vein deposits from the late 1800?s to 1953. Today, waters draining from waste rock piles adjacent to the mine, as well as the main adit, are acidic with elevated concentrations of several transition metals and sulphate. Abundant iron oxide coatings form on existing rock surfaces, and precipitates form within this drainage up to several kilometers from the mine site. This situation is typical in AMD environments.

Experimental. AMD sediments from the Mike Horse Mine described in this study were collected just outside the main adit, sieved through a 63 μm nylon screen, and stored in plastic bottles. The samples were dried at 70°C before preparation for the TEM. A portion of dried sediment was added to a glass centrifugation tube filled with an epoxy resin. The sediment was spun and lightly compacted in the bottom of the tube. After curing, the tube was sectioned with a diamond saw. These sections were cemented to glass slides and carefully polished to a thickness of 10 μm. The sections were released from the glass slides and embedded into another epoxy block. This block was sectioned with a diamond knife ultramicrotome to a thickness of 100 nm. The ultrathin sections were floated on a water pool, and were recovered onto 400-mesh copper grids. The sections/grids were carbon coated before insertion into the TEM.

A JEOL 3010 TEM was used in this study at a beam energy of 300 kV and magnifications up to 300,000 ×. Peripheral systems on the microscope also used included an Oxford Instruments energy dispersive X-ray (EDX) analysis system and a Gatan electron energy loss spectrometer (EELS) for

EFTEM imaging. No beam or vacuum induced sample degradation was observed during extended viewing and analysis of our samples in the TEM.

The samples from Mike Horse Mine were also studied by optical microscopy both in reflected and transmitted light, as well as by scanning electron microscopy (SEM, JEOL JSM-840A) and associated EDX system. X-ray diffraction (XRD) analyses of the samples were performed on a Philips X?Pert diffractometer (monochromatic Cu radiation) and in a Debye-Scherrer camera (Fe radiation to prevent Fe fluorescence).

Results and discussion. Transmitted light microscope examination of the Mike Horse Mine samples show rounded grains in the range of 10 to 60 μm. All grains in normal light appear reddish-brown (rusty) in colour. The interior of the grains are mottled, but any more detail is beyond the resolution of the optical microscope.

The SEM reveals a very complicated grain character. Primary grain size appears to be in the range of 5 to 60 μm. Ultrafine particles, with sizes ranging down to 0.1 μm, adhere to all of these grains. The ultrafines are evenly dispersed over the larger grains so that EDX analysis of the larger grains could not be obtained without including the ultrafines. All SEM/EDX spectra from these samples show major Fe, followed in abundance by Zn and Si, with lesser amounts of Cu, Ca, Al, Mn, and S.

The XRD patterns of these samples are nearly featureless. Only three very weak but sharp lines are observed, two representing the primary lines of quartz (d = 4.25 and 3.34 Å), and one a diagnostic line for akaganéite (d = 7.6 Å). The only other features on the XRD patterns are very broad and weak humps characteristic of ferrihydrite.

TEM and EFTEM reveal the true and highly complex nature of these AMD precipitates and coatings. The apparent grains seen in optical microscopy and SEM are actually aggregates of much smaller particles. About 90% (by volume) of the samples studied consists of rounded masses of ferrihydrite between 10 and 100 nm (0.01 to 0.1 μm) in diameter, although occasionally particles up to 2 to 3 microns in diameter are observed. All of these masses produce a diffuse but distinct two-ring electron diffraction pattern (maxima at approximately 2.5 and 1.5 Å), corresponding to a two-line ferrihydrite pattern. The fact that these diffuse ring patterns can be obtained from even the smallest particles directly demonstrates that ferrihydrite crystallites are exceptionally small, that is in the size range of a few nanometers. Also, although ferrihydrite diffraction patterns can have as many as six distinct lines, the ferrihydrite in these samples is more typical of samples collected from AMD environments in showing the least possible structural order for this phase.

TEM/EDX spectra of the ferrihydrite in these samples show major Fe and O, as expected, with small amounts of Si and Al. Natural ferrihydrites are typically reported to contain Si. It is significant here, but not surprising, to also find small amounts of Al apparently substituting for Fe in the ferrihydrite structure. Also, all EDX spectra of this ferrihydrite show the uptake of significant amounts of Zn and smaller amounts of Cu. This is also not surprising, in that ferrihydrite is known to be one of the single most important sinks in nature for both cationic and anionic species via adsorption processes over surface areas that range up to several hundred m^2/g (see, for example, Waychunas *et al.*, 1993, and references therein). It is notable that Zn and Cu are also found in several other phases intimately associated with ferrihydrite in these samples (see below). In addition, Mn and Pb are major components of other phases observed in these samples, but neither metal has been adsorbed by ferrihydrite.

A number of other phases have been found in these samples, cumulatively making up the remaining 5–10% of the total sample, as follows: 1) Fibrous particles, typically 100 to 200 nm long and less than 10 nm wide, primarily a Mn oxide (or hydroxide / oxyhydroxide) in composition. Major amounts of Zn also seem to be associated with this phase, although the association is not clear, along with lesser amounts of Cu and minor amounts of S. Electron diffraction patterns have not as yet been obtained from this phase (or phases) due to their size and morphology. These fibres often aggregate relatively tightly and form rims around large ferrihydrite aggregates, and are typically intermixed with very small ferrihydrite particles. 2) Fibrous particles, typically less than 200 nm long and 10 nm wide, with only Zn, Al, and O in the EDX spectra. Electron diffraction patterns have also not been obtained from these fibres. These fibres are typically grouped in very loose (open) and small aggregates, and are not associated with ferrihydrite aggregate surfaces. 3) Quartz crystals up to a micron in size. EDX analysis of these grains typically show minor amounts of Cu and S presumably sorbed to their surfaces. 4) Rare subhedral particles typically around 100 nm in diameter which give single crystal diffraction patterns. This is a Fe, Pb oxide, with lesser amounts of Cu and K. This phase may also contain S, although the principal S emission line is fully interfered with by the principal Pb line. This phase has not yet been positively identified.