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Origin of high manganese concentrations in coal mine drainage, eastern Tennessee

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Abstract

The origin of high dissolved manganese concentrations in slightly acidic mine runoff from a surface mine operated by the Cumberland Coal Company in eastern Tennessee was investigated. Mineralogical and chemical analyses were performed on 31 samples of sandstone, shale, coal, and mudstone from the mine to identify the sources and stratigraphic distribution of high extractable manganese contents in the spoil materials. The samples were analyzed for their bulk mineral content by X-ray diffraction, net acid-base potential, and reaction to 2 or 4 chemical extraction procedures. A limited number of samples were analyzed for petrographic characteristics, clay mineral composition by X-ray diffraction, and mineral compositions by electron microprobe. Analysis of the data and consideration of the geochemical conditions at the mine were used to identify probable sources for the high extractable manganese contents.

The results indicate 2 prominent, independent sources of extractable manganese. The first source is exchangeable manganese on clay minerals (mainly illite + muscovite and chlorite) and is concentrated in shale and mudstone rock types. The second and more significant source is manganese in siderite concretions and cement, mainly in shale and mudstone. Comparison to other coal-bearing strata indicates that manganese-rich siderite is common in fresh- to brackish-water subaqueous sediments that overlie coal. This is especially the case for coals formed in wet, tropical environments.

Ratios of manganese to calcium and magnesium in mine runoff suggest that manganese from siderite is the major cause of the high dissolved manganese contents. A conceptual model is developed to explain the high manganese contents of the mine runoff. Oxidation of pyrite creates mildly acidic waters that are subsequently partially neutralized by reaction with impure siderite. Solubilized manganese remains dissolved in the slightly acidic runoff water, whereas dissolved iron precipitates as ferric hydroxide or goethite. Consideration of data from other coal mining regions suggests that similar reactions involving impure siderite may be responsible for high manganese concentrations in acidic to slightly acidic mine runoff. Geochemical reaction path modeling of pyrite and impure siderite with rainwater illustrate how resulting water compositions may vary depending on pyrite to siderite ratios in spoil materials. Spoil water compositions from the Cumberland mine are largely consistent with reaction of pyrite and impure siderite in proportions observed in the

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sediments; however, deviations may be explained by minor mixing with waters that reacted only with impure siderite or clay mineral exchange reactions.

Keywords: Manganese; Chemical extraction; Pyrite; Siderite; Coal-mine drainage

1. Introduction

Weathering of pyrite and other sulfide minerals in tailings and mine workings at coal and metal sulfide mines results in acid mine drainage, a well known environmental problem. Acid mine drainage typically contains high mineral acidity, and high sulfate and transition metal concentrations due to oxidation of sulfide minerals, primarily pyrite (see Langmuir, 1997 for review). In some cases, reactive minerals with neutralizing capacity, such as calcite or other carbonate minerals, may also be present at the mine workings. Reaction with carbonate minerals neutralizes acidity, which decreases the solubility of many transition metals. Iron concentrations in acid-mine drainage are typically high (>10 mg/L), but decrease dramatically during oxidation of subsurface waters and neutralization of acidic waters, leading to precipitation of solid iron hydroxide and oxyhydroxide, and iron sulfate oxyhydroxide (Bigham et al., 1990; Winland et al., 1991; Bigham et al., 1996). Many transition metals, such as copper and chromium, coprecipitate or sorb to the iron oxyhydroxides and hydroxides and are removed from solution (Kinniburgh et al., 1976; Chapman et al., 1983; Filipek et al., 1987; Winland et al., 1991; Kimball et al., 1995). Manganese, however, is more soluble in slightly acidic to neutral waters than many other transition metals and can persist in the neutralized acid drainage (Kimball et al., 1995; Verplanck et al., 2000). Little work has been completed toward determining the source of manganese in coal overburden rocks; however, impure siderite has been proposed as a prominent source in western Pennsylvania coal fields (Morrison et al., 1990a; Brady et al., 1998; Rose and Cravotta, 1998).

In this study, the origin of high manganese concentrations (as much as 50 mg/L) in slightly acid to neutral drainage from a coal mine in eastern Tennessee was investigated. Manganese is an effluent limit on mine runoff and can be expensive to remove from runoff solutions because it is not as easy to precipitate through oxidation as iron in natural conditions. The problem was approached using stratigraphic, mineralogic, and chemical extraction data to identify the chemical and mineral sources of high extractable manganese contents in overburden strata. Manganese minerals, such as rhodochrosite and pyrolusite, are typically not abundant in coal bearing strata. However, manganese substitutes into sedimentary minerals such as ferromagnesian clay minerals (Curtis et al., 1985; Hillier, 1994) and carbonate minerals (Curtis and Coleman, 1985; Mozley, 1989). Manganese oxides and hydroxides precipitate from oxidized waters at slightly alkaline pH values, but the reaction rates are slower than those of iron (Stumm and Morgan, 1981; Senkayi et al., 1986; Lind and Hem, 1996). The distributions of authigenic clay, oxide and hydroxide, carbonate and sulfide minerals coal-bearing strata are closely related to depositional environments (Berner, 1982; Donaldson et al., 1985; Cecil et al., 1985), paleoclimate (Cecil et al., 1985), and geochemical and microbial conditions (Postma, 1982; Curtis and Coleman, 1985; Coleman, 1993). The stratigraphic and mineralogical data in the present study are used to assess the importance of depositional conditions and associated processes on extractable manganese contents.

The results of overburden analysis in this study are evaluated in relation to the water chemistry and environmental conditions at the mine to identify potential processes by which manganese-rich acid mine drainage can develop. Iron and manganese concentrations are commonly coupled in sedimentary mineral chemistry; however, their precipitation and sorption behaviors in acid mine drainage are complex (Theobald et al., 1963; Lind and Hem, 1996; Lee et al., 2002). A conceptual model is proposed involving reaction of acid mine drainage with clay mineral- and siderite-bound manganese