Synthesis, characterization, and thermodynamics of arsenates forming in the Ca-Fe(III)-As(V)-NO₃ system: Implications for the stability of Ca-Fe arsenates

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ABSTRACT

Arseniosiderite and yukonite are among the important arsenate minerals occurring as secondary alteration products in relation to the oxidation of arsenopyrite and arsenian pyrite and as discrete grains in some gold ores, mine tailings, and contaminated soils. Characteristics of these Ca-Fe arsenate species are not well known and our understanding of the conditions promoting their formation and dissolution is limited. Long- and short-range structural characteristics and thermodynamic properties of the Ca-Fe arsenates forming in the Ca-Fe(III)-As(V)-NO₃ system were determined to better predict the mineralogical transformations taking place in neutralized sludge and tailings environments, and their influence on arsenic mobilization. Yukonite and arseniosiderite readily form from solutions with highly variable compositions at a wide pH range from slightly acidic to alkaline conditions. Calcium concentrations corresponding to molar Ca/(Ca+Fe+As) ratios as low as 0.1 appear to be adequate for their formation. Our experimental results confirm observations in natural settings and mine tailings where scorodite is progressively replaced by yukonite and arseniosiderite. The initial amorphous precipitates made of small oligomeric units of edge-sharing FeO₆ octahedra with bridging arsenate evolve to yukonite through the establishment of corner linkages between the FeO₆ chains. Yukonite represents a nanocrystalline precursor and Ca-deficient variety of arseniosiderite. Formation of arseniosiderite is kinetically controlled with faster development of crystallinity at neutral to slightly acidic pH and slower kinetics under alkaline conditions. Calorimetric measurements provided an enthalpy of formation value of –1950.3 ± 3.1 kJ/mol and standard entropy of 237.4 ± 4.4 J/(mol·K) for arseniosiderite [with composition Ca₀.₆₆₃Fe₁.₉₉₃(AsO₄)(OH)₁.₆₀₅·0.₈₂₇H₂O], the corresponding Gibbs free energy of formation is –1733 ± 3.4 kJ/mol. A rough estimate of the thermodynamic properties of yukonite is also provided. Arseniosiderite is a stable arsenate between pH 3.5 and 7.5 in solutions saturated with respect to soluble Ca minerals such as calcite, gypsum, anorthite, or Ca-montmorillonite. Arsenic release from mine wastes and contaminated soils can be effectively controlled by arseniosiderite and the conditions promoting its formation such as lime-treatment leading to gypsum saturation in ferric arsenate solutions would prove to be desirable for stabilizing arsenic in the form of arseniosiderite in mine wastes. Keywords: Arsenic, arsenate, arseniosiderite, yukonite, arsenic control, mine wastes

INTRODUCTION

Ca-Fe arsenates such as yukonite and arseniosiderite are important constituents of mine wastes resulting from the processing of some gold and base metal ores and neutralization of acidic mine effluents (Paktunc et al. 2004). Cyanide leaching of gold ores under highly alkaline conditions with the use of lime promotes the formation of Ca-Fe arsenates from Fe- and As-rich process solutions. Calcium, which is widely available in some process solutions, appears to increase the solubility of ferric arsenate compounds (Swash and Monhemius 1995), and it has a detrimental effect on arsenic stabilization because of the co-precipitation of arsenosiderite-like oligomeric units during adsorption of As on goethite (Paktunc et al. 2004). Disposal and immobilization of arsenic in the form of Ca arsenate compounds in mine and industrial wastes was deemed to be inappropriate due to their high solubilities (Robins and Tozawa 1982). Arseniosiderite and yukonite were reported in gold ores and mine tailings occurring as secondary alteration products after arsenopyrite, arsenian pyrite, or arsenate minerals such as scorodite (Paktunc et al. 2003, 2004). Ca-Fe arsenates were also reported in naturally contaminated soils at the Mokrsko-west gold deposit (Filippi et al. 2007; Drahota et al. 2009), impacted soil near an industrial site in France (Cancès et al. 2008), mine tailings and contaminated soils at several abandoned gold mine sites in Nova Scotia (Walker et al. 2009), mine wastes in the Mojave desert (Kim et al. 2012), and historic gold mine wastes at Empire Mine State Historic Site, California (Burlak 2012). Arseniosiderite