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ScienceDirect
Applied Geochemistry 22 (2007) 2486–2508
Applied Geochemistry
www.elsevier.com/locate/apgeochem

Formation of sequences of cemented layers and hardpans within sulfide-bearing mine tailings (mine district Freiberg, Germany)

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Received 9 February 2007; accepted 11 July 2007
Editorial handling by B. Kimball
Available online 21 July 2007

Abstract

The roles of mineral dissolution, precipitation, transformation and mass transport processes related to formation of characteristic cemented layer–hardpan sequences were studied in low sulfide and low carbonate Freiberg polymetallic mine tailings. Using high resolution profiling, combined geochemical, geomicrobiological and geophysical methods allowed description of the process of weathering of reactive mineral phases and the position of the oxidation front in detail, as well as revealing the mechanisms of cementation of tailings predominantly by the formation of gels/poorly crystalline phases. Autochthonous and allochthonous gels reduced the porosity of cemented layers to values $\leqslant 1\%$, whereas secondary crystalline phases were less efficient in filling the pore space. Electron microprobe analysis of cemented tailings showed that common jarosite-group minerals contained up to about 8 wt.% PbO and 0.2–1.9 wt.% As_2O_5. Iron–As–Si gels reached contents of up to $\sim$44 wt.% As_2O_5 in gel-rich cemented layers. Zinc was below the detection limit in the studied secondary phases. Sequential extraction of cemented and related oxidized brown silt layers confirmed that the bulk of As was bound to amorphous/poorly crystalline hydrous oxides of Fe, whereas Pb was often bound to jarosite. Zinc was found preferentially in the water-soluble and the exchangeable fractions. In the grey silt and the sand directly underlying the oxidized layers, As, Pb and Zn occurred as sulfide minerals. The main effects of the cemented layer–hardpan sequences at the studied site are (1) a temporary natural attenuation of the toxic compounds, (2) a restriction of the downward movement of the oxidation front, and (3) a reduction of the extent of the erosion of the surface of the tailings impoundment by wind and water. The potential of a heap to form cemented layers and hardpans is greatly increased by a heterogeneous distribution of grain sizes and reactive materials in the topmost zone, as well as by the occurrence of sulfide-rich tailings on top of layers with low permeability.

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doi:10.1016/j.apgeochem.2007.07.002

1. Introduction

The study of natural attenuation (NA) processes on Acid Mine Drainage (AMD) formation in mine waste deposits is of great importance, because NA may counteract serious pollution threats to the water systems. Mobilisation of As, Zn and Pb from metallic mine tailings is known to be induced by oxidative weathering of metal sulfides. For example, oxidation of arsenopyrite (FeAsS) and Fe^{2+}-bearing sphalerite ((Zn,Fe)S) results in AMD containing H_2SO_4, Fe(III) as amorphous ferric oxyhydroxide precipitates, Fe(II) as soluble Fe species, As(III) as arsenite (AsO_3^{3-}), As(V) as arsenate (AsO_4^{3-}), and Zn(II). Microorganisms are known to catalyze sulfide oxidation (e.g. *Acidithiobacillus ferrooxidans*, *Thiomonas* sp.; e.g. Tuovinen et al., 1994; Blowes et al., 1998; Bruneel et al., 2003; Schippers, 2004; Morin and Calas, 2006). Several contaminant attenuation processes in mine waste deposits must be considered, like precipitation, sorption, and ion substitution. For example, arsenate may precipitate as scorodite, $FeAsO_4 \cdot 2H_2O$ (Ehrlich, 2002) or more commonly as ferric arsenate (Paktunc et al., 2004), sorb to amorphous ferric oxyhydroxide phases and clay minerals (e.g. Korte and Fernando, 1991), or substitute for sulfate in jarosite, $KFe_3(SO_4)_2(OH)_6$ (e.g. Paktunc and Dutrizac, 2003; Waychunas et al., 1995). Because hardpans and cemented layers may consist of reactive secondary minerals, they are expected to play a crucial role in contaminant attenuation.

Cemented, indurated layers in sulfide-bearing mine tailings (so-called hardpans) have been studied for their physical, chemical and mineralogical properties (Blowes and Jambor, 1990; Tassé et al., 1997; Coggans et al., 1999; Johnson et al., 2000; McGregor and Blowes, 2002; Courtin-Nomade et al., 2003; Giere et al., 2003; Gilbert et al., 2003; Moncur et al., 2005; Gunsinger et al., 2006). Field studies have reported on hardpans in e.g. Canadian tailings impoundments (McGregor and Blowes, 2002; Moncur et al., 2005; Gunsinger et al., 2006). The thickness of the hardpans varied from a few cm up to ~4 m. They consisted of ferrihydrite ($Fe_2O_3 \cdot 0.5\ H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), jarosite, lepidocrocite (γ-FeOOH), melanterite ($FeSO_4 \cdot 7H_2O$), and rozenite ($FeSO_4 \cdot 4H_2O$). The highest concentrations of originally dissolved metals were observed directly above and within a hardpan layer, thus the hardpans may have restricted the movement of dissolved metals through the tailings and may have acted as a zone of metal accumulation. In addition, the permeability of the hardpans was lower than that of uncemented tailings. Column experiments verified that hardpans that are situated between reactive tailings and cover material, improved leachate water quality and reduced the rate of sulfide oxidation (Gilbert et al., 2003).

The terms hardpan and cemented layer are widely used, but these terms are not exactly defined in the literature. In the authors' understanding, hardpans are zones at the capillary fringes where agglutination of particles is basically due to processes driven by capillary transport within an O_2 dominated environment. Supersaturation results in the precipitation of secondary phases and gels, which may coat particles, agglutinate them, and reduce the porosity. Cemented layers on the other hand, can be observed at the transition between oxidized and reduced zones, which often occurs at the transition between saturated and unsaturated zones. At these transitions, variations in master geochemical variables, such as Eh and pH, occur.

Despite that hardpan layers probably play a pivotal role in the NA of unwanted metals that may originate from sulfide-bearing mine tailings, their formation processes have not been thoroughly studied. A combination of processes such as dissolution of primary mineral phases, transport processes, and precipitation of secondary phases seems to be responsible for hardpan/cemented layer formation in mine tailings. The formation of amorphous phases (gels) and/or poorly crystalline phases plays a key role in this process. Gel formation has been documented for a wide range of geochemical conditions; they occur in alkaline (pH 9–14; Wan et al., 2004; Rammlmair et al., 2005) and also in neutral to acidic, sulfate-rich environments ($pH < 1$–6; e.g. in AMD; Rousel et al., 1999). However, the mechanisms of formation of gel-rich layers in tailings, their distribution characteristics and stability, as well as possible genetic relationships between gel-rich layers and sulfate-rich hardpans are controversially discussed or lacking in the literature.

A multi-disciplinary approach based on geochemical, mineralogical, geophysical and geomicrobiological methods was applied to study (i) the mechanism of formation of gel-rich and gel-poor cemented layers and hardpans in an AMD environment, and (ii) the NA capacity of the cemented layers and hardpans for As, Pb and Zn. The low-sulfide and low-carbonate tailings deposited at the studied site represent a major type of tailings impoundment of great international importance (e.g. Diaby et al., 2007).