



## Environmental stability of the processing waste from sulfide mining districts of Namibia – A model rhizosphere solution approach



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### ARTICLE INFO

#### Article history:

Received 14 June 2013

Accepted 31 October 2013

Available online 9 November 2013

#### Keywords:

Metals

As

Low-molecular-weight organic acids

Flotation waste

Rhizosphere

### ABSTRACT

Kinetic batch leaching of the flotation wastes from Berg Aukas and Kombat mining districts (northern Namibia) in 500  $\mu\text{M}$  solutions of citric, oxalic and acetic acids was performed to simulate the release of trace metals and As in the rhizosphere-like environment. The obtained data demonstrate that citric acid may significantly contribute to mineral waste alteration accompanied by contaminant mobilization; the maximum dissolution rates corresponded to 7% (Cu), 3% (As), 2% (Cd), 0.8% (Pb) and 0.3% (Zn) of their total amounts. In contrast, the role of oxalic and acetic acids in the complex process of contaminant leaching was usually negligible and/or comparable with water. The precipitation of newly formed Fe (hydr)oxides followed by the adsorption of Pb, Cd and eventually Zn from the model solutions seems to be the key mechanism which led to the metals' stabilization, as predicted by speciation modeling. Considering the neutral and slightly alkaline (and lowly organic) character of soils around the investigated flotation waste dams, Cu and As, present as neutral or anionic species, are suggested to be contaminants with the highest potential for rhizospheric mobilization and subsequent vertical mobility in local soils and/or transfer to plants.

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### 1. Introduction

Low-molecular-weight organic acids (LMWOAs), which are mainly simple organic acids such as citric, oxalic and acetic acids released by plant roots in the rhizosphere, play a key role in pedogenic processes, particularly in the weathering of soils (Ettler et al., 2009). Despite the fact that LMWOAs are potentially unstable in the soil environment due to microbial degradation (Evangelou et al., 2008), they significantly affect dissolution/alteration processes (Jones, 1998). After root exudation, LMWOAs enter the rhizosphere and, through chelation and  $\text{H}^+$ -promoted reactions, enhance the dissolution of soil minerals and facilitate the uptake of dissolved elements into plants (Ettler et al., 2009). Depending on the dissociation properties and the number of carboxylic groups, ligands of LMWOAs have negative charges, thereby allowing the complexation of nutrient cations (e.g., Fe, Ca, and K) in the soil solution and affecting their release from soil (Jones and Darrah, 1994). In contaminated environments, LMWOAs may increase the mobility of inorganic contaminants in soils polluted by mineral wastes. Such a geochemical situation can typically be observed in the

vicinity of base-metal smelters, where fly ash emitted by the smelter stacks represents the main source of soil pollution by trace metals/metalloids (e.g., Douay et al., 2008; Ettler et al., 2005a; Rieuwerts et al., 2000). Enhanced mobilization of these elements was also demonstrated by leaching experiments performed on metallurgical slags in model soil solutions, indicating a significantly greater effect of LMWOAs (e.g., citrate) than of high-molecular-weight organic acids (HMWOAs; e.g., fulvic acid and peat water) (Ettler et al., 2004, 2005b).

The present study aims to test the environmental stability of the flotation wastes, derived by sulfide ore separation, from two former mining districts of northern Namibia, Africa – Berg Aukas and Kombat. There is evidence of wind (and water) erosion of local tailing dams followed by substantial dispersion and deposition of fine-grained tailings at both sites. Large amounts of trace metals/metalloids (mainly Pb, Zn, Cd, Cu, V, As) have entered the surrounding soils in this way (Křibek and Kamona, 2006; Mapani et al., 2010). However, to our best knowledge, there is no information available about the reactivity of these flotation wastes when present in the soil rhizosphere. In other words, the question of the role of LMWOAs in the waste dissolution/alteration related to the contaminant mobilization remains unresolved. The batch leaching experiments with LMWOA solutions (citric, oxalic and acetic acids) at concentrations analogous to rhizospheric soil

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solutions (500  $\mu\text{M}$ ) supplemented by thermodynamic speciation-solubility modeling were conducted in this study.

## 2. Materials and methods

### 2.1. Flotation wastes

Flotation tailings from Berg Aukas (GPS: S 19° 30' 40.89", E 18° 15' 40.45") and Kombat (GPS: S 19° 43' 37.06", E 17° 42' 52.80"), former Zn–Pb–V and Cu–Pb–Zn mining districts, respectively, situated in the Otavi Mountain Land (northern Namibia) were investigated in this work. Principal ore minerals documented in Berg Aukas include sphalerite (ZnS), galena (PbS), pyrite (FeS<sub>2</sub>), descloizite ((Pb,Zn)<sub>2</sub>(OH)VO<sub>4</sub>) and minor mottramite (PbCu(VO<sub>4</sub>)(OH)) and vanadinite (Pb<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>Cl); dominant phases occurring at the Kombat deposit are as follows: chalcopyrite (CuFeS<sub>2</sub>), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), chalcocite (Cu<sub>2</sub>S), galena and sphalerite (von Bezing et al., 2008).

At each locality, a mixed sample from the surface layer (0–20 cm) of flotation waste dams was collected using an auger drill, as the top of waste deposits tends to be easily eroded and may be deposited in the adjacent soils, especially during the dry season. It should be noted that no remediation practice has been carried out at Berg Aukas dam and the remobilization of fine wastes has led to the significant contamination of local soils and vegetation (Mapani et al., 2010). In the case of the Kombat flotation deposit, there was an attempt at dam slope stabilization in the past, using vegetation in the form of tree and shrub plantation. Nevertheless, this practice only partially reduced wind (or water) erosion of the material because of the gradual denudation of plants' roots, as well as, the vegetation stress caused by the toxicity of tailings (Křibek and Kamona, 2006).

In order to determine bulk element concentrations in the samples, a pseudo-total digest according to the standardized *aqua regia* extraction protocol (ISO 11466:1995) was performed. A flame atomic absorption spectrometer (FAAS, Varian SpectrAA 280 FS, Australia) was used for element determination; three replicates were applied. During the analytical procedure, deionized water (Milli-Q Element, Millipore, France) and chemicals of analytical grade (Lach-Ner, Czech Republic) were used. The quality control (QC) was evaluated using the standard reference material (CRM 7001, Analytika, Czech Republic) with the RSD < 10%. To determine the cation exchange capacity (CEC), the soil was saturated with Ba<sup>2+</sup> cations using 0.1 M BaCl<sub>2</sub>. Barium was subsequently released using MgSO<sub>4</sub> (ISO 11260:1994). Excess Mg present in the solution was determined using FAAS. The concentrations of inorganic carbon (TIC) and total S (S<sub>tot</sub>) were determined by catalytic oxidation (1350 °C) using Metalyt CS 500 and Metalyt CS 530 elemental analyzers (ELTRA, Germany). Particle size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The pH at the point of zero charge was assessed by the immersion technique of Fiol and Villaescusa (2009).

Data on waste mineralogy were obtained using the X-ray diffraction method (PANalytical X'Pert Pro diffractometer, The Netherlands) applied on bulk and pre-concentrated samples (separated in 1,1,2,2-tetrabromethane as a heavy liquid with a density of 2.96 g cm<sup>-3</sup>). The analyses were performed under the following conditions: CuK $\alpha$  radiation, 40 kV, 30 mA, step scanning at 0.02°/150 s in the range of 5–80° 2 $\theta$ . Qualitative and semiquantitative analysis was performed with X'Pert HighScore software 1.0d, equipped with the JCPDS PDF-2 database (ICDD, 2003).

### 2.2. Leaching experiments

Batch leaching experiments were performed according to Ettler et al. (2009) at a solid-to-liquid (S/L) ratio of 1/10 (2 g of air dried waste in 20 mL of solution) in 500  $\mu\text{M}$  LMWOAs, i.e., citric, oxalic and acetic acids. These acids are commonly observed in rhizospheric soil solutions (Evangelou et al., 2008; Jones, 1998). Despite the fact that the LMWOA

concentrations are strongly variable in the rhizosphere (various plant species, etc.), we selected a value of 500  $\mu\text{M}$  to simulate the higher concentration range observed in soil solutions (Jones, 1998). The LMWOA solutions were prepared from chemicals of analytical grade (Lach-Ner, Czech Republic) and deionized water. The leaching was conducted at a constant temperature of 21  $\pm$  3 °C in acid-cleaned 50-mL centrifugation tubes (PP) shaken on an end-over-end shaker in dark (to prevent LMWOA photodegradation) for 0.5, 1, 2, 12, 24, 48 and 168 h and then sampled. Deionized water was used as a control. The experiments were performed in two replicates for all sampling times and treatments. At each sampling time, the suspensions were centrifuged for 5 min (at 3500 rounds min<sup>-1</sup>) and the pH and temperature were measured immediately using a pH-meter handylab pH 11 (Schott, Germany). Leachates were then filtered to 0.45  $\mu\text{m}$  using nylon syringe filters (Nalgene, USA). The solutions were analyzed for major and trace elements (Ca, Fe, Mn, Zn, Pb, Cd, Cu, As) and anions (Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>) using a combination of FAAS and IC (ICS 1600, Dionex, USA). The quality of the FAAS measurements was controlled using the standard reference material NIST 1640a (National Institute of Standards and Technology, USA); the accuracy was <10% RSD. The residual LMWOA concentrations in the leachates were analyzed using IC (ICS 1600, Dionex, USA). Alkalinity was measured by back titration using a Schott TitroLine Easy (Schott AG, Germany) automatic microtitrator and 0.05 M HCl. All of the analytical data were further used for speciation modeling and element complexation.

### 2.3. Speciation modeling

The PHREEQC-2 speciation-solubility code (Parkhurst and Appelo, 1999), version 2.18 for Windows, was used to determine the metal and As speciation in the experimental solutions and the saturation indices (SI) of possible solubility controlling phases. The minteq.dat database was used for all the calculations and was supplemented by stability constants of Me-LMWOA complexes from Smith et al. (2004). Both predicted metal and As species as calculated by speciation modeling, and the concentrations of free inorganic and LMWOA ligands as determined by IC are summarized in Tables S1 and S2 (Supplementary data). Although the studied system does not reach real geochemical equilibrium within the time of experimental leaching, the thermodynamic calculations propose probable mechanisms controlling metal/As behavior and stabilization.

## 3. Results and discussion

### 3.1. Geochemical and mineralogical composition of the flotation wastes

Detailed data relating to the physico-chemical characteristics, chemical and mineralogical composition of leached flotation tailings are reported in Table 1. The particle size distribution of the wastes was quite different with a majority of sand (82%) at Berg Aukas and silt (77%) at Kombat. Similarly, the higher clay content (9%), representing potentially the most reactive fraction, was found in the latter material. The pH of both tailings was alkaline (8.3 and 8.6 in water suspension), as influenced by carbonates forming the mineral matrix. The identified slightly alkaline pH<sub>ZPC</sub> suggests preferential adsorption of cations at alkaline conditions. Very low CEC values were detected in both wastes (<2 cmol kg<sup>-1</sup>), resulting probably from small specific surface areas of the primary phases (see below). As far as major contaminants are concerned, Zn, Cd and Pb dominate in the waste from Berg Aukas, with a maximum for Zn (>5 wt.%). The latter one was significantly enriched in Cu, Pb, Zn and As (Table 1).

XRD analysis indicated that the mineralogy of both materials was dominated by carbonates (dolomite, CaMg(CO<sub>3</sub>)<sub>2</sub>; calcite, CaCO<sub>3</sub>) and quartz. At Berg Aukas, the material also contained a small amount of magnesite (MgCO<sub>3</sub>) and willemite (Zn<sub>2</sub>SiO<sub>4</sub>). In the heavy mineral

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