Available online at www.sciencedirect.com
ScienceDirect
Catena 71 (2007) 497–506
CATENA
www.elsevier.com/locate/catena

Weathering of sulphide minerals and trace element speciation in tailings of various ages in the Guanajuato mining district, Mexico

Yann René Ramos Arroyo [a,*], Christina Siebe [b]

[a] Facultad de Ingeniería en Geomática e Hidráulica, Universidad de Guanajuato, México, Juárez 77, Guanajuato, Gto., 36000, Mexico
[b] Instituto de Geología, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 Mexico

Abstract

We studied the behavior of the trace elements (TE) As, Cu, Pb and Zn associated with sulphide minerals in tailings of different age at the Guanajuato mining district, Mexico. The objective was to determine the dominant fractions into which the TE move as tailings age and to identify how much time is needed until the dominant metal fractions approach equilibrium. We collected 21 samples from the surface of mine waste deposits of different ages (0, 2 , 4, 16, 70, 75, and 100 years), and measured their *aqua regia* extractable contents of As, Cu, Pb and Zn. We also applied a sequential extraction procedure to quantify water soluble TE as well as TE associated with carbonates, iron oxides, sulphides and the residual fraction. The mineralogy was analysed by X-ray diffraction, and selected samples were studied on polished specimens through a stereoscopic microscope. The TE in samples extracted with *aqua regia* ranged between 10 and 168 mg kg^{-1} for As, 12 to 194 mg kg^{-1} for Cu, 31 to 308 mg kg^{-1} for Pb, and 122 to 1129 mg kg^{-1} for Zn, and varied in a wide range within each age group of tailings. Water soluble Cu, Pb and Zn contents were below detection limits in almost all samples, which was attributed to the alkaline pH (7.17 to 8.61) in the tailings. Water extractable As was detected only in tailings older than 16 years, and concentrations ranged between 0.06 and 7.58 mg kg^{-1}. The proportion of TE associated with sulphides decreased in the tailings as they age, while the proportion of TE associated with iron oxides increased with time of exposure to the atmosphere, approximating equilibrium after 60 years for As, Cu and Zn, and after 40 years for Pb. Observations of polished specimens suggests that oxidation proceeds until coatings of secondary minerals cover and protect sulphide mineral grains from further weathering. First order rate equations were adjusted to the proportions of TE associated with either sulphides or iron oxides. Assuming that the TE in sulphide fractions correspond to arsenopyrite (FeAsS), chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS), the relative oxidation rate of sulphides followed the order: $PbS > ZnS > FeAsS \approx CuFeS_2$, while the relative affinity of the elements with iron oxides followed the sequence $Cu \approx Zn > As > Pb$.

Keywords: Mine wastes; Arsenic; Copper; Lead; Zinc; Trace element fractionation

1. Introduction

Mine wastes containing metal sulphides will oxidize when they are exposed to atmospheric oxygen and rain water. This process releases protons and trace elements (TE) into the environment, which in turn may deteriorate soil and water quality (Plumlee, 1999).

Iron sulphides (as pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and arsenopyrite (FeAsS)) oxidize under atmospheric conditions and are transformed into ferrihydrite, goethite and hematite, and into sulfates, which can precipitate, for example as gypsum, if evaporation exceeds precipitation (Jambor, 1994; Plumlee, 1999; Hammarstrom et al., 2005). Trace elements associated with these iron sulphide minerals, and also to other sulphide minerals such as galena (PbS) and sphalerite (ZnS), either are adsorbed on the iron oxide neoformations or might precipitate as siderite ($FeCO_3$), malachite ($Cu_2(OH)_2CO_3$), cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$), if ion activities are large enough and if few specific adsorption sites provided by humic substances, clays and iron oxides are present in the soil (Brümmer et al., 1986; Nordstrom and Alpers, 1999).

The weathering rates of sulphides in tailings depend on the mineralogical composition of the ore residues, the prevailing humidity and temperature conditions at the site, and the particle

---

* Corresponding author.
E-mail addresses: yannramos2004@yahoo.com.mx (Y.R. Ramos Arroyo), siebe@servidor.unam.mx (C. Siebe).

0341-8162/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.catena.2007.03.014

size distribution. The latter influences water infiltration rates, water retention and hydraulic conductivity as well as aeration conditions (Lefebvre et al., 2001).

Many procedures have been developed to evaluate and forecast possible environmental impacts of mine waste deposits. They range from general simulations of extreme scenarios using thermodynamic models, by which the maximum acidity production and mobilization of TE can be estimated, to specific numeric transport models adjusted to case studies considering particular environmental conditions. The parameters of the models are obtained by laboratory experiments (Strömberg and Banwart, 1994; Li, 1997; Brown et al., 2000) or from field data (Elberling and Nicholson, 1996; White et al., 2005). However, neither laboratory nor field data can consider long time frames, not only because the costs are unaffordable, but also because decisions on the fate and management of mine wastes can not be delayed until results from long term experiments are available. On the other hand, Malmström et al. (2000) discovered that kinetic parameters estimated from laboratory experiments could differ up to 4 orders of magnitude from those that occur under field conditions; therefore their extrapolation and application must be done with caution.

One way to study the fate of trace elements over long time intervals is to analyse waste deposits of different ages that are composed of materials of similar origin. An important disadvantage of these kinds of chronosequences is the implicit heterogeneity within any natural system (Eppes and Harrison, 1999; Wilcke et al., 2003), and which is generally increased when the system is altered by human activities. Few sites exist that allow the study of weathering processes in mine tailings for a time long enough to develop the apparent equilibrium that these systems tend to reach (Maskall et al., 1996; Gee et al., 2002).

The surface horizons of tailings in the Guanajuato mining district represent a good opportunity to study the evolution of mineral phases that contain TE under temperate climate conditions, since these tailings have been exposed to the atmosphere for different lengths of time. We studied seven mine tailings that have been exposed for 0, 2, 4, 16, 70, 75 and 100 years. All sampled sites have similar epithermal geological origin, grain size and moisture conditions. The objective was to determine the dominant fractions into which the different elements move as tailings age and to identify how much time is needed until they approach equilibrium.

2. Materials and methods

2.1. Study area

The Guanajuato mining district is in central Mexico, 360 km northwest from Mexico City between 21°05′00″ and 21°00′00″ northern latitude and 101° 20′00″ and 101°10′00″ western longitude, and it covers approximately 320 km^2 (Fig. 1). It is situated at the contact between two physiographic units: the Mesa Central and the Trans-Mexican Volcanic Belt. The relief is abrupt and the altitude varies from 2000 to 2800 m above sea level. The climate is sub-humid with summer rains and a mean annual precipitation of 670 mm. The mean annual temperature is of 18 °C, with a seasonal range between 5 and 35 °C.

In this region gold and silver ores have been exploited continuously since 1550; during this period approximately 100 million tons of mine wastes have been generated (Ramos-Arroyo, 2004). At this district mineralization was of epithermal origin. Three main vein systems exist: La Luz (LL), La Sierra (LS) and Veta Madre (VM). They are embedded in different lithologies, and the exploited minerals are silver and gold sulphides, pyrite, chalcopyrite, sphalerite and galena. Other minerals contained in the ores are quartz, calcite, feldspars, plagioclase and clay minerals (Randall-Roberts et al., 1994).

More than 20 areas of tailings exist in the district. We identified 7 areas of tailings of different ages (0, 2, 4, 16, 70, 75 and 100 years). Each area only received deposits during a short time and remained undisturbed thereafter (Fig. 1).

All tailings are a mixture of materials extracted from different mines, but all ores come from epithermal vein systems. Therefore, their general mineralogical composition is assumed to be similar at the time of deposition. Particularly, we can assume that TE were dominantly associated with sulphide minerals at the time of deposition, and iron oxides were present only in small proportions. However, the absolute concentrations of the different sulphide minerals that contain TE vary within the tailings.

2.2. Sampling

Within the tailings areas, particles were sorted into different sizes during the construction process; close to the dumping site coarse grained materials were deposited, while far from it only fine grained materials and precipitates accumulated (Ramos-Arroyo, 2004). All samples were collected at sites close to the dumping area, so that textures and general mineralogical composition are comparable. Sampling was done in January and February 2000, during the dry season. At each tailing area three composite samples were collected at random, giving a total of 21 samples for the 7 tailings. Each composite sample consisted of a mixture of 12 cores of 100 cm^3 taken from 0 to 10 cm depth within a 5 × 5 m surface. Samples were put into plastic bags, which were sealed and labelled. It was not necessary to protect the samples from oxidation, since all sampling sites were well aerated and the tailings were dry at their surface.

In the field we determined the soil colour with Munsell Colour Charts, the texture by hand, and we estimated the carbonate content by observing the sample effervescence after adding HCl 10% (Siebe et al., 1996). Once in the laboratory all samples were air dried and sieved (<2 mm) to homogenize them. No particles larger than 2 mm exist in the tailings, since the materials are crushed during the ore extraction process.

2.3. Mineralogical analyses

Mineralogical analyses were done by X-ray diffraction on seven powder specimens with a SIEMENS D-500 equipment at the Centro de Investigaciones en Química Inorgánica