



Arsenic and lead mobility: From tailing materials to the aqueous compartment



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ABSTRACT

This study concerns the mineralogy of the tailings of a former Ag–Pb mine (Auzelles district, France) and the contribution of the waste materials to the heavy metal dissemination in the environment. Accumulation of metals in fish flesh was reported and this pollution is attributed to past mining activities. Tailings were studied to establish the major transfer schemes of As and Pb in order to understand their mobility that leads to contamination of a whole ecosystem. Mineralogical investigation, solubility and compliance tests were performed to assess the stability of the metal-bearing phases. Among the various metallic elements measured, As and Pb show the highest bulk concentrations (up to 0.7% and 6.3% respectively) especially for samples presenting near neutral pH values. According to X-ray diffraction (XRD), Scanning Electron Microscopy (SEM-EDX), Electron Probe Micro-Analysis (EPMA) and micro-Raman spectrometry (μ RS), tailings mineralogy still contain primary minerals such as sulfides (*e.g.*, galena, pyrite), phosphates (monazite, apatite) and/or carbonates (*e.g.*, (hydro-)cerussite, dolomite, siderite). Sulfates (*e.g.*, anglesite, lanarkite, plumbojarosite and beudantite) are the main secondary metal-bearing phases with other interesting phases accounting for metals mobility such as Fe and/or Pb and/or Mn oxides (*e.g.*, lepidocrocite, goethite -up to 15 wt% of Pb was measured-, plumboferrite-type phase, mimetite). The lowest Pb solubilities were obtained at pH 8–9 and at a larger range than for As for which the lowest solubilities are reached around pH 6–7. At this minimum solubility pH value, Pb concentrations released still over exceed the National Environmental Quality Standards (NEQS), whatever the samples. The highest solubility is reached at pH 2 for both elements whatever the considered sample. This represents up to 51% of total Pb and up to 46% of total As remobilized and concentrations exceeding the NEQS. As and Pb released mainly depends on the Fe/Mn oxides (*e.g.*, goethite, lepidocrocite) and carbonates (cerussite) which are the less stable phases. Compliance tests also show that Pb concentrations released are higher than the upper limit for hazardous waste landfills. Determination of the mineralogy allows understanding both the solubility and leaching test experiments results, as well as to forecast the impact of the residues on the water quality at a mid-term scale.

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1. Introduction

Numerous waste dumps and tailings are common leftover of former mining activities all over the world and the French Massif Central in France is no exception. This region was one of the highest

polymetallic producers in Europe until the mid-20th century. These activities led to contamination of soils, sediments, biota and alter water quality of the rivers at various scales (see examples for this area, *e.g.*, Bossy et al., 2010; Courtin-Nomade et al., 2012, 2010, 2003; Grosbois et al., 2012, 2009, 2007; Pascaud et al., 2013). Numerous studies have demonstrated the high toxicity of As and Pb in aqueous medium (water column and sediment) at all trophic levels: microorganisms, fish and algae (*e.g.*, Macdonald et al., 2000; Moriarty et al., 2014; Shuhaimi-Othman et al., 2012; Wetzel et al.,

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2013). Mineralogy of As and Pb host phases in mining environments has been also extensively studied (Courtin-Nomade et al., 2003; Donahue and Hendry, 2003; González-Corrochano et al., 2014; Hayes et al., 2012; Savage et al., 2000; Smuda et al., 2007; Yang et al., 2009) showing the importance of sulfates and Fe/Mn oxides in their sequestration. Depending on the mineralized vein paragenesis and the local lithology, Pb is identified as anglesite, the most frequent sulfate, plumbojarosite or beudantite (Arenas-Lago et al., 2014; Frau et al., 2009; Murray et al., 2014; Néel et al., 2003; Romero et al., 2010; Roussel et al., 2000) and its affinity with Fe and Mn compounds have been also highlighted (Courtin-Nomade et al., 2009; Miller and Gosar, 2012; Sejkora et al., 2012). Arsenic can be naturally attenuated in mining environments when associated to jarosite, iron oxides or present as scorodite or pharmacosiderite (Asta et al., 2009; Bossy et al., 2010; Craw et al., 2002; Drahota et al., 2009; Gault et al., 2005; Kocourková et al., 2011; Lee et al., 2005).

This study concerns a watershed affected by former Ag–Pb extraction belonging to the Auzelles district in the French Massif Central, and where only no-kill fishing practice is allowed (local French regulation) because of too high metal contents in fish flesh according to European limits. Results presented here concern tailings samples, characterized by complementary techniques (X-ray Diffraction, Scanning Electron Microscope (SEM), Electron Probe Micro-Analysis (EPMA) and micro-Raman spectroscopy (μ -RS)) and for which stability of metal host phases was assessed using various leaching experiments.

This study is the first one concerning the Ag–Pb Auzelles district and thus aims: (i) to characterize the mineralogy of the tailings, and especially to identify the As and Pb host phases; (ii) to determine the evolution with time of these host-phases (e.g., weathering susceptibility, remobilization of As and Pb, impact on the water quality, natural attenuation) and establish the major transfer schemes of the metallic elements from the tailings in order to understand their mobility that leads to the contamination of the aqueous compartment.

2. Materials and methods

2.1. Site and materials description

The Auzelles district is located in the southeastern part of the French Massif central. The lithology of this area corresponds to migmatites with intrusive granite. The Miodet River (30 km long) crossed through this district and is a sub-tributary of the Loire River by the Dore River then by the Allier River (Fig. 1). The Miodet basin has a total surface area of approximately 100 km². Around 6t of Ag and 6000t of Pb were extracted from the district of Auzelles until the last 19th century (<http://www.sigminesfrance.brgm.fr>) to be treated in the Pontgibaud fundery located several thousand kilometers away on the western part of Clermont-Ferrand (Fig. 1). The activities began in 1869 and ceased in 1901 even if exploration operations occurred until 1960 (<http://www.sigminesfrance.brgm.fr>). The main mineralization consists of galena (PbS) and the accessory mineralization consists of sphalerite (ZnS), chalcopyrite (CuFeS₂), pyrite (FeS₂), arsenopyrite (FeAsS) and cerussite (PbCO₃) in a gangue of granite, quartz and clays, barite and carbonates (dolomite CaMg(CO₃)₂, calcite CaCO₃, siderite FeCO₃, ankerite Ca(Fe,Mg,Mn)(CO₃)₂) (<http://www.sigminesfrance.brgm.fr>).

These previous mining activities generated large volume of waste, estimated here to represent 100 000 m³. These residues are treatment residues from physical–chemical processes (crushing and flotation) and are deposited on a slope overhanging the Miodet River (Fig. 1). They constitute large heaps of more or less coarse sandy material affected by retrogressive erosion due to meteoric

water runoffs and present scarce vegetation if any. Thus erosional processes led to solid transport by runoff waters, wind and gravity toward this river. Tailings particles could directly feed the sediments affecting their quality. Alteration processes may also occur, leading to remobilization of heavy metals by oxidation and hydrolysis.

Furthermore the waste dumps are located 21.7 km away from a dam reservoir constituting a favorable settling system that may accumulate heavy metals. A prefectural decree was established in March 2010 prohibiting consumption of fishes caught all along the Miodet River. Indeed, Pb and Cd were measured within the trout fished near the tailings and downstream, exceeding the European consumption regulation (CE n°1881/2006) set at 0.3 and 0.05 mg/kg respectively (<http://www.puy-de-dome.gouv.fr>).

Twenty-seven samples of tailings have been collected with a plastic scoop on the heap according to the following criteria: texture, grain size, color and location. They have been air dried at room temperature and then sieved at <2 mm with Teflon mesh to remove any vegetation debris. Part of this fraction was used to prepare 30 μ m thick thin sections using epoxy resin polymerized at low temperature (<40 °C) and another part was crushed with an agate mortar for X-ray diffraction, chemical analysis, solubility and leaching experiments.

2.2. Analytical techniques

2.2.1. Chemical parameters and characterization

The pH values of the waste materials were determined according to the normalized protocol NF ISO 10390. Chemical compositions were obtained by ICP-MS or ES (Inductively Coupled Plasma-Mass Spectrometry or Emission Spectrometry, ACME, certified laboratory, Can) following a Lithium metaborate/tetraborate fusion and nitric acid digestion. An aqua regia digestion was also performed for the precious and base metals. Some chemical analyses were also done by AAS-GF and AAS-F (Atomic Adsorption Spectrometer-Graphite Furnace or Flame, GRESE, Fr) after a four acid digestion using HNO₃, HF + HClO₄ and HCl using a hot plate. All measurements were performed on duplicates and some measurements were triplicate randomly. Reference materials were also used for quality control (STD SO-18 ACME standard). Analytical error was within 1% for major elements and within 10% for trace elements.

2.2.2. Solid characterization

The grain size distribution has been determined by the INRA certified laboratory (Laboratoire d'Analyses des Sols d'Arras, Fr) using five grain size classes according to the normalized protocol NF \times 31–107. X-ray diffraction (XRD) was performed using a BRUKER D8 advance diffractometer (SPCTS, Limoges, Fr) and obtained from 2 to 80° 2 θ with a step size of 0.02° and an acquisition time of 2s/step using CuK $\alpha_{1,2}$ (λ = 1.5418 Å) radiation. Indexation was obtained with the EVA software and ICDD database.

Secondary (SE) and backscattered electron (BSE) images were obtained with a Philips XL30 scanning electron microscope (SEM) equipped with an EDX system (electron dispersive spectrometer X-ray analyzer) (SERMIEL, SPCTS, Limoges, Fr). The accelerating voltage was fixed at 20 kV and samples were coated with carbon prior analysis.

Micro-Raman spectroscopy (μ RS) analyses were performed using a Jobin Yvon 6400 Raman spectrometer (SPCTS, Limoges, FR), combined with a 100 \times objective, which results in a spatial resolution of one micron. The excitation source is an Ar⁺ laser (Coherent Radiation or Spectra Physics) operating at 514.5 nm. The incident power was limited to 2–5 mW with additional filters (D1 or D2). More experimental details on this setup have already been described in Courtin-Nomade et al. (2010).

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