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Natural weathering of slags from primary Pb–Zn smelting as evidenced by Raman microspectroscopy

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ABSTRACT

Lead (Pb) and zinc (Zn) smelters produce high amount of granulated slags which are currently stored on unconfined slag heaps and exposed to weathering. The environmental risk related to slags disposals can be estimated through the results of a variety of characterization methods coupled with laboratory leaching experiments and *in situ* monitoring. The present study is focused on the Raman characterization and distribution at a microscopic scale of secondary products resulting to the alteration of glassy slags exposed to natural weathering for at least ten years. The slag alteration is characterized by the formation of a crack network around iron sulfide inclusions and Pb droplets embedded in the glassy matrix. The Raman images clearly point out the gradually weathering processes. The dissolution of the FeS species lead to the formation of Fe (oxy-hydr)oxide phases. The successive layer formation highlights a probable local pH/Eh changes. The fluids-containing sulfates issued from the alteration of sulfide species are conveyed in the crack network inducing a local alteration of the crack edges together with the formation of (Al,Fe)-hydroxide phases. The fluids-containing sulfates when in contact with Pb droplets induce a progressive dissolution of the droplets from the edge to the core to form Pb sulfate species (mainly basic lead sulfates) and Pb oxides in complex mixture. In a last step, carbonation occurs with local increasing pH due to the presence of CO_2 from air or HCO_3^-/CO_3^{2-} in fluids originating from glassy matrix alteration.

1. Introduction

The smelting of non-ferrous metals such as Pb, Zn or Cu, produce high amounts of wastes, which contain potentially toxic metals (Pb, Zn, Cu, Cd, Sn, Hg,…) and metalloids (As, Sb,…). In the treatment of these toxic substances, the immobilization of hazardous materials is the major concern to prevent pollution; therefore the technique of vitrification is widely applied to encapsulate the hazardous wastes in the glassy matrix of slags. Slags are the most abundant waste from Pb–Zn smelting. Historically, large amount of Pb and Zn granulated slags have been stored in unsupervised area and exposed to weathering for a long period of time (several decades). Their safe disposal or possible recycling has been extensively discussed (Davranche et al., 2003; Ettler and Johan, 2014; Ettler et al., 2009a, b, 2004, 2001, 2003; Gee et al., 1997; Lassin et al., 2007; Murari et al., 2015; Sueoka and Sakakibara, 2013; Vanaecker et al., 2014). Observations from *in situ* slag weathering and from laboratory leaching experiments indicate that metals could be released and could affect the surrounding environment (Ettler et al., 2002; Gee et al., 1997; Lima and Bernardez, 2011; Lottermoser, 2002; Parsons et al., 2001; Seignez et al., 2006; Sobanska et al., 2000) For example, the negative environmental impacts of slags include soil and water degradation at numerous former smelting sites (Courtin-Nomade et al., 2012; Ettler et al., 2009a, b; Lottermoser, 2002; Navarro et al., 2008). The environmental risk related to slags disposals can be estimated through the results of a variety of characterization methods including chemical analyses but also mineralogical examination of wastes coupled with laboratory leaching experiments and *in situ* monitoring (Bril et al., 2008; Kierczak et al., 2010; Pareuil et al., 2010; Piatak and Seal, 2012; 2010; Piatak et al., 2004; Vanaecker et al., 2014; Wilke et al., 2008) (Bril et al., 2008; Ettler et al., 2009a, b; Kierczak et al., 2010; Seignez et al., 2007, 2008; Vítková et al., 2009, Vítková et al., 2013). The weathering processes are mainly

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established on the basis of the leaching procedures that combine batch experiments and/or chemical extractions with thermodynamic modelling using geochemical codes. Additionally, the characterization of the newly formed products or processed at the microscopic level using analytical scanning electron microscopy provides accurate information about the elemental concentration variations within the hosted phases that occurred during weathering process (Deneele, 2002; Ettler and Johan, 2003; Ettler et al., 2009a, b, 2012, 2004, 2001, 2002, 2003; Kierczak et al., 2013; Seignez et al., 2006, 2007, 2008; Sobanska et al., 2000; Vanaecker et al., 2014). Complementary, Raman microspectroscopy was used in punctual mode to characterize the molecular species as shown in few studies (Seignez et al., 2007; Vanaecker et al., 2014; Courtin-Nomade et al., 2012). However, to our knowledge the detailed description of the chemical weathering at micrometric scale through molecular characterization of altered entities has not yet been investigated. The present study is especially based on application of the Raman imaging characterization (i.e. molecular identification) and micro-scale identification of the alteration products of Pb–Zn smelting slags which have been stored on a sprawling unsurpervised area and exposed to natural weathering for at least ten years. The confocal Raman microspectroscopy which combines the molecular analysis capabilities of Raman spectroscopy and the spatial resolution of optical microscopy is well adapted for obtaining direct molecular information on microscopic volumes of crystalline, amorphous or liquid phases with *in situ* conditions (Jehlička et al., 2009). Moreover, semi-automated systems are currently available for acquiring two-dimensional Raman data with a lateral resolution only limited by light diffraction. However, the large compound heterogeneity of slags often results in severe overlapping of spectral information even for regions as small as 1 μm^2 area. Fortunately, the chemical information contained in Raman maps can be significantly improved using data processing based on multivariate curve resolution (MCR) methods (De Juan et al., 2008, De Juan and Tauler, 2006, Jaumot et al., 2005; Windig et al., 2002). Applying MCR to Raman maps can yield information about the number of Raman active species, what pure compounds are present and where in the sample they are located as demonstrated in previous works (Batonneau et al., 2004, 2006; Sobanska et al., 2006). In this work, we demonstrate the effectiveness of the combined use of Raman mapping analysis and elemental X-ray analysis to get detailed characterization of altered slags. This approach provides unique information to understand chemical weathering processes of slag at microscopic scale. Furthermore, comparisons between the micro-imaging results and the macroscopic approach reported in the literature are discussed.

2. Materials and methods

2.1. Description and composition of fresh smelting slag samples

Generally, the technology used in the zinc and lead production consists of three successive steps: sintering, reduction and refining. The sintering step corresponds to the oxidation of lead and zinc ores (including mainly PbS and ZnS) at high temperature (900 °C) by the Dwight–Lloyd process. Then, coke and melting agents (SiO_2, CaO and iron oxides) are added to the sintering product in order to decrease the melting temperature and to make easier the ore gangue extraction. Afterwards, reduction of this charge in a Lead Blast furnace (LBF) or an Imperial Smelting furnace (ISF) leads to the transformation of lead and zinc oxides into native Pb and Zn (ISF has the advantage to produce lead and zinc simultaneously from mixed Pb and Zn ores). During the reduction process, the products accumulate in the base of the furnace and are separated by decantation as molten lead layer (which will be refined), a speiss layer (which mainly consists of iron arsenide but also contains Ni, Cu and Co), a matte layer (which is principally composed of metal sulfides including iron, nickel and copper sulfides) and finally, the molten slags in the form of a silicated liquid representing the main waste of the lead and zinc production. Because the decantation process is not complete, some traces of Pb, speiss and matte are trapped in the molten slag. The molten slag is regularly evacuated from the furnace and granulated by a quenching with cold water shortly after the exit of the furnace to form slag grains of about 2 mm sized.

The pyrometallurgical slags studied in this work come from historic Pb–Zn smelter plant located at Noyelles-Godault in the North of France. From s to the factory closing date in 2003, the LBF and ISF pyrometallurgical smelters have produced more than 4 million tons of granulated slags as wastes (Deneele, 2002; Seignez et al., 2007, 2008). Until 2003, ISF and LBF slags have been discharged together outdoors on the plant site without protection, and today they cover about 9 ha, reaching 1.800.000 m^3 and 70 m in height.

Typically, fresh slags are black granulated materiel with a vitreous sheen (luster) and slag grains do not exceed several millimeters in diameter. The average chemical composition and mineralogy of granulated slags directly issued from the smelting furnace have been previously detailed (Deneele, 2002; Ettler et al., 2009a,b, 2001, 2002; Piatak et al., 2015; Seignez et al., 2006, 2007, 2008). They were mostly composed of $FeO–SiO_2–CaO$ glass matrix for about 80 wt% and various other phases dispersed in the glass matrix for about 20 wt%. The glassy matrix composition (in weight %) plots within the olivine field of $SiO_2–CaO–FeO$ diagram (Piatak et al., 2015). The crystallized phases were mainly identified as iron-rich oxide inclusions such as plurimicrometric dentritic wuestite ($Fe_{0.85}O$) or Zn substituted wuestite ($Fe_{0.85-x}Zn_xO$ with $0.085 < x < 0.170$) and various solid solutions of spinels (from magnesiochromite: $MgCr_2O_4$, to franklinite: $ZnFe_2O_4$, and magnetite: Fe_3O_4 poles). Sulfide-rich phases such as $Fe_{1-x}S$ (pyrrhotite), $FeCuS_2$ (chalcopyrite) and $(Fe_x,Zn_y,Cu_z)S$ (complex sulfides with huge variation of x, y and z with $x + y + z = 1$) were also identified in both ISF and LBF slags. These sulfur-containing phases mainly appeared as droplets embedded in the glassy matrix with a maximal 500 μm size. Numerous metallic particles (mono or polymetallic assemblages) with size ranging from few nanometers (Pb droplets) to several micrometers (~400 μm – speiss) were encountered in ISF and LBF slag particles and resulted from liquid metal droplets trapped within slag particles during the industrial process. The slag particles were enriched in metals i.e. Zn (7–12 wt %), Pb (0.5–3.5wt%) and toxic elements such as Cr, Cd and As (Seignez et al., 2006) distributed either in the oxides, metallic assemblages (including lead droplets), sulfide phases or in the glassy matrix. The distribution of Pb and Zn in the various host-phases of ISF and LBF fresh slags is shown in Fig. 1.

2.2. Sampling of aged smelting slags

A sample of 10 kg of granulated slags was collected from the first 30 cm of the surface on the top of a slag pile. This sampling procedure allows collecting slag samples having an estimated direct exposure time to natural weathering of about 10 years. After homogenization and drying, a set of 100 slag grains was selected and these particles were embedded in epoxy resin and polished to plates for easy observation due to the surface roughness of slags. During the polished section preparation, contact between water and polished plates were avoided to limit further alteration of the reactive phases. The polished sections were examined using optical and electronic microscopes to observe the general morphology of the grains and Raman mapping was performed later on selected