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Environmental characterization of Sarcheshmeh Cu-smelting slag, Kerman, Iran: Application of geochemistry, mineralogy and single extraction methods

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ABSTRACT

Annually, more than 370,000 tons of slag waste is produced in Sarcheshmeh Copper Complex, the biggest Cu-producer in Iran. Geochemical, mineralogical and single extraction methods were used in order to evaluate the contamination potential of metal(loid)s associated with Sarcheshmeh smelting slags. Results showed that, like the other non-ferrous or base metal slags, Sarcheshmeh slags are considered as one of the metalliferous smelting wastes with the multi-elemental contamination potential of most of the potentially toxic elements. Mineralogical studies revealed that the mineral assemblage of the investigated samples is controlled by at least three main factors, including: (1) primary mineralogy of the ore concentrate (chalcocite, chalcopyrite, covellite ± pyrite); (2) smelting process (magnetite, fayalite, pyroxene); and (3) weathering reactions in arid to semiarid climate conditions [thenardite (Na_2SO_4), bonattite ($CuSO_4 \cdot 3H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$)]. Results obtained from the U.S. EPA toxicity characteristic leaching procedure (TCLP) and water soluble tests revealed that the order of leachability of target elements from the most to the least in the slag samples is as S ≫ Cu> > Zn > Fe > Mo > Pb > Ni > Mn > Co > As > Se > Sb > Cd > Cr = Sn = Ag = Bi. The maximum contamination potential, higher than the considered toxicity regulatory levels (one-hundred times the U.S. EPA maximum contamination level in drinking water), of As (9.35 mg/L), Mo (186.7 mg/L), Sb (3.50 mg/L) and Se (6.12 mg/L) was observed in the alkaline leached solutions (pH 9.67) of the sediments associated with the slag dump drainages, while the maximum concentrations of the other investigated elements such as Cu, Co, Cd, Fe, and Zn were measured in the acidic (pH < 5) leached solutions. Annually, about 18.7% of Sarcheshmeh reverberatory slags are used for other purposes such as sandblasting. Wind blowing slag particles, produced from the grinding and sieving facilities, are responsible for the enrichment of elements such as As, Cu, Mo, Pb, Sb, Sn, Zn, Cr, S and Fe in the topsoils around the slag preparation site. Based on the acid acetic (0.43 mol/L) and EDTA (0.05 mol/L) leaching tests, the solubility and thus the bioavailability of these potentially toxic elements also were increased in the surface contaminated soils, a subject that is very important from environmental point of view. Obtained results also emphasize on the need for the greater caution in the slag waste management.

1. Introduction

From the environmental point of view, pyrometallurgical slags are undesirable materials that must be considered as one of the anthropogenic threats to the natural environments due to the presence of high amounts of potentially toxic trace elements (metals and metalloids) such as Ag, As, Ba, Cd, Cu, Pb, Sb and Zn (Parsons et al., 2001; Ettler et al., 2005; Costagliola et al., 2008; Scheinert et al., 2009; Piatak and Seal, 2010; Kierczak et al., 2013; Lima and Bernardez, 2013; Dung et al., 2014; Jin et al., 2014; Potysz et al., 2015; Piatak et al., 2015). Several studies have investigated the role of slag particles in the soil (Sobanska et al., 2000; Sterckeman et al., 2000; Ettler, 2016), air (Sobanska et al., 1999) and river sediment contamination (Isaure et al., 2002; Vdovic et al., 2006). Traditionally, these wastes have been considered relatively inert in most of the weathering environments, based on the opinion that the potential contaminants are encapsulated in low soluble silicates, oxides, and glass compounds (Scales, 1986). Today, it is well understood that slag wastes can also contribute to the environmental contamination through the weathering and leaching processes (Manz and Castro, 1997; Parsons et al., 2001; Lottermoser, 2002; Piatak et al., 2004). For example, base-metal slag deposits at the Penn Mine in Calaveras County, California, are a source of environmental

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contamination through leaching of potentially toxic elements (Parsons et al., 2001).

Concentrating, roasting, and smelting are three critical steps in the processing of Cu porphyry sulfide ores. Slag waste is produced during smelting, converting, and some possible additional refining steps (Biswas and Davenport, 2002). A part of these wastes is recycled to the smelter because of their high metal content. Although, the amount of slag in comparison to the amount of metal produced varies based on the commodity (Piatak et al., 2015), it is estimated that the production of 1 ton of copper generates approximately 2.2–3 tons of copper slag (Shi et al., 2008). Based on the worldwide estimate, 2.2 tons of slag is produced per ton of Cu and about 24.6 million tons of slag is generated from the world copper production (Gorai et al., 2003). Dumping or disposal of such huge quantities of slag can cause environmental and space problems. These waste dumps have received a large amount of attention as potential pollutant sources (Kierczak et al., 2013). Recently, smelting slags are used as additives for several purposes including building and construction materials, concretes and abrasive materials (Shi et al., 2008; Potysz et al., 2015).

Characterization of slags according to the chemical, textural, and mineralogical studies is recommended as the first step of environmental investigations (Ettler et al., 2009a, 2009b; Piatak et al., 2015; Potysz et al., 2015). Mineralogical characteristics of the slag wastes have been well described by a number of studies (e.g. Parsons et al., 2001; Lottermoser, 2002; Piatak et al., 2004; Puziewicz et al., 2007; Ettler et al., 2009a, 2009b; Piatak and Seal, 2010). Although, each slag type usually contains a specific chemical, mineralogical and therefore the specific elemental assemblages that may be of environmental concern, generally non-ferrous slags such as Cu ore slag may have a higher potential to negatively impact the environment compared to the ferrous slags (Piatak et al., 2015). Today, due to the presence of high concentrations of potentially contaminant trace elements and the sulfide minerals, most studies emphasize on the mobilization potential of pollutants of the slag waste dumps (Vdovic et al., 2006; Shanmuganathan et al., 2008; Yang et al., 2010; Kierczak et al., 2013; Dung et al., 2014). Release of toxic metals from smelting slags is controlled by several factors including pH, metal content, texture, and geochemical/mineralogical composition of slags (Ettler et al., 2009a,b; Ash et al., 2013; Kierczak et al., 2013; Jin et al., 2014). Leaching tests are more common methods used to assess the environmental risk associated with the slag wastes (Potysz et al., 2015, 2016). For example, the leachability of potentially toxic trace elements from copper slags have been investigated by several studies (e.g. Lagos and Luraschi, 1997; Shanmuganathan et al., 2008; Yang et al., 2010; Kierczak et al., 2013; Dung et al., 2014). Most of these studies (Lagos and Luraschi, 1997; Parsons et al., 2001; Lim and Chu, 2006; Shanmuganathan et al., 2008; Ettler et al., 2009b; Piatak et al., 2015) have used the adopted U.S. EPA toxicity characteristic leaching procedure (TCLP) test for determining the leachability of trace toxic elements.

The Sarcheshmeh smelting plant is the biggest Cu producer in Iran, which produces about 2 tons of slag per ton of Cu. Annually, more than 370,000 tons of slag are produced and dumped around the smelting site in Sarcheshmeh industrial complex. This study was conducted in order to investigate the environmental characterization of Sarcheshmeh smelting slags. The main objectives are as follows:

1- Identifying the concentration, leachability and toxicity potential of the toxic trace elements in the smelting slags;
2- Identifying the mineralogical composition of Sarcheshmeh slag;
3- Determining the role of grinding and sieving facilities in the trace element contamination of the surrounding soils;
4- Predicting the leachability and thus the contaminant potential of metal(loid)s in the contaminated soils by using the single extraction methods.

2. Material and method

2.1. Site description

The Sarcheshmeh mine as one of the largest porphyry copper deposits in the world is located at 29°58′N and 55°51′E and about 160 km southwest of Kerman city. The geological map around this mine is shown in Fig. 1A. Several studies have been investigating the ore forming processes including alteration and mineralization in Sarcheshmeh porphyry copper mine (e.g. Hezarkhani, 2006; Shahabpour and Doorandish, 2007; Atapour and Aftabi, 2007; Aftabi and Atapour, 2010). Mineralization in the Sarcheshmeh mine is associated with a complex intrusive body, named Sarcheshmeh Stock, which intruded into a folded and faulted Early Tertiary volcano–sedimentary series comprising trachybasalt/trachyandesite and andesitic lavas, tuffs, ignimbrites, and agglomerates (Shahabpour and Kramers, 1987; Aftabi and Atapour, 2010). Eocene basic-to-intermediate volcanic rocks, including trachybasalt, trachyandesite, and/or andesite are the primary rocks in Sarcheshmeh area (Atapour and Aftabi, 2007; Dimitrijevic, 1973). The main host rocks around Sarcheshmeh porphyry copper deposit are Eocene trachybasalts intruded by Miocene quartz monzonite and granodiorite (Aftabi and Atapour, 2010). Sarcheshmeh Stock is exposed over an area of about 1.2 km by 2.2 km and contains 450 Mtons of ore with average grades of 1.13% Cu and 0.03% Mo and a cutoff grade of 0.4% Cu (Waterman and Hamilton, 1975). The copper–molybdenum mineralization/alteration zones occur both in the porphyry stock and the surrounded trachybasalt rocks (Aftabi and Atapour, 2010).

The Sarcheshmeh area has a semi-arid climate conditions with an annual temperature between −20 and 32 °C, a mean rainfall of 440 mm, and annual evaporation of about 1170 mm (Khorasanipour and Eslami, 2014). The wind speed, sometimes exceeds 100 km/h (Doulati Ardejani et al., 2008).

Approximately, 374,000 tons of reverberatory furnace smelter slag and 12,800 to 12,900 tons of converter smelter slag (with 3.5 to 4% of Cu) are produced in Sarcheshmeh industrial complex, annually. As noted earlier, most of the converter slag is recycled and recharged to the reverberatory furnace smelter. Therefore, the reverberatory slags are the most important smelting wastes in Sarcheshmeh Copper Industrial Complex. These wastes are dumped near the smelting plant (Fig. 1B). Annually, about 70,000 tons or 18.7% of the produced reverberatory slags are used for the other purposes such as sandblasting. The preparation site is located near the Sarcheshmeh Township, where large amount of reverberatory slags is dumped for the grinding and sieving processes (Fig. 1C). The older parts of the reverberatory slag dump were weathered and the signs of weathering products were observed in the slag dump drainages (Fig. 2).

2.2. Sampling and sample preparation

In this study, 8 samples of the reverberatory slags and 2 samples of the converter slags were sampled from the Sarcheshmeh slag wastes. Collected samples were from fresh slag, powder slags around the grinding and sieving facilities and also the sediments of the slag dump drainages (Fig. 2). For the geochemical investigations, slag samples were pulverized to <75 μm and stored in polyethylene bottles.

Field studies showed a remarkable contamination layer of the wind-dispersed slag particles on the top of the soils around the grinding and sieving facilities of the preparation site close to Sarcheshmeh Township. Surface (0–5 cm) and subsurface (20–40 cm) soils were sampled in order to investigate the role of these slag particles in the contamination of the surrounding soils (Fig. 1C). The Sarcheshmeh slag dump, near Sarcheshmeh smelting plant, also has a remarkable effect on its surrounding soil through wind-dispersed slag particles. Surface soil (0–5 cm) around this