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Geochemical investigations of slags from the historical smelting in Freiberg, Erzgebirge (Germany)

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Abstract

The Freiberg area in the Saxon Erzgebirge (Ore Mountains) represents one of the oldest mining districts in Germany. Argentiferous ore mineralizations with lead, zinc and copper are dominating in this region. Various waste products of mining can be found around Freiberg. In particular, the slags from ore smelting were and are regarded as unusable waste products. However, they preserve information on the smelting and weathering behaviour of slag, which makes them very useful sources of information for our purposes. To reconstruct the chemical processes during ore smelting, historical slag represents a most valuable archive. Therefore, the historical slag dump in Halsbach (Germany) was examined exemplarily for the Freiberg deposit. The slag was dumped approx. 400 years ago and is rich in lead. An interrelation between the slag and the metallurgical process applied can be made on the basis of chemical composition, appearance and microscopic results. The slags of the heap in Halsbach contain high concentrations of heavy metals (average contents in mg kg^{-1}: Zn 40,000; Pb 10,000; Cu 1500; U 1000). Enrichments of heavy metals in the organic-rich soil horizons within the range of the dump foot (maximum contents in the A-horizon in mg kg^{-1}: Zn 3719; Pb 9198; As 3017; Cu 963) imply a faint discharge of metals from the dump.

Keywords: Saxon Erzgebirge; Mining; Smelting; Slags; Waste dump; Heavy metals; Radionuclides; Rare earth elements (REE); Chalcophile elements; Weathering stability

1. Introduction

Important centres of the central European silver mining industry were situated in the low mountain ranges of Germany such as the Harz (since 968), the Schwarzwald (since 1028) and the Erzgebirge (since 1168) (Steuer, 1993; Meier, 2001). The Freiberg area is the oldest mining district in the Erzgebirge. Up to the 19th century, the 800-year-old mining activities in Freiberg were concentrated mainly on silver (Wagenbreth and Wächtler, 1986). Besides pure silver ores (e.g. argentite), silver-containing minerals such as galena and sphalerite were mined and smelted increasingly (Baumann et al., 2000). Two procedures of smelting can be differentiated in Central Europe: the one-step Roast-Reaction process and the recent, more modern two-step Roast-Reduction method (Heimbruch et al., 1989; Brockner et al., 1995). Heterogeneous slags with portions of concomitant ore minerals characterize the one-step procedure at process temperatures of 900–1000 °C (Brockner et al., 1995). In the two-step procedure a rather glassy, homogeneous slag develops at higher process temperatures (1100–1200 °C) under

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addition of charcoal as a reducing agent and partly slag-forming additives like Baryte (Eckstein et al., 1994; Brockner et al., 1995). Besides chemical analyses of the slag, microscopic investigations are necessary required exact metallurgical allocation of the slag to the smelting process and their solidification.

Depending on the geochemical behaviour of the elements, caused particularly by their valency and ion radii, fractionating processes take place during smelting (Mingram, 1995; Galonska, 2000). After the classification of Goldschmidt (1930) it can be differentiated between lithophile, chalcophile and siderophile elements. In general, lithophile elements such as Ba, U, Th, Ti, Sr and rare earth elements (REE) are incompatible elements with large ion radii. These elements are mainly oxidic-siliceous bound during the smelting process and are enriched in the remaining slag melt (Galonska, 2000). However, chalcophile elements such as As, Cd, Cu, Pb and Zn are mostly sulfidic bound or become reduced to metals during the smelting process (Galonska, 2000). If metallic–sulfidic compounds occur in the siliceous melt during the separation of the silicate–sulfidic phase in the smelting process, these toxic metals will be enriched in the slag (Ihl, 1972). For being able to describe the metallurgical smelting processes, the slags must be classified (Eckstein et al., 1994).

In this study, the chemical composition of slag from mining in Freiberg had been determined. By analyzing the main and trace element concentrations and the distribution of the REE in both, the slag and the mined ore, assessments on the chemical composition of the slags and the kind of the Freiberg smelting process can be made.

Due to the high concentrations of heavy metals and the high sulphide content in the slag, investigations were carried out to detect a potential mobilization of pollutants from the waste dump (Wolf, 1999; Scheinert, 2002; Kupsch et al., 2004). Important tools for the evaluation of the weathering stability of the slag are autoradiographic measurements. By means of the lateral radionuclide distribution in slag hand specimen, possible weathering influences can be revealed. They are indicated by a depletion of the radionuclides in the surface area of the samples. However, Scheinert (2002) and Kupsch et al. (2004) could not show a significant mobilization of radionuclides in the surface area of slag samples from the dump Halsbach. Only a thin weathering zone in the μm-range was detected near and at the surface of the slag. For detailed conclusions in terms of weathering stability of this slag, further investigations with respect to element distribution in the surface area of slag samples are necessary, e.g. by the use of scanning electron microscopy (SEM). In general, no strong weathering influence was detected in mining slags (Eckstein et al., 1994; Galonska, 2000; Müller, 2003). Probably slags exhibit a high weathering stability, analogous to the resistance of natural glass (Heide et al., 2003).

Nevertheless, a faint element discharge from the dump could be detected. This discharge is demonstrated by an enrichment of heavy metals and radionuclides in the organic-rich soil horizons (A-horizon) at the corresponding dump foot (Wolf, 1999). On the one hand, because of the slow weathering, no direct observation of the process is possible on single slag pieces. On the other hand, despite of low discharges, the metals are concentrated in natural organic matter (NOM) in the A-horizon over time. In particular humic substances, as main part of the NOM, are able to bind metals permanently due to their functionality and high reactivity (e.g. Ziechmann, 1980; Schnitzer, 1982; Stevenson, 1982; Mason and Moore, 1985; Frimmel and Christman, 1988; Kördel et al., 1997). The NOM in the soil is acting as a natural geochemical barrier for toxic and radiotoxic elements in the surrounding of mining dumps (Franke et al., 2000; Franke, 2003). In addition, other pathways for heavy metals and radionuclides such as direct sedimentation of fine-grained slag material or input of sediment material from the close river Freiberger Mulde must be considered.

Following a risk analysis, the dump Halsbach has been taken off and reorganized. This was due to the above-average heavy metal and radionuclide concentrations in the slag (Saxonia, 1999).

2. Characterization of the study area

These investigations are focused on smelting residues (slags) originating from mining in Freiberg. As a model, the historical slag dump Halsbach near Freiberg in the Saxon Erzgebirge, Germany was studied (Fig. 1). The waste dump covers a surface of approx. 9100 m^2 and contains approx. 70,000 t of slags (Saxonia, 1999). The slag derived from the smelter Thurmhofer 3., 4. Maß. This smelter was located in the eastern part of Freiberg near the river Freiberger Mulde and was operated between 1442 and 1754 (Wagenbreth and Wächtler, 1986). The resulting slag was dumped on the eastern riverside of the Freiberger Mulde.

2.1. Geography

The slag dump Halsbach is located in the central part of the mining district of Freiberg. This district covers nearly 1340 km^2 in the Northeastern part of the Erzgebirge, a 150 km long mountain range between Germany and Czech Republic. With more than 1000 metalliferous lodes, the site of Freiberg is considered to be one of the largest ore occurrences in Europe. The once very extensive silver deposits had been exhausted over 800 years of mining activities (Baumann et al., 2000).