Mine Water and the Environment (2003) 22: 2–6 © IMWA Springer-Verlag 2003

Technical Article

The Weathering Behavior of Heavy Metals in Ore Processing Residues (Mansfeld Region, Germany)

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Abstract. One of the ore processing residues in the Mansfeld region of Germany is a flue dust, which was scrubbed out of the smelter process gases by spraying water into the hot gas stream. During the many years of ore processing, the resulting fine-grained sludge was washed into ponds for storage. These sludge deposits were covered by water and thus sealed off from the atmosphere. However, after the local copper works shut down in 1990, the ponds dried up, causing the sludge in the uppermost layers to oxidize. The need to assess the risk posed by these deposits today prompted questions over the depth to which the dried sludge can be altered by weathering and the extent of heavy metal emissions. A drill hole was bored at the center of a dry pond and the core samples analyzed. The samples indicated relatively constant levels of Cu and Pb with depth, but other metals, such as Cd, Mn, and Zn, were relatively depleted in the upper 50 cm of the sludge body. Such behavior can be explained by the solubilities of the respective secondary phases. It appears that the oxidation of metal sulfides and the subsequent dissolution of the respective secondary phases, especially sulfates, pose a potential problem for the quality of the nearby ground and surface water.

Key words: Copper ore processing; risk assessment; scrubber dust; Theisen sludge

Introduction

For more than 800 years, the Mansfeld region of Saxony-Anhalt, Germany was known for the mining of Kupferschiefer (copper shale), a black shale of Permian age, which in addition to copper, contains high concentrations of lead, zinc, cadmium, and other heavy metals (Matheis et al. 1999). However, due to economical and ecological reasons, mining and the related regional industrial activities ended in 1990. The shutdown of the smelters had an immediate positive effect on local air quality, but contamination of ground and surface water continues, and is closely linked to the former pyrometallurgical activities. Now that the plants have been demolished, the sources of this contamination are the various by-products left behind by mining and ore processing. The two major by-products that can still be found abundantly in the area are waste rock and slag. Both materials were piled up in huge heaps (up to 9,000,000 m^3) during the 20th century and are a characteristic feature of the local landscape (Wege 2000). Another by-product with a less striking impact on the topography but an even more noticeable effect on the local soil and groundwater quality is a extremely fine-grained material called ‘Theisen sludge’.

Theisen sludge is named after the inventor of a special gas scrubbing process, which was used at the copper works in the Mansfeld region from 1904 to 1990. The scrubber washed the flue dust out of the process gases, leaving the blast-furnaces at temperatures of about 400°C. A mist of water was sprayed into the gas stream, binding and concentrating the dust particles in a slurry of about 3 g/L of flue dust solids. The cleaning effect has been reported to exceed 99% (Wege 2000).

Aside from the substantial water content, the main components (> 10% by dry weight) of the resulting sludge are Zn (~ 20%), Pb (~ 13%), SiO_2 (~ 18%), S_{total} (~ 18%) and C_{total} (~ 13%), the latter resulting from the high concentrations of organic matter in the original black shale. The actual sludge particles are agglomerates of inorganic compounds and a matrix of various polyaromatics with relatively high boiling points. The agglomerates have a median diameter of 1.25 μm but range in size up to 100 μm.

The inorganic compounds in the sludge consist mainly of amorphous sulfidic particles, which can be characterized as complex solid solutions of Pb, Zn, Cu, and Fe sulfides. X-ray diffraction studies carried out by others (Weiss et al. 1997; Morency et al. 1998) also indicated the presence of sphalerite/wurzite (ZnS) and galena (PbS), both with extensive ionic substitutions, as crystalline structures. However, the small grain size of the material complicates further mineralogical identification. For a more detailed discussion of the physical and chemical properties of the sludge, see Weiss et al. (1997) and Morency et al. (1998).

Due to its high metal concentrations, Theisen sludge was originally reprocessed at a nearby lead smelter. This reprocessing went on until 1978 when the lead smelter was closed. However, the sludge production went on. By 1990, a total of about 220,000 t of unprocessed sludge had accumulated. Several attempts to establish a process to extract zinc, lead, and other valuable metals such as silver, rhenium, and germanium have not yet yielded an economically feasible solution (e.g., Morency et al. 1998). Hence, in spite of its high concentrations of valuable metals, Theisen sludge had to, and must still be considered an industrial waste product, requiring careful storage.

Initially, the sludge was stored in small concrete cells that were less suitable for long-term storage. Later on it was dumped into huge hollows or ‘ponds’ located on top of the local slag and waste rock heaps. Today the most significant Theisen sludge disposal site is ‘Pond 10’, which is situated inside a basin on top of a waste rock heap. Pond 10 contains about 200,000 m^3 of Theisen sludge, with a thickness of about 9 m. Most of the sludge was brought there between 1982 and 1990 directly from the scrubbers. The sludge was washed into the basin using huge amounts of water (1,000-1,200 m^3/d). During these active years, the sludge in the pond was covered with water and thus virtually sealed off from atmospheric oxygen. However, after the copper works closed in September 1990, Pond 10 dried up and remained virtually untouched for about three years.

With the goal of making Pond 10 the central Theisen sludge deposit, the transfer of some additional 10,000 t of Theisen sludge and similar materials began in summer 1993. These materials had previously been deposited at less appropriate sites. The conditions under which the materials had been stored before being transferred to Pond 10 are not reproducible and their composition is quite inhomogeneous. This local concentration of waste materials at Pond 10 was completed by the end of 2001. The additional material transferred to Pond 10 since 1993 covers the whole 25,000 m^2 area of pond 10 with a layer about 0.5 m thick.

The oxidation of the heavy metal sulfides in the sludge and the subsequent dissolution of the respective secondary phases can release significant concentrations of heavy metals from the sludge deposit into the surrounding environment. The “Stadtborn” spring, which is located at the base of a nearby disposal site comparable to the pond 10 deposit is heavily contaminated with heavy metals (Table 1). Oxidation processes also destroy the organic matrix of the sludge, which intensifies the erosion of the extremely fine-grained material.

Table 1. Heavy metal concentrations (mg/L) of water samples from the Stadtborn spring (analytical techniques: *ICP-AES; **ICP-MS)

Al*	17.9	Mn*	15.9
Cu*	19.2	As**	0.087
Fe*	<0.05	Cd**	3.3
Mg*	196.5	Cr**	0.003
Zn*	2111	Pb**	2.4

Given the ultimate aim of assessing the risk posed by the Theisen sludge deposit in Pond 10, a key question is the depth to which the sludge body can be altered by weathering. Since Theisen sludge is a very dense clay-like material, it was expected that oxidation and solution processes only occur within a relatively thin top layer of the sludge body. However, occasional weathering of Theisen sludge via mud cracks, several tens of centimeters deep, has also been reported (Schreck 1998). Provided a significant chemical alteration of Theisen sludge in the top layer can be observed in the first place, attention would have to be focused on the question of which metals are primarily mobilized by oxidation and dissolution processes.

Experimental

Samples and sampling

The goal of the investigation discussed in this paper was to examine the weathering behavior of Theisen sludge under the conditions prevailing at Pond 10. In order to investigate the influence of weathering (oxidation and solution) on the chemical composition of the Theisen sludge and to examine the degree of its chemical alteration as a function of depth, a 15-cm diameter drill hole was bored at the center of Pond 10. It penetrated the entire 9 m of the sludge body and reached the gravel base of the pond. Thus, the drill core material represents all of the waste material that has been dumped into the basin.

Subsequent to the drilling the core material was stored in the dark under cool, damp conditions. The core was examined visually for inhomogeneities in characteristics such as grain size distribution, color, and moisture content. Then it was studied for alterations to its chemical composition using x-ray fluorescence spectrometry analysis (XRF). The samples for analysis were taken from the axis of the core and are thus representative of the material under the actual conditions in the pond.

XRF analysis

The total concentrations of silica, aluminum, iron, zinc, manganese, cadmium, lead, and copper were determined in dried material (105°C) by both wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence. For the quantitative analysis of heavy metal concentrations that are outside the range of the available reference materials, the original Theisen sludge was diluted with SiO_2 powder (Riedel de Haen). Dilution factors of 5-10 reduced the concentrations of the elements of interest to the desired level and yielded sample compositions that matched the working range of calibrations performed by the EDXRF spectrometer (XLAB 2000). Al_2O_3 and SiO_2 were determined by WDXRF measurements of the undiluted material. For both sets of samples, the prepared sample material was mixed with 20% wax (Hoechst wax for XRF analysis) as a binder, and compacted in a hydraulic press at a pressure of 100 MPa.

Results

Visual examination of the drill core material confirmed the expected homogeneity of the sludge body. Virtually the entire core could be described as a clay-like, silty, black, moist material. However, small amounts of the sludge body were sandy rather than clay-like and differed in color from the Theisen sludge. These grayish sandy layers appear only rarely and are less than 1 cm thick. Thus, they were assumed to be irrelevant to the chemical composition and the weathering behavior of the sludge body as a whole. The samples discussed in this paper were hence all taken from the clay-like Theisen sludge, and the sandy bands were ignored.

Figures 1 and 2 illustrate the XRF data determined in the drill core material. A sample collected from the gravel base of the pond, at a depth of 9 m, is not representative of the sludge and is thus not referred to in the diagram. Moreover, the concentrations of the samples taken from depths of < 50 cm are not referred to since this layer of material was, as mentioned above, added to the original sludge after mid-summer 1993 and cannot be considered as original Theisen sludge. To enable better comparability, all concentrations were normalized to a mean composition of Theisen sludge (Table 2), derived from the XRF results of the samples taken from the drill core section between 2.5 and 8.0 m. This material can be assumed to be chemically unaltered and ought therefore to represent the chemical composition of the fresh Theisen sludge as it came from the scrubbers.

Figure 1 shows the normalized concentrations of silica, aluminum, and iron. It can be seen that the concentrations of these elements vary only within a ± 20 % range, confirming the assumption that the sludge body is fairly homogeneous.

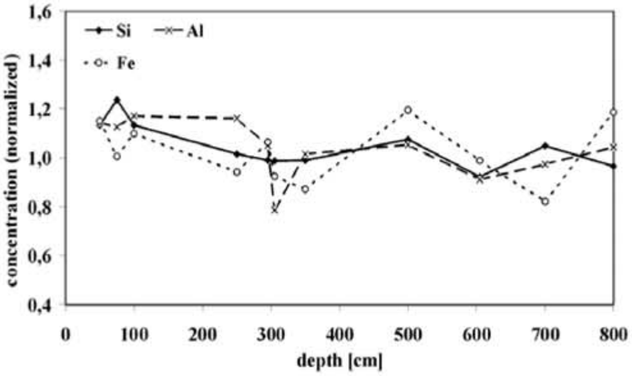

Figure 1. Normalized concentrations of silica, aluminum, and iron in a Theisen sludge drill core

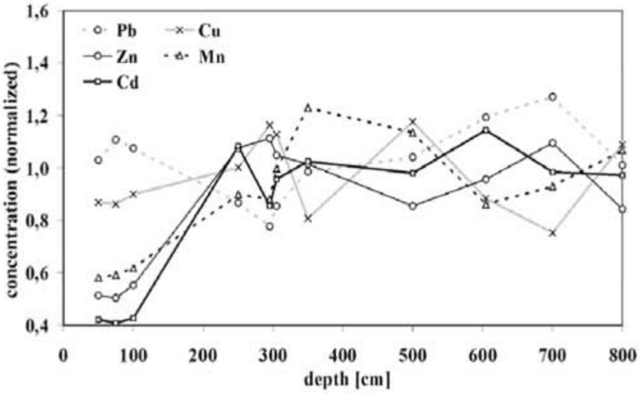

Figure 2. Normalized concentrations of heavy metals in a Theisen sludge drill core

Table 2. Theisen sludge 'mean concentrations' (MC) and the respective relative standard deviations (RSD) for the elements discussed (n = 8)

	MC [g/kg]	RSD [%]
Si	4.5	85.3
Al	10.4	15.3
Fe	12.9	24.1
Zn	9.9	208
Pb	15.9	130
Mn	12.5	0.78
Cu	15.5	15.9
Cd	8.1	0.54

Figure 2 shows the normalized concentrations of the heavy metals of concern. It can be seen that the concentrations of heavy metals in the deeper layers of the sludge body are rather constant, too. However, the samples taken at depths of 50, 75, and 100 cm differ distinctively from the composition of the fresh sludge in the concentrations of cadmium, manganese, and zinc. The cadmium concentration determined in the uppermost sample is about 40% of that in the fresh sludge; zinc and manganese were about 50% and 60%, respectively. In contrast, the concentrations of lead and copper were the same in the upper as in the lower section, varying within a ± 20 % range.

Discussion

The significant reduction in the concentrations of zinc, manganese, and cadmium, and the more or less stable behavior of iron, lead, and copper can be explained by the solubilities of the respective secondary phases, especially of the metal sulfates, relative to the respective sulfides. In the fresh Theisen sludge, the metals discussed appear mainly as metal-II-sulfides, some of which appear as crystalline sphalerite / wurzite (ZnS) and galena (PbS) (Weiss et al. 1997; Morency et al. 1998). The solubility product constants of the relevant metal sulfides are summarized in Table 3. The constants were calculated from the Gibbs energies of the substances as solids and are valid for the pure substances at 25°C (Lide 1992). As can be seen, the sulfides of the discussed metals are virtually insoluble.

As long as the sludge was covered with water, the reducing conditions in the actual sludge body were stable. After the pond had dried up, oxidation processes started at the surface of the sludge deposit and the sulfides were transformed into the respective secondary phases, especially sulfates. The solubilities of the discussed sulfates are summarized in Table 4. The data are valid for the pure substances in 'cold water' (Lide 1992).

Since the sludge deposit was still exposed to rainfall, the highly soluble sulfates were washed out of the material into the surrounding environment. As can be seen in Table 4, the solubilities of the sulfates discussed decrease in the order $ZnSO_4$ > $CdSO_4$ > $MnSO_4$ > $CuSO_4$ > $PbSO_4$ > $FeSO_4$. This tallies well with the data illustrated in Figures 1 and 2. The concentrations of Zn, Cd, and Mn, the metals with easily soluble sulfates, are considerably reduced in the upper sludge layer exposed to oxidation. On the other hand, the concentrations of Fe, Cu, and Pb, metals that have sulfates with low or very low solubilities, do not show any changes due to oxidation and dissolution.

Because the discussed results suggest that the environmental risk posed by the deposited waste is closely linked to the oxidation state of sulfur, methods for directly determining the valence state of sulfur in the sludge are being examined. Figure 3 shows an example of a direct determination using valence X-ray spectrometry (VXR), as carried out in a related project (Seidel et al. 1998). The diagram illustrates the different solubilities of zinc and lead phases depending on the degree of oxidation of the sulfur. Unfortunately, this method could not be applied to this investigation since the extremely high lead concentration in the Theisen sludge prevents precise analysis of the sulfur spectrum due to interference. To overcome this, we plan to use X-ray absorption spectrometry (XANES) in the future.

Table 3. Solubility product constants (K_{sp}) of the metal-II-sulfides of iron and the heavy metals discussed (Lide 1992)

	K_{sp}
PbS	9.04×10^{-29}
CuS	1.27×10^{-36}
ZnS	2.93×10^{-25}
CdS	1.40×10^{-29}
MnS	4.65×10^{-14}
FeS	1.59×10^{-19}

Table 4. Solubilities of the metal-II-sulfates [g/cm³] of iron and the heavy metals discussed (Lide 1992)

	Pb	Cu	Zn	Cd	Mn	Fe*
M-II-Sulfate	0.00425	14.3	s	75.5	52	sl s

s=soluble, sl s =slightly soluble, *=$FeSO_4 \cdot H_2O$

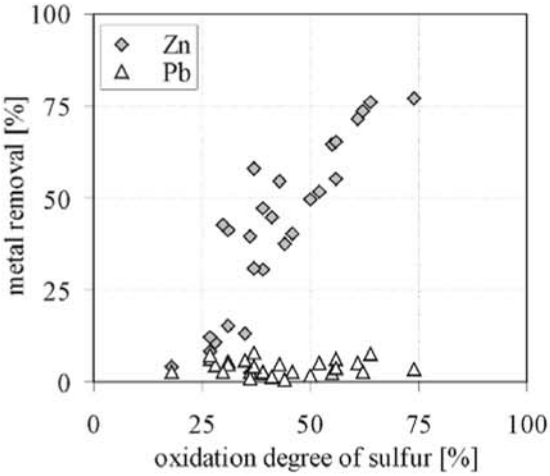

Figure 3. Comparison of the metal removal (ratio of the metal content in a sediment before and after leaching with water) for Zn and Pb depending on the measured oxidation degree of sulfur (ratio of S^{6+}/S_{total}) in the sediment specimens (Seidel et al. 1998)

The affinity of metals to organic matter might also contribute to the different weathering behavior. Lead and copper exhibit a much higher tendency to form metal-organic complexes than do zinc, manganese, and cadmium (Gruhn et al. 1985; Asche and Beese 1986; Hornburg and Bruemmer 1993). This means that in the presence of organic matter, lead and copper are likely to become adsorbed or chemically bound and thus fixed in complex metal-organic structures, whereas zinc, manganese and cadmium are much more mobile. Since Theisen sludge contains up to 20% organic compounds, the formation of metal-organic complexes is likely to be of some importance for the fixation of lead and copper in the oxidized zone of the Theisen sludge deposit.

Due to the clay-like consistency of the Theisen sludge, the oxidation front only penetrated down to a depth of about 0.5 m. Thus, the low permeability of the sludge limits the actual quantity of heavy metals that can potentially be mobilized by oxidation, even without remediation. However, this statement only applies to the Theisen sludge body in the pond, not to the sludge particles that might have oozed into the highly permeable slag heap that contains Pond 10.

The oxidation front in the deposit was indicated by a change in the chemical composition of the sludge. However, due to the grain size distribution of the inorganic material (< 1µm), its high degree of ionic substitution, and the high share of amorphous phases, a mineralogical examination of the sulfide/sulfate boundary did not appear promising and was not carried out.

Conclusions

The fresh Theisen sludge was chemically homogeneous despite the varied composition of the processed copper ore.

Si, Al, and Fe, and the heavy metals, Pb and Cu, show concentration changes in a range of only about ± 20% of the respective mean concentrations of the "fresh" sludge. The concentrations of Zn, Mn, and Cd also vary in the deeper layers in a ± 20% range, but display considerably lower concentrations in the upper 50 cm of the original sludge body.

The significant reduction in the concentrations of Zn, Mn, and Cd and the more or less stable behavior of Fe, Pb, and Cu is due to the weathering of the material. After the sludge had dried up, oxidation processes started at the surface and the sulfides were transformed into mainly sulfates. The sulfates showing high solubility were washed out.

Another reason for the different metal mobilities might be the dissimilar affinity of the metals to form metal-organic complexes.

The clay-like consistency of the sludge limits the actual quantity of heavy metals that can potentially be mobilized by oxidation and dissolution.

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