5. On the Weathering Behaviour of Theisenschlamm

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Abstract

For several centuries the Mansfeld region of Saxony-Anhalt / Germany was known for the mining and processing of 'copper shale' which came to an end in 1990. One of the residues of the former pyrometallurgical activities is 'Theisenschlamm' - a flue dust which was washed out of the hot process gases. Scrubbing was done by spraying water into the hot gas stream to bind the dust particles, resulting in an extremely fine-grained sludge which had to be stored and was for that purpose washed into 'ponds'. When copper ore was still being processed, these sludge deposits were permanently covered by water and thus virtually sealed off from the atmosphere. However, after the shutdown of the works in 1990, the ponds dried up, causing the oxidation of the sludge in the upper most layers. The need to assess the risk posed by Theisenschlamm deposits that have become exposed to weathering prompted the question over the depth to which the sludge can be chemically altered by weathering. To tackle this question, a 9 m drill hole was bored at the center of such a "pond". The core material was examined for alterations to its chemical composition using XRF analysis. The results indicate that there is a substantial influence of oxidation in the upper 0.5 m of the material. In particular the weathering of the heavy metal sulfides abundant in the Theisenschlamm and the subsequent dissolution of the respective sulfates are nowadays a major problem for the quality of the nearby groundwater and surface water. Significant differences in the weathering behavior of the analyzed heavy metals, depending on the solubility of their sulfates, could be observed.

Introduction

For more than 800 years the Mansfeld region of Saxony-Anhalt / Germany was known for the mining of Kupferschiefer or "copper shale", a marine black shale of a Permian age. However, for economical and ecological reasons the mining and the related regional industrial activities came to an abrupt end in 1990. Whereas the shut down of the smelters had an immediate positive effect on the local air quality the groundwater and the surface waters even now, about ten years later, still suffer a continuing contamination which is closely linked to the former pyrometallurgical activities. Now that the actual works are closed and pulled down, the sources of that contamination are the various by-products left behind by the former mining activities and the copper production.

The two major by-products which can still be found abundantly in the area are waste rock and slag which were piled up in huge heaps during the 20th century and which are still a characteristic feature of the local landscape (WEGE et al., 2000). However, another by-product with a less striking impact on the topography but which, on the other hand, has an even more noticeable effect on the local soil and groundwater quality is the “Theisenschlamm".

Aside from its substantial water content its main components (by dry weight) are Zn (ca. 20%), Pb (ca. 13%), SiO_2 (ca. 18%), S_{total} (ca. 18%) and C_{total} (ca. 13%). By the end of the copper production in 1990 a total of about 220,000 t of unprocessed Theisenchlamm had been piled up. Initially the sludge had been stored at several only more or less suitable sites. Besides small concrete cells it was dumped in huge hollows or “ponds” that sat at the top of the slag and waste rock heaps. To enable a further dewatering of the sludge the basis of these ponds had not been sealed. Neither had the ponds been protected from rain by covering because there was practically permanently sludge being pumped into the ponds. As a consequence considerable amounts of the extremely fine grained sludge oozed away into the bodies of the slag and waste rock heaps where it spread out uncontrollably. Particularly these sludge particles which are diffusely scattered inside the slag and waste rock heaps are nowadays one of the main sources for the inorganic and organic contaminants that are found in the groundwater and the surface waters of the region and will therefore be subject to further investigation.

The major Theisenschlamm disposal site today is the so called “Pond X” which sits in a basin at the top of a waste rock heap. Pond X contains about 225,000 m³ of Theisenschlamm. Most of it has been brought here between 1982 and 1990 when it came directly from the production site, i.e. from the scubbers. It was washed into the basin using huge amounts of water (1,000 – 1,200 m³/d). During these years the sludge in the pond was permanently covered with water and thus virtually sealed from atmospheric oxygen. However, after the shut down of the copper works, in September 1990, Pond X dried up. It remained virtually untouched until mid summer 1993.

In 1993 a transfer of some additional 10,000 tons of Theisenschlamm and alike materials to Pond X began. These materials had previously been deposited at sites which were less suitable for long term storage. That local concentration of waste materials at the Pond X is planed to be finished at the end of 2001. The goal of the re-storage of waste materials is to establish Pond X as the central Theisenschlamm deposit and to finally transfer all the Theisenschlamm, which is still stored at other sites to Pond X. The material which has been transferred to Pond X after 1993 covers the whole 25.000 m² site with a layer of an average thickness of about 0.5 m.

A central problem for the quality of the groundwater and surface waters in the vicinity of the “old” Theisenschlamm deposits as well as the “new” Pond X is the weathering of the Theisenschlamm. The oxidation of heavy metal sulfides which are abundant in the sludge and the subsequent dissolving of the sulfates gives rise to a considerable heavy metal emission out of the deposit sites into the surrounding environment.

With the final aim to assess the risk potential of the Theisenschlamm deposit in Pond X the question was posed down to which depth the sludge body can be chemically altered by weathering. Since Theisenschlamm is a very dense clay-like material it was expected that oxidation and solution processes do only occur within a relatively thin top layer of the sludge body. Provided that a significant chemical alteration of the Theisenschlamm in this top layer can be observed at all, the question which metals are mainly mobilized by the oxidation and solution processes would come into focus.

Experimental

Samples and sampling

With the aim to investigate the influence of weathering (oxidation and solution) on the chemical composition of the Theisenschlamm and with the intention to examine the degree of its chemical alteration as a function of depth a drill hole was bored at the center of Pond X. The hole had a diameter of 15 cm. It penetrated the whole 9 m of the sludge body and reached the gravelly basis of the pond. Thus the drill core material represents the Theisenschlamm that has been dumped into the basin from the very beginning in 1982 to the deposits washed into the basin just lately.

The drill core was stored under dark, cool and damp conditions. Initially the drill core was examined visually for inhomogeneities in its physical characteristics such as grain size distribution, color and moisture content. Subsequently the core material was logged for alterations in its chemical composition using XRF–analysis. The samples for analysis were taken from the axis of the core and are thus representative for the material under the actual conditions in the pond.

XRF analysis

The total concentrations of the elements Fe, Zn, Cu, Pb, Cd, Mn, Si, and Al were determined in dried material (105°C) by both wavelength dispersive (WDXRF) and energy dispersive X-ray fluorescence (EDXRF). For the quantitative analysis of heavy metal concentrations that are out of the range of the heavy metal concentrations in available reference materials, the original Theisenschlamm was diluted with SiO_2 powder (Riedel de Haen). Dilution factors of 5 - 10 reduce the concentrations of the elements of interest to the desired level and yield sample compositions which match the working range of calibrations performed by the EDXRF spectrometer (XLAB 2000). In contrast to this the determination of the matrix constituents Al_2O_3 and SiO_2 was provided by WDXRF-measurements of the undiluted material.

In any case 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

The visual examination of the drill core material confirmed the expected homogeneity of the sludge body. Virtually the whole drill core could be described as a clay-like, silty, black, moist material. Yet, some strata which were rather sandy than clay-like and which differed also in color from the actual Theisenschlamm were found. However, these grayish sandy layers appear only scarcely and show a thickness of less than 1 cm. Therefore it can be assumed that the sandy strata are not relevant for a discussion of the chemical composition and the weathering behavior of the sludge body as a whole. The samples discussed in this paper have all been taken from the clay-like Theisenschlamm. No closer attention has been paid to the sandy bands.

Figures 1 and 2 illustrate the XRF data determined in the drill core material. The sample which was taken in a depth of 9 m, i.e. from the gravel basis of the pond, is not representative for the sludge and has thus not been referred to in the diagram. Also the concentrations of the samples taken from a depth of < 50 cm have not been referred to since that layer of material was, as mentioned above, added to the original material after mid summer 1993 and can not be considered as fresh Theisenschlamm. To enable better comparability all concentrations were normalized to a “mean composition” of the Theisenschlamm. That mean composition was derived from the XRF results of the samples taken from the drill core section between 2.5 and 8.0 m. That material can be assumed to be chemically unaltered and should therefore represent the chemical composition of the fresh Theisenschlamm as it came from the scubbers. The used “mean concentrations” of the elements discussed here were defined as summarized in Table 1.

Table 1: Theisenschlamm "mean concentrations" (MC) and the relative standard deviations (RSD) for the discussed elements (n = 8)

	Si	Al	Fe	Zn	Pb	Mn	Cu	Cd
MC [g/kg]	85.31	15.32	24.06	208.78	130.56	78	15.89	0.54
RSD [%]	4.5	10.4	12.9	9.9	15.9	12.5	15.5	8.1

Figure 1 shows the normalized concentrations of silica, aluminum, and iron in the drill core samples. The results confirm the assumption of a rather homogeneous composition of the sludge body.

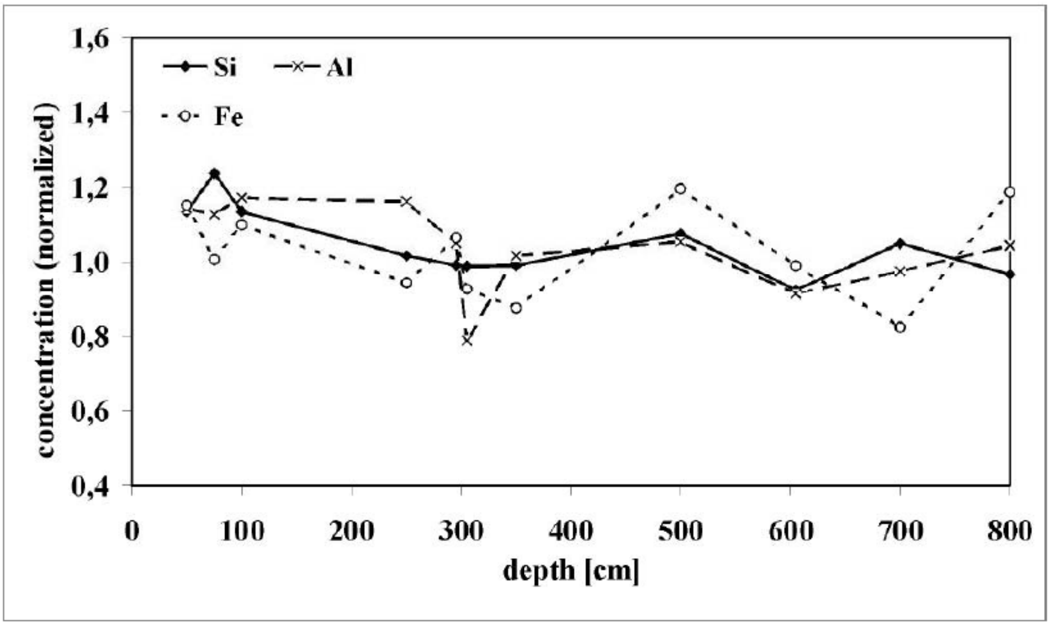

Figure 1: *Normalized concentrations of silica, aluminum, and iron in a Theisenschlamm drill core*

Figure 2 shows the normalized concentrations of the heavy metals of concern. It can be seen that the heavy metal concentrations in the deeper layers of the sludge body remain quite stable, comparable to silica, aluminium, and iron. That implies once more the homogeneous composition of the fresh sludge. However, the samples taken in 50, 75 and 100 cm show concentrations of cadmium, manganese, and zinc which differ distinctively from the composition of the fresh Theisenschlamm. In these upper samples the concentrations of the three elements are significantly lower than the respective mean concentrations. In contrast to this the concentrations of lead and copper do not change considerably in the upper samples.

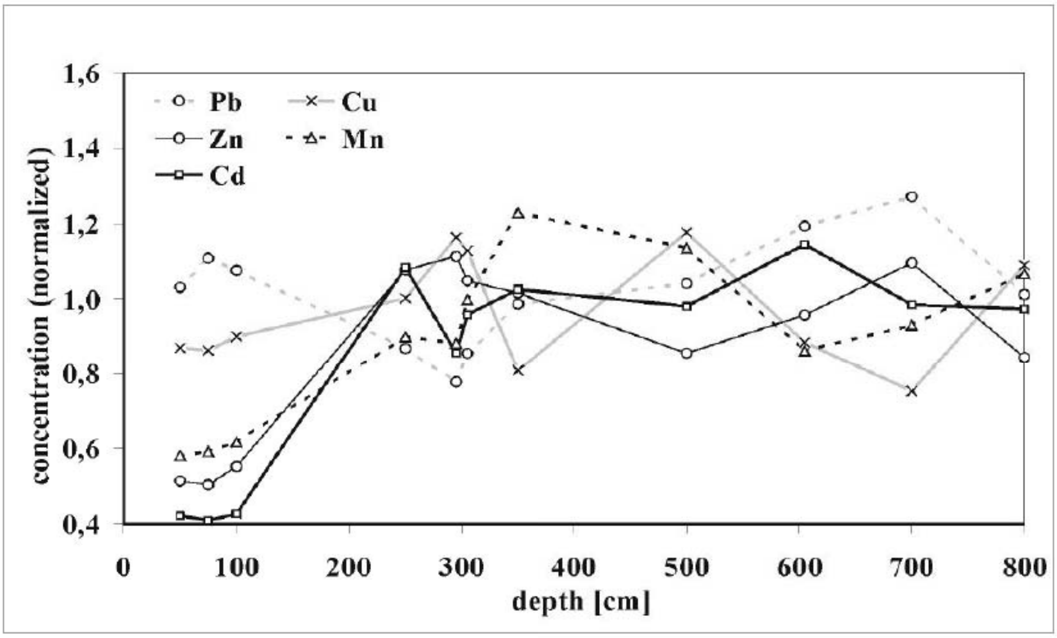

Figure 2: *Normalized concentrations of heavy metals in a Theisenschlamm drill core*

Discussion

Before discussing the results, let us summarize the historical and the experimental facts.

- The sludge body in Pond X has a thickness of about 9 m. The material in Pond X consists virtually entirely of Theisenschlamm.
- The sludge that has been washed into Pond X continuously between 1982 and September 1990 was brought here directly from the scrubbers and can be considered as “fresh” Theisenschlamm. In this period the sludge body was permanently covered with water.
- Following September 1990 the sludge body remained practically untouched for about three years. During that time the pond dried up and its surface was exposed to the atmosphere and thus to oxidization.
- Starting in mid summer 1993 additional Theisenschlamm and alike materials have been brought to the Pond X. That material, which is now represented by the top 0.5 m layer of the sludge body had previously been stored at several other sites and can not be considered as “fresh” Theisenschlamm. The conditions under which the material had been stored before being transferred to Pond X are not reproducible.
- The concentration profiles which are illustrated in Figures 1 and 2 indicate that the fresh Theisenschlamm was chemically fairly homogeneous in spite of the changing composition of the processed copper ore. Figure 1 illustrates the changes in concentrations for the “main” elements silica, aluminum, and iron i.e. of elements which have barely been affected by solution processes as a result

of the oxidation of the sludge. The concentrations of these elements change in a range of only about ± 20%.

- Figure 2 illustrates the changes in the heavy metal concentrations. In the lower part of the depth profile the concentrations do also change in a range of just about ± 20%. However, in the upper 50 cm of the discussed section the concentrations of zinc, manganese and cadmium are considerably lower than in the "standard" Theisenschlamm. The cadmium concentration determined in the most upper sample is only about 40% of the cadmium concentration in the fresh standard sludge. Zinc and manganese show concentrations of about 50 and 60%, respectively, compared to the standard Theisenschlamm. On the other hand can be seen that the concentrations of lead and copper do not show such a general decrease in the upper section. The concentrations remain in the ± 20% range just as in the lower part of the drill core.

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 with the solubility of the sulfates of the respective heavy metals. In the fresh Theisenschlamm the discussed metals appear mainly as metal-II-sulfides. The respective solubility product constants are summarized in Table 2. The constants are calculated from the Gibbs energies of the substances as solids and are valid for the pure substances at 25°C (LIDE, 1993). As it can be seen the sulfides of the discussed metals are virtually insoluble.

Table 2: *Solubility product constants (K_{sp}) of the sulfides of the discussed heavy metals and iron*

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

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 sulfates. The solubilities of the discussed sulfates are summarized in Table 3. The data are valid for the pure substances in "cold water" (LIDE, 1993).

Table 3: *Solubilities of the sulfides and sulfates [g/100 cm³] of the discussed heavy metals and iron; s = soluble, sl s = slightly soluble, * = $FeSO_4 \times H_2O$*

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

After the pond had dried up the oxidation front penetrated into the sludge. Since the pond was still exposed to rainfall the sulfates that show generally a much higher solubility than the sulphides, were washed out of the material. As it can be seen in Table 3 the solubilities of the discussed sulfates decrease in the order $ZnSO_4$ > $CdSO_4$ > $MnSO_4$ > $CuSO_4$ > $FeSO_4$ > $PbSO_4$. That is in good correspondence with the data illustrated in the figures 1 and 2. The concentrations of Zn, Cd, and Mn, i.e. of the metals that have easily soluble sulfates, are considerably reduced in the upper sludge layer which was exposed to oxidation. On the other hand the concentrations of Fe, Cu, and Pb, i.e. of the metals that have sulfates with only low or very low solubilities, do not show any changes due to oxidation and solution.

Another effect that might be responsible for the different weathering behavior of the discussed metals is their affinity for organic matter. Lead and copper exhibit a much higher tendency to form metal-organic complexes than zinc, manganese and cadmium (HORNBURG et al., 1993; ASCHE & BEESE, 1986; GRUHN et al., 1985). That means that in the presence of organic matter lead and copper become adsorbed or chemically bound and thus fixed in complex metal-organic structures, whereas zinc, manganese and cadmium are much more mobile. Since Theisenschlamm consists of up to 20% of 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 Theisenschlamm deposit.

Due to the clay-like consistence of the Theisensludge the percolating rain water and thus the oxidation front penetrated into the sludge down to a depth of only 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 actions being carried out. Yet this statement is only valid for the actual Theisenschlamm body in the pond itself but not for the sludge particles that have oozed into the highly permeable bodies of the slag and waste rock heaps.

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A case study from the Mansfeld District, Germany

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