6. Environmental Impact of Smelting Residues Affected by Weathering

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Abstract

Even today, a decade after mining and smelting was abandoned in the district of Mansfeld, smelting residues, in particular Theisenschlamm, significantly contribute to the pollution of the environment. The extremely fine grained sediments are subject to erosion by wind and water. The most effective dissemination mechanisms are deflation (wind erosion), mechanical erosion and leaching. Environmentally significant pollutants derived from Theisenschlamm comprise metals (zinc, lead, copper, arsenic, cadmium), organic components such as PAH and dioxins and radionuclides (^{210}Pb, ^{210}Po). These pollutants can be found in lake and river sediments, in soils, in the surface water and in the groundwater of the former mining district. The most serious environmental hazards of Theisenschlamm are (a) the pollution of the surface water and groundwater by harmful, soluble and bioavailable organic and inorganic compounds; (b) the mechanical erosion of metalliferous sediments in the mining area and their accumulation in the lakes of Mansfeld, a potential threat to wildlife and vegetation; (c) harm to human health by inhaling radioactive particles.

Dispersion mechanisms for environmentally hazardous components in mining and smelting residues

The major pollutants released from the mining and smelting residues are metals (mainly Zn, Pb, Cu, Cd, As), radionuclides (^{210}Pb, ^{210}Po), hydrocarbons (PAH, dioxins) and salts (sulphate, chloride). All these components are remarkably enriched in the smelting residues such as Theisenschlamm, carbonised Theisenschlamm, flue dust and finally the neutralisation sludge from leachate treatment. Other residues, namely slag and mining waste, are only of minor importance for the environment. The extremely fine grained sediments (average particle size of about 1 micron) are subject to erosion by wind and water. The most effective dissemination mechanisms are deflation, mechanical erosion by torrential waters and leaching by precipitation.

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Climate and precipitation

The area around Eisleben is of low rainfall intensity with an annual average of about 490 mm of precipitation (Figure 1). This extraordinarily low precipitation rate, the lowest in Germany, results from the geographical position of the mining region in the foothills of the Harz mountains. Nevertheless, in summer heavy rainfalls may occur and result in torrential waters and flooding of the low grounds.

Precipitation rate at Helbra in mm/day

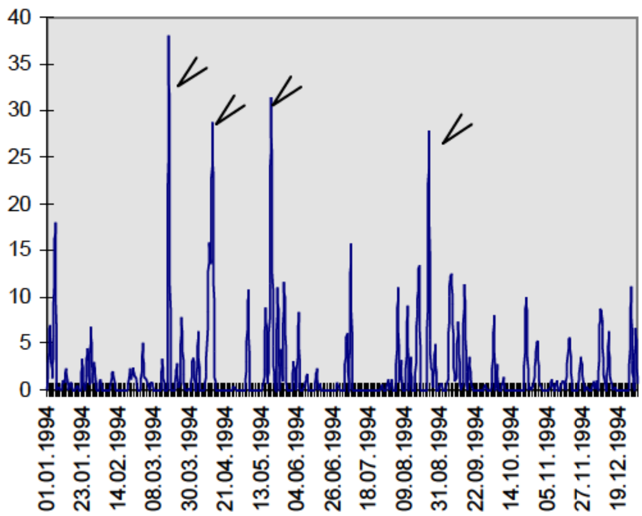

Figure 1: *Diurnal precipitation record at Helbra in 1994. Data from Mansfeld Rohhütten GmbH i.L, Helbra*

Arrows: events of major precipitation

This flooding is accompanied by extensive erosion and resedimentation and finally leads to a silting-up of the adjacent lakes (SCHMIDT, 1997). The average annual temperature is 8°C, ranging from -0.2°C in January to 18.2°C in July.

Major pollutant dispersion mechanisms

Pollutants derived from Theisenschlamm and related metalliferous sediments are spread to the environment by three mechanisms (Figure 2):

- Deflation of dried sludge (dust) by the wind
- Erosion of the fine grained metalliferous sediments by heavy rain falls and torrential waters, removal by the surface water
- Leaching of pollutants from the sediments by precipitation and dispersion in the surface and the groundwater

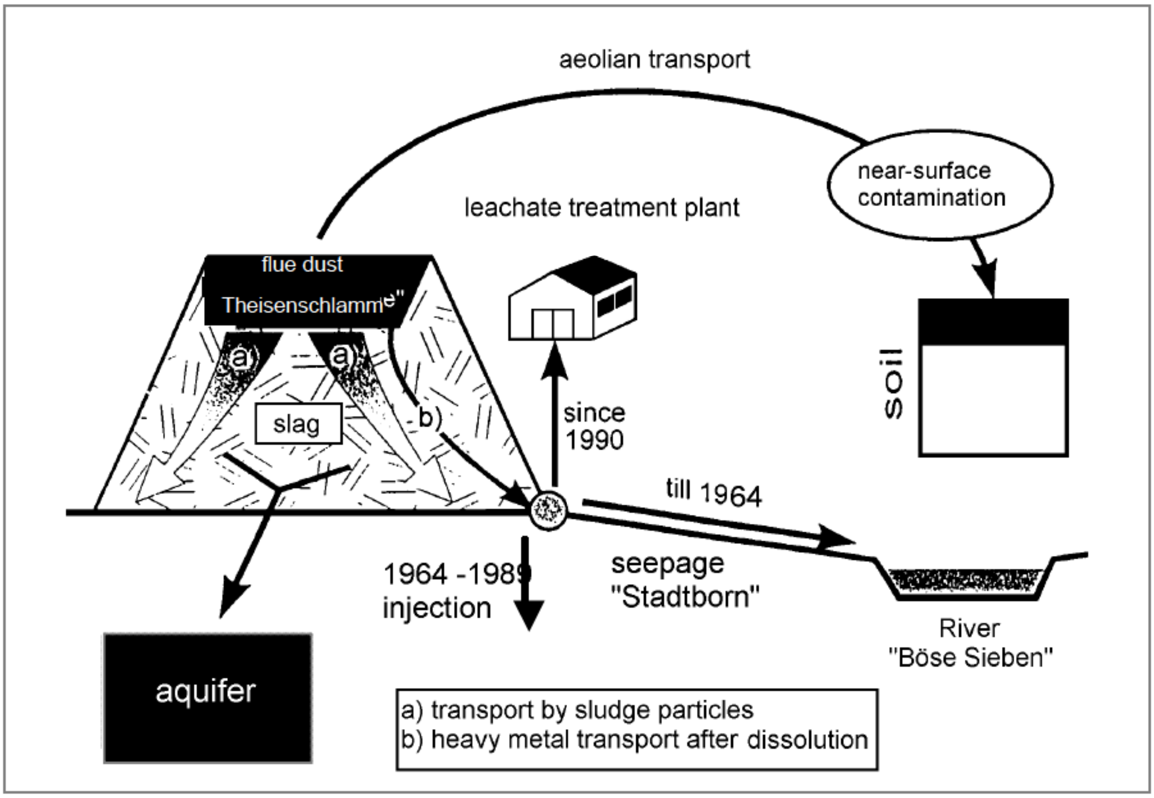

Figure 2: *Paths of pollutant migration by the weathering of Theisenschlamm. Modified after* J*AHN et al. (1997)*

Airborne dispersion of pollutants

Airborne dispersion (deflation) affects all unprotected fine-grained surficial sediments. Desiccation of the sludge results in the formation of mud cracks, several tens of centimetres deep (Annex, A5). Proceeding from the mud cracks, precipitation and oxygen destroy the protective binding agent of the sediments, i.e. organic matter in Theisenschlamm, and the remaining dust is easily scattered by the wind.

This metalliferous dust is responsible for metal enrichments in soils close to unprotected Theisenschlamm dumps. MARQUARDT (1997) sampled soil profiles below and along the southern flank of the Helbra slag heap (Annex, A1), 0.5 - 1.5 km distant from a Theisenschlamm storage basin on top of the heap. He observed distinctly increased contents in heavy metals in the upper 20 cm of the soil profiles, in particular in elevated terrain. The metal ratios in the enriched soil samples correspond to those in Theisenschlamm, a proof for the airborne dispersion of metalliferous dust.

More distant from the smelters one has to distinguish between different overlapping mechanisms for heavy metal dissemination: flue dust emissions in the early years of copper shale smelting without top gas scrubbing, metal emissions during production until 1990 and the recent deflation of deposited sludge. LORENZ (1994) calculated the amount of lead emitted as flue dust between 1870 and 1910 by only one smelter to be 11,900 tons and postulated an emission corridor of 400 m x 1,600 m in size. TÜV BAYERN/LUB (1991) carried out a wide grid screening of soil samples around the former smelters. They registered above-average metal enrichments in soils, originating from the smelters and spreading to the environment for a distance of about 1.5 km (As) to 7 km (Cd), following the main wind direction. Soil samples taken from the smelters (sample 20002, smelter Helbra) may contain up to 5,890 mg/kg Cu, 2,640 mg/kg Zn, 1,220 mg/kg Pb, 119 mg/kg As and 8 mg/kg Cd. Only 3-4 km to the East, the soil contains only 156 mg/kg Cu, 240 mg/kg Zn, 162 mg/kg Pb, 13 mg/kg As and 2 mg/kg Cd (sample 20017, Steinmetzgrund).

Mechanical dispersion of metalliferous sediments by the surface water

In the early years of the century furnace top gas scrubbing in Helbra suffered from various technical shortcomings and a lack of environmental awareness (TÜV BAYERN/LUB, 1991). Several times Theisenschlamm storage basins leaked or spilled over and suspended flue dust was spread to the environment. In times of increased smelting activities, and lacking storage capacities, the flue dust suspension was passed into the mining waste and slag dumps (heap filtration) or even directly released to the surface water. Today we find about 30,000 tons of metalliferous sediments in the wetlands of the river Glume (Annex, A 3) close to the former smelter. Lenticular intercalations of Theisenschlamm in flood plain sediments are common in the river channel between Helbra and Eisleben. Even 15 km to the East, in the sediments of the lakes of Mansfeld, particles from Theisenschlamm have been found (KLÖCK, 1997). The major mechanism for Theisenschlamm dissemination and redeposition is erosion by torrential waters caused by isolated but heavy rainstorm events (Figure 4). This mechanism affects unprotected Theisenschlamm dumps as well as redeposited metalliferous flood plain sediments.

Leaching of pollutants from Theisenschlamm by precipitation

Flue dust and Theisenschlamm, in particular when carbonised, are easily leached by water. This is the result of sulphide mineral oxidation generating soluble sulphates of zinc, copper and cadmium while lead sulphate is more resistant to leaching.

Most of the Theisenschlamm deposits and flue dust accumulations set up on slag heaps are either unprotected or lightly covered by tarpaulins to avoid deflation. This measure does not prevent the leaching of the smelting residues by precipitation. Even after the relocation of most of the Theisenschlamm from temporary dumps to the central deposit Pond X, many thousand tonnes of metal-contaminated waste material and slag (“mixed material”) remained on site and are subject to leaching by precipitation.

Several springs can be found at the base of the Helbra slag heap. This seepage is enriched in metals and organic pollutants leached from smelting residues by precipitation. At two locations, Stadtborn and Vietsbach, metal and sulphate concentrations far surpass the accepted environmental norms, making leachate treatment necessary (Tab. 1).

Table 1: *Average zinc, copper and sulphate contents (1992-2000) in leachate-dominated water of the Stadtborn well*

mg/l	1992	1993	1994	1995	1996	1997	1998	1999	2000
Zn	1,457	2,363	2,655	3,241	2,541	2,082	1,758	1,733	1,581
Cu	13.65	14.33	20.36	16.64	11.96	9.61	10.68	10.01	10.83
Sulphate	5,267	5,918	6,494	7,260	7,199	6,334	6,326	5,913	5,908

Data from Mansfeld Rohhütten GmbH i.L., Helbra, with permission (Analyst: Pfeiffer)

The distinct increase in zinc and sulphate values between 1993 and 1996 is probably due to Theisenschlamm relocation measures in Pond 9, situated above the Stadtborn well on the Helbra slag heap. Aeration and artificial wetting (dust prevention) accelerated sulphide oxidation and the subsequent leaching considerably. The gradual decrease in metals and sulphate after 1995 is a proof for the effectiveness of the relocation measures.

Around the Stadtborn well pebbles and leaves are coated by a greenish precipitate, the mineral glaucocerinite $[Zn_{8-x}Al_x(OH)_{16}]\ [(SO_4)_{x/2}(H_2O)_9]$, first described by WITZKE (1997). Glaucocerinite is a “reservoir mineral” of hydrotalcite structure. It possesses a hybrid layer-lattice structure and may absorb bivalent metal cations such as Cu, Pb, Cd and Zn. Precipitation is triggered by changes in pH, the abundance of trivalent cations in solution such as Al, Fe or Cr, and a sufficient amount of anions (sulphate, chloride, carbonate) available. Details are given in SCHRECK and WITZKE (1999) and SCHRECK et al. (2000).

The impact of Theisenschlamm on the quality of the surface water can be followed from the smelters downstream to the lakes of Mansfeld, a distance of about 15 km. Both heavy metals and organic pollutants (PAH) act as tracers and point to its source - Theisenschlamm. Location 1 (see Figure 1 of Chapter 1 and Table 2) is unpolluted water upstream from the smelters (geogenic background). Locations 2 and 3 are leachate affluents from the smelters at Helbra and Eisleben to the river “Böse Sieben”, location 4 is about 1 km west of the lakes of Mansfeld and location 5 is the outlet of the lake. It is evident that Zn, Cu and Cd contents in the river water can be attributed to leachates from smelting residues while Pb seems to remain stable and does not seriously contribute to the pollution of the water.

Table 2: *Metal content [µg/l] in water samples along the river "Böse Sieben"*

Element	1	2	3	4	5
Zn	< 10	3149	10150	395	90
Pb	< 0.4	14	< 0,4	< 0.4	< 0.4
Cu	3.8	21	30	10	4
Cd	< 0.2	5	6	3	0
As	< 0.2	< 0.2	20	10	28

Dissolved metals and suspended metalliferous sediments from heap leaching and erosion pass into the lakes of Mansfeld and are temporarily trapped in this geochemical sink. Here precipitation of metal sulphides in a partly reducing environment and the settling of metalliferous particulate matter takes place. The lake bottom sediments close to the inflowing river exhibit the highest concentrations in Zn, Pb, Cu, Cd and As whereas sediments from the centre and the outlet of the lake contain much lower amounts of metals (Table 3).

Table 3: *Average metal content in sediments from the lakes of Mansfeld (Süßer See), uppermost layer. From SCHRECK (1996)*

metal (mg/kg)	lake inflow	lake centre	lake outlet
Zn	2,865	51	63
Pb	581	13	13
Cu	458	20	26
Cd	7	< 0.3	< 0.3
As	64	6.5	5.5

Organic components released from the smelting residues can also be used as geochemical tracers. The PAH content of Theisenschlamm (Pond 9) is 1,030 mg/kg (SCHRECK 1997a). Leachates from Theisenschlamm deposits contain 1,736 ng/l PAH (Stadtborn, analyst Dermietzel, UFZ). The distribution pattern of the 16 EPA PAH's in leachates from Theisenschlamm shows typical enrichments in lighter PAH such as naphthalene (1), acenaphthene (3), phenanthrene (5) and fluoranthene (7) and only minor amounts of heavier PAH (Figure 4). A similar distribution pattern, the "finger print" of Theisenschlamm, can be found in the water of the lakes of Mansfeld. The lower percentage of naphthalene in lake water, about 15 kilometers away from the source, probably results from biological degradation or from the high degree in volatilization to more heavy PAH molecules.

GÖTZELMANN et al. (1996) describe similar PAH patterns in groundwater contaminated by gasworks. They conclude from calculated transfer potentials that the lighter PAH from naphthalene (1) to pyrene (8) are more transferable in (ground-) water than the heavier ones and thus will preferentially be found in water samples.

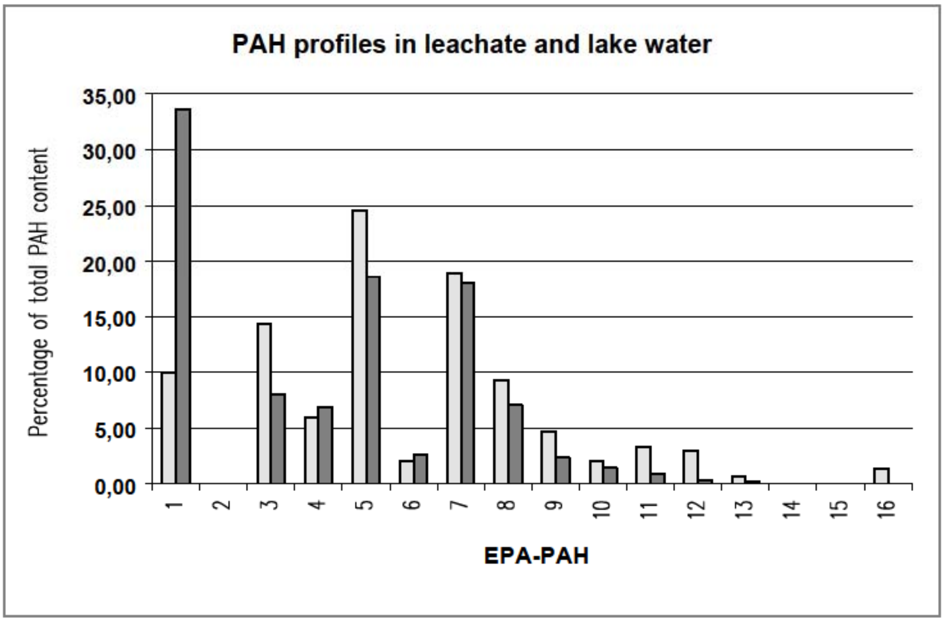

Figure 4: *PAH profiles in seepage from Theisenschlamm (Stadtborn, dark grey, total PAH = 1,736 ng/l) and in lake water (light grey, total PAH = 301 ng/l). Numbers 1-16: EPA-PAH from naphthalene (1) to indeno(1,2,3-cd)pyrene (16).*

However, Theisenschlamm, the PAH source, is already enriched in lighter PAH such as phenanthrene (5), fluoranthene (7), pyrene (8) and benz(a)-anthracene (9). Additional research on PAH migration is required to confirm the reliability of PAH patterns.

Pollutants leached from the smelting residues by precipitation contaminate the shallow aquifer in the surrounding of the former smelters. In Helbra sixteen groundwater observation wells have been installed in three different aquifers. As an example, data from well 2 (shallow aquifer, 4.77 m deep) and well 2A (deeper aquifer, 31.06 m deep) are presented (Tab. 4).

Table 4: *Groundwater characteristics of two aquifers close to Pond X at Helbra.*

component (mg/l)	groundwater observation well 2 (depth 4.77m)	groundwater observation well 2A (depth 31.06m)
Zn	16.54	0.024
Pb	< 0.0008	< 0.0008
Cu	< 0.0003	< 0.0003
Cd	< 0.0003	< 0.0003
As	0.017	< 0.0003
SO_4	2,325	247
Cl	463	82
NO_3	96	0.55
pH	7.2	6.5

From SCHRECK (1997b). Analyses UFZ: AAS and IC (C. BÖHNISCH, A. SAWALLISCH)

Compared with the deeper aquifer, the shallow aquifer is enriched by a factor of 700 times in zinc, 175 times in nitrate, about 10 times in sulphate and about 5 times in chloride. The level of pollution in the shallow groundwater sampled from more remote wells in discharge direction is much lower than the presented values.

Decomposition of Theisenschlamm by weathering

Theisenschlamm is mainly composed of metal sulphides and sulphates, quartz, amorphous silica and organic compounds. The most common metal containing minerals are wurtzite, sphalerite, galena and anglesite (MORENCY 1994, WEISS et al. 1997). LEIPNER (1994) mentioned additional chalcopyrite, stannite and pyrrhotite. Most of these minerals were formed during the cooling of the furnace top gas in a reducing environment and thus are not stable under oxidizing conditions.

Once exposed to weathering, Theisenschlamm is decomposed by atmospheric oxygen and a subsequent leaching of the soluble compounds occurs by precipitation. Oxidation also destroys the organic matrix of the sludge and converts the sludge into dust. Wurtzite and sphalerite are converted into easily soluble zinc sulphate and galena changes to anglesite, which is resistant to weathering. In consequence Theisenschlamm becomes distinctly impoverished in zinc, cadmium and copper while the lead content is stable or slightly enriched (Tab. 5). On the other hand leachates from Theisenschlamm deposits exhibit high zinc and sulphate concentrations.

Table 5: *Chemical composition of Theisenschlamm and leachate.*

component	Theisenschlamm, non-weathered, Pond 9 (ppm)*	Theisenschlamm, weathered, Pond 9 (ppm)*	seepage, Stadtborn well, 1995 (ppm)**
Zn	140,209	73,590	3,507
Pb	119,345	95,475	3.2
Cu	23,920	14,790	18
Cd	790	420	5
As	3,280	3,690	0.018
sulphate	24.17 %	15.6 %	7,980

From SCHRECK (1996). Analyses: *XRF, Technical University Berlin, **AAS and IC, UFZ

The weathering of Theisenschlamm was studied by MARQUARDT (1997). He took core samples from Pond 9, a basin containing up to 5 m of consolidated sludge (Annex, A 4). Pond 9 is situated on the Helbra slag heap, above the Stadtborn well. The decomposition of Theisenschlamm starts from the sediment surface and continues to depth via mud cracks, several tens of centimeters deep. Along the mud cracks the sediment changes its colour from black to olive green and translucent, tabloid crystals of anglesite appear. The final step of Theisenschlamm disintegration can be observed at the surface of the deposited sediments: after decomposition of the organic matrix the sludge turns into dark brown dust and is easily blown away by the wind. The preferential leaching of metals and sulphate from Theisenschlamm starting on mud cracks can be read from a vertical profile of 60 cm length (Figure 5). Here mud-cracked layers (samples 7, 12, 13, 14) are characterized by a strong depletion in zinc and sulphate, a moderate decrease in copper and constant lead-values.

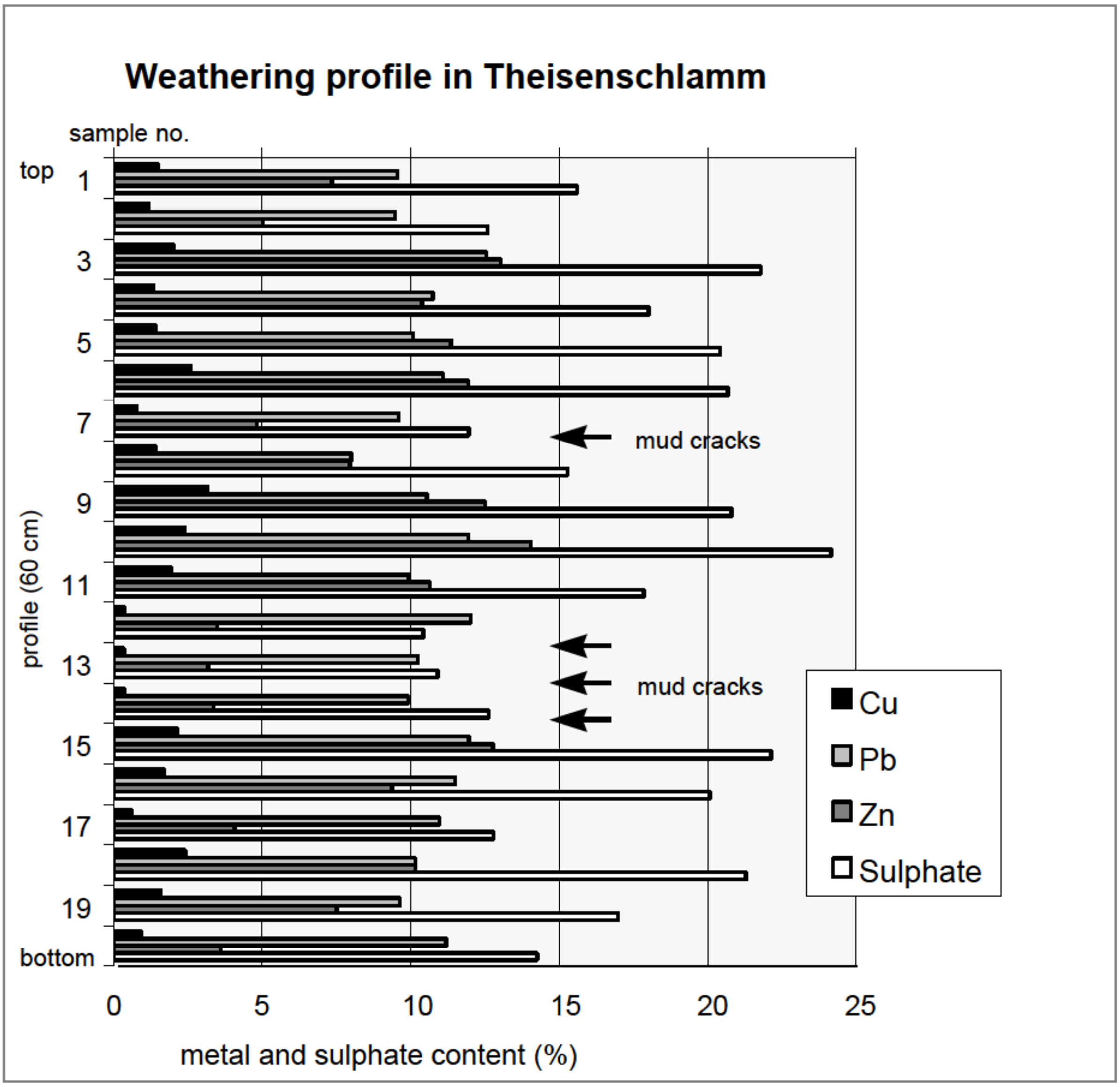

Figure 5: *Vertical profile in consolidated Theisenschlamm, Pond 9. From* MARQUARDT *(1997).*

Additional information on the weathering of Theisenschlamm is given by JAHN et al. (1997). The authors carried out field experiments in Helbra to determine the leaching potential of six different mining and smelting residues by natural precipitation. The experiments included original Theisenschlamm, carbonised Theisenschlamm, neutralisation sludge, copper slag, copper shale and limestone. 6 boxes of 30 liters each were filled with different heap materials from Helbra and exposed to precipitation for about 6 months. The leachate was collected and analysed every month (Tab. 6). Leachate from Theisenschlamm shows low pH, starting from 4.2 to finally 5.7. This acidification is caused by sulphide mineral oxidation and results in sulphate concentrations of up to 15,400 mg/l in leachate. Zinc, cadmium and sulphate are preferentially leached from the sludge and maximum values are achieved after two months. Lead and copper obviously exhibit lower mobilisation potentials. The initial zinc content in leachate from Theisenschlamm is about 7% of the value in solid sludge whereas the corresponding lead content is only 0.005%

Table 6: *Chemical composition of leachates from Theisenschlamm (field leaching experiment, natural precipitation).*

mg/l	after 1 month	after 2 months	after 3 months	after 4 months
Zn	5,270	6,370	5,910	2,980
Pb	4.4	5.8	4.9	1.1
Cu	0.3	0.2	0.1	< 0.1
Cd	9.3	11.8	10.6	5.0
SO_4	14,100	15,400	12,300	7,580
Cl	337	283	266	111
pH	4.2	4.3	4.9	5.7

Data from JAHN et al. (1997). Rain water pH 6.2

Conclusions

The environmental impact of Theisenschlamm and related metalliferous residues from copper shale smelting was assessed in early 1990 and extensive redevelopment concepts for the region were developed (1991, 1994, 1997). At present, 11 years after smelting was abandoned in the Mansfeld mining district, almost only temporary measures to prevent environmental hazards were put into practise. These measures include the dismantelling of the technical installations, the relocation of Theisenschlamm from different unprotected dumps to Pond X, the continuation of leachate treatment and a small monitoring program. Many of the recommended and necessary, but expensive, measures such as the capping and sealing of contaminated areas, the relocation of metalliferous sludge from the wetlands and the technical improvement of the leachate treatment plant are still in the planning stage.

Today, pollutants derived from smelting residues, in particular from Theisenschlamm, can be found in the surface water and in the groundwater, in sedimentary sequences of the wetlands, in soils and even in the sediments of the lakes of Mansfeld. In recent years the district of Mansfeld has changed from a mining and industrial region to tourism and recreation. This new objective, together with the hope for job creation and prosperity, is based on a clean environment, unpolluted lakes and attractiveness for leisure-time activities. To keep this vision alive, it is high time to realize the regional redevelopment concepts now.

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Fine-grained residues from copper smelting and their environmental impacts

A case study from the Mansfeld District, Germany

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