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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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1. Introduction

As a consequence of Germany´s reunification in 1990, the majority of the primary industries in East German were completely restructured, i.e. partially or totally closed down. The reason for this unprecedented upheaval in the East German national economy was related to the obsolete technological level and the top-down production based on local raw materials. These industries, particularly in the mining, chemical and metallurgical fields caused serious and even outrageous environmental problems.

One of these industrial activities was the traditional mining of so-called Kupferschiefer, a low-grade metalliferous Permian black shale, in the Mansfeld region. This region is located in Sachsen-Anhalt southeast of the Harz mountains (Figure 1). Mining and metallurgy is documentated from this district for more than 800 years; for a detailled description of its outstanding significance for European history see EISENHUTH & KAUTZSCH (1954) and JANKOWSKI (1995).

The bituminous shale was smelted in coke-fired blast furnaces at temperatures of about 1300°C to produce a copper stone (matte) containing about 40% Cu. The bulk of the raw material formed a silicic slag, whereas the volatile compounds and some fine particles were concentrated in the scrubber dust. A special type of scrubber was developed for the Mansfeld smelting process in 1904, and is known, in honour of the inventor, as the Theisen-scrubber. The flue dust, leaving the furnace at about 400°C, was collected by a washing procedure, resulting in a slurry of about 3 grams per liter of solids. This was concentrated to about 60 grams per liter prior to decantation and drying. The product was named "**Theisenschlamm**", which means Theisen sludge (LORENZ; 1994). The material is composed predominantly of lead and zinc, but also contains significant amounts of rare metals including Ag, Re, Ge (LORENZ, 1994; LORENZ et al., 1992).

The Theisenschlamm was used as the raw material feedstock for a lead smelter until 1978, when this smelter was closed down (LORENZ et al., 1992). Nevertheless, the production of copper stone continued which in turn left the Theisenschlamm (about 500 kg per ton copper stone) as an industrial waste by-product that had to be stored.

This by-product of metal extraction has caused serious environmental problems. The closure of the plant had an immediate positive effect on the environment by stopping air and surface water pollution, however contaminations of soils, ground- and surface waters are still present and require remediation.

By 1990, when ore mining and copper production were stopped, a total of about 220,000 tons of Theisenschlamm had been deposited at several sites, among them small-scale cement cells, on top of slag heaps and in a large pond constructed on a waste rock heap. These deposits were neither sealed from the ground, nor covered and therefore were a major source of contamination to surface waters, ground water and soils.

Since 1990 several environmental studies have been undertaken in the Mansfeld region (Arbeitsgemeinschaft TÜV Bayern/L.U.B. Lurgi-Umwelt-Beteiligungs-Gesellschaft, 1991; Noell Umweltdienste GmbH, 1993; Flachowsky et al., 1992; Freyer & Treutler, 1992; Gläser et al., 1993) as well as a radiological study by the German Federal Agency for Radiation Protection (Bundesamt für Strahlenschutz, 1992). By now the former smelter works have been demolished, highly contaminated materials from the sites have been removed and contamianted percolate waters are being collected and treated; though, the voluminous deposits of Theisenschlamm continue to pose a major environmental risk in the Mansfeld district.

The present report begins with a detailed depiction of the technical features of mining and smelting of copper shale in the Mansfeld region. The following contributions compile results of research activities executed by scientists from UFZ and the Université du Québec à Montréal (Canada) since 1993. Main objectives were the characterisation of Theisenschlamm and its environmental impacts on the freshwater systems of the region (see Figure 1). Additionally, studies dealing with reuse technologies and a feasibility study for a treatment process have been carried out.

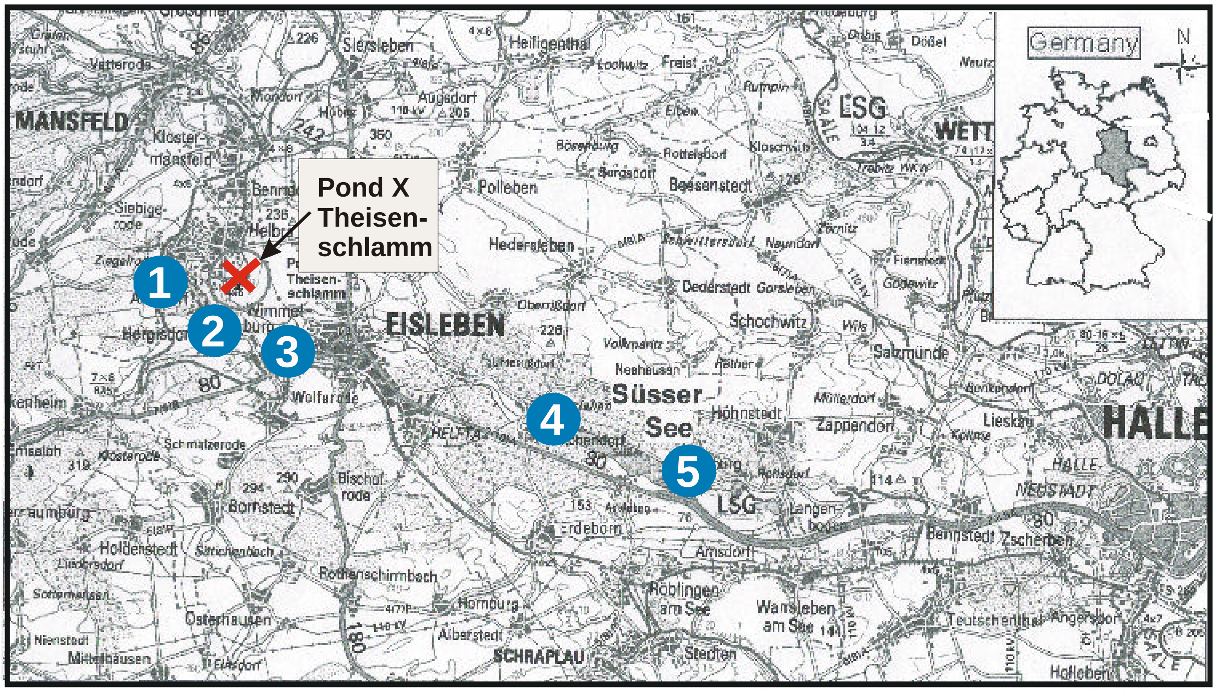

Figure 1: *Map of the Mansfeld Mining Area. Numbers 1-5 are sampling sites, mentioned in chapters 6 and 7. Pond X is the central deposit of Theisenschlamm*

It is anticipated that the present work will not only contribute to the solution of local and regional environmental problems, but also elucidate risk assessment parameters for heavy metal bearing residues posed into the environment elsewhere.

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2. The Mansfeld Copper Smelting Process and the Accumulation of Theisenschlamm

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Copper shale mining in the Mansfeld region

The spoilheaps and slag heaps from mining and the metallurgical industry in the Mansfeld and Sangerhausen region are relicts of the extraction of copper here for almost 1,000 years. Beginning with plain gathering of the ore at its outcrop, and continuing with trail pits on the edge of the Mansfeld syncline and the construction of a main gallery for water handling and regulation, mining in the Mansfeld syncline and the Sangerhausen region experienced its heyday with deep mining in the 1950s and 1960s, before finally being closed down in 1990.

Copper is thought to have been first used in the Mansfeld region in around 1700 BC. This is indicated by the numerous bronze finds in the district from the eastern foothills of the Harz mountains to the area of Halle-Dieskau dating back to 1700–1600 BC and attributed to local production (MARSCHALL, 1981). More information about the 800-year history of copper extraction and processing in the Mansfeld syncline and the Sangerhausen district is available elsewhere (JANKOWSKI, 1995).

Ore extraction in the Sangerhausen district had been stopped in 1885 owing to the prohibitive costs involved. However, in 1951 the ore extraction was shifted again from the Mansfeld region to the Sangerhausen district and the end of Mansfeld as the centre of the non-ferrous metallurgical industry was put off. Activities finally ceased in 1990 when extraction was terminated in the Sangerhausen mines and the smelting furnaces for the production of low-grade matte in Helbra were demolished. However, numerous spoilheaps and slag heaps as well as a considerable number of waste dumps remain. These 'monuments' to technological development contain modest reserves of metals and other raw materials.

Copper shale

The copper deposits first mentioned in around 1200 are morphologically bounded by the Harz foothills, the hills between Halle and Hettstedt, the Hornburger Sattel, the Kyffhäuser mountains, and the range of hills of the Schmücke and the Hohe Schrecke. The out-cropping copper shale at the above-mentioned boundaries dips with 3–8° towards the centre of the syncline and is covered by the thick carbonate, sulphate and chloride rock of the Permian Zechstein, sandstone, claystone and limestone of Triassic age, as well as sands and gravel's from the Tertiary and Quaternary. The entire series of strata above the copper shale can be up to 1,000 m thick. The whole sequence is cut by numerous faults with displacements ranging from a few centimetres to over 1,000m.

The copper shale is a laminated fine-grained, bituminous marl with an average thickness of 35 – 40 cm. The seam contains a large number of sulphidic ore minerals in various quantities in the form of granules, flasers and lenses surrounded by gangue (KNITSCHKE, 1995). In geological terms it can be classified as sediment rock, which petrographically is defined as carbonaceous slate. The main mineral components of the gangue are listed in Table 1 (AK MANSFELD, 1999).

Table 1: *Mineral analysis of Mansfeld copper shale*

Calcite	$CaCO_3$	41 %
Dolomite	$CaMg[(CO_3)]_2$	
Gypsum	$CaSO_4$	
Anhydrite	$CaSO_4 * 2\ H_2O$	
Quartz	SiO_2	5 %
Feldspar	$KAlSi_3O_8$	7 %
Kaolinite	$Al_2[(OH)_4][Si_2O_5]$	5 %
Sericite	$KAl_2[(OH,F)_2/AlSi_3O_{10}]$	2 %
Silica gel	$(SiO_2)_m * nH_2O$	29 %
Organic substances	$C_xH_yO_z$	9 %
Metal sulphides and trace elements	MeS	2 %

The distribution (AK Mansfeld, 1999) of metals in the shale stocks depends on several factors. As the profile from foot wall to hanging wall in Figure 1 indicates, the shale seam ("Flöz") is followed by low and unmineralized marl layers ("Dachklotz" and "Fäule") and Permian limestone ("Bankkalk").

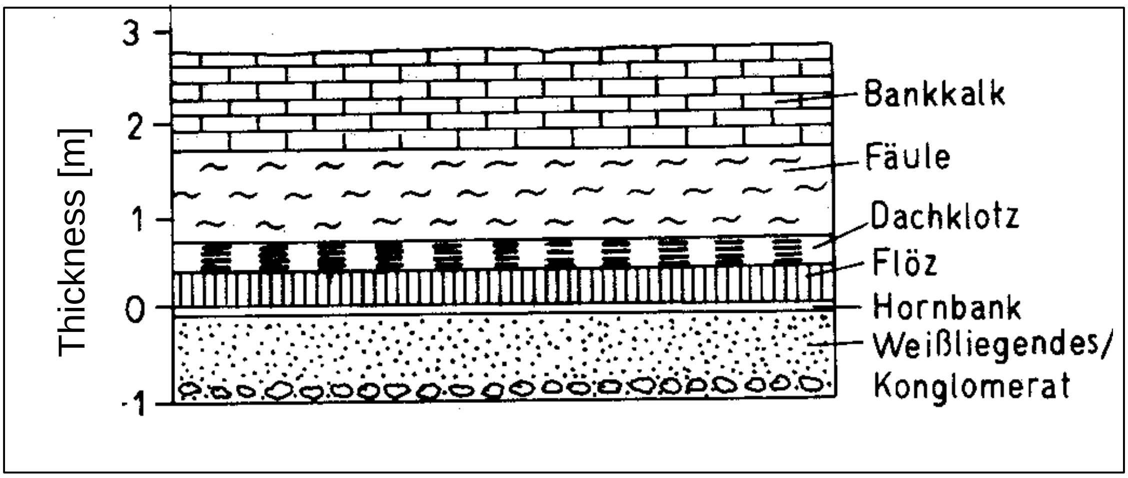


Figure 1: *Stratigraphic section of the shale (VOLKMANN et al., 2000)*

The elemental composition varies throughout the deposit depending on depth and faults, as shown in Table 2.

Table 2: *Quantitative details of main and trace elements in copper shale (KNITZSCHKE, 1961)*

	Cu	Pb	Zn	As	Cd	Hg	Ni	Co	Se	V	Mo	Tl	Ag	Ge	Re	Te	Sb	Bi
	g/kg			mg/kg														
Dachklotz	1.4	1.4	1.8	22	5	<2	37	16	5	74	43	3	9	8	20	<3	<10	<2
Schwarze Berge	2.3	4	5	74	8	<3	61	28	8	141	73	6	14	8	21	<3	10	<2
Schieferkopf	6.9	5.7	13	87	20	3	78	46	20	315	119	7	36	8	21	3	11	2
Kammschale	18	7.6	17	146	29	3	111	86	34	751	253	15	107	8	21	3	12	2
Coarse Lette	29	8.6	19	327	34	3	140	144	48	914	308	13	191	9	21	3	30	3
Fine Lette	26	6,1	9,6	855	18	3	147	159	48	877	251	20	183	9	21	3	44	2
Sand ore	30	8,4	10	162	45	<2	90	102	13	115	79	14	147	8	22	<3	45	<2

The metals are mainly incorporated in the copper shale in the form of sulphides. Beside the economically important metals copper and silver, the shale also contains several other useful metals such as lead, zinc, cobalt, nickel, vanadium, molybdenum, selenium, rhenium, cadmium, thallium, and germanium. Moreover, tellurium, arsenic, antimony, mercury and bismuth as well as gold, platinum and palladium have all been extracted at times.

The main ore minerals found are:

- Bornite (Cu_5FeS_4)
- Neodigenite (Cu_9S_5)
- Native silver
- Chalcosine (Cu_2S)
- Tennantite ($Cu_{12}As_4S_{13}$)
- Sphalerite (ZnS)
- Marcasite (FeS_2)
- Chalcopyrite ($CuFeS_2$)
- Tetrahedrite ($Cu_{12}Sb_4S_{13}$)
- Galenite (PbS)
- Covellite (CuS)
- Idaite (Cu_5FeS_6)
- Pyrite (FeS_2)

The following trace minerals are also to be found:

- Pyrrhotite (FeS)
- Enargite (Cu_3AsS)
- Linneite (Co_3S_4)
- Bravoite ($(Ni, Fe, Co)S_2$)
- Safflorite ($CoAs_2$)
- Native bismuth
- Molybdenite (MoS_2)
- Arsenopyrite ($FeAsS$)
- Stromeyerite ($Cu_2S \cdot Ag_2S$)
- Millerite (NiS)
- Nickelite ($NiAs$)
- Maucherite (Ni_4As_3)
- Uraninite (UO_2)
- Castaingite ($CuS \cdot 2MoS_2$)

In the deposit's zone of Rote Fäule, the copper shale additionally contains the oxidic ore minerals hematite (Fe_2O_3) and magnetite (Fe_3O_4).

A special feature of the gangue in both the Mansfeld syncline and the Sangerhausen district is the bitumen fraction. These partly anthracite-like, partly bituminous carbon compounds interfere with the smelting process and necessitate higher furnace temperature. Both the bitumen fraction and higher furnace temperatures led to a reducing furnace atmosphere, causing effects such as the (undesired) by-production of sows ("Eisensau") in the smelter process.

Mining, transport and treatment of the ore

The methods used for copper shale mining changed several times during the 800-year history of mining. Whereas wedge picks, hammers and mallets were originally used, black powder was first employed in the early 18th century. The introduction of steam power into mining in 1785 opened up new possibilities. A further step was taken when dynamite was used for the first time in 1866. The usage of compressed air allowed deeper parts of the deposit to be exploited. Productivity was boosted in the early 20th century by technical innovations based on electricity. After 1949, great efforts were made to mechanise ore extraction.

The main aim was always to minimise the proportion of barren rock. When manual extraction was still practised, the barren rock was sometimes used as stowage or even left where it was found. However, mechanisation increased the proportion of barren rock. To avoid smelting the barren rock, sorting took place at the surface. Problematic geological conditions, rising demand and inefficiency finally resulted in ore production being halted in 1960 in the Mansfeld syncline and shifted to the Sangerhausen district.

Enrichment trials using float-and-sink analysis and flotation were not as successful as had been hoped, subsequently the first enrichment stage of the ore consisted in smelting on low-grade matte in the blast furnace.

Ore was transported by rail from the shafts in the Sangerhausen district to the smelting works in Helbra. Mineral processing comprised primary crushing, followed by riddling and sizing. The riddled fine ore was compressed into circular briquettes accounting for 25–35% of the total burden.

The smelting process

Over the centuries, the procedure developed for smelting copper from ore was mainly shaped by the specific features of the deposit. Its basic characteristics remained unchanged as of the 16th century.

As mentioned above, the shale contained a considerable fraction of organically bound carbon, which was removed prior to smelting by combustion. For this purpose, the ore was stacked on piles of brushwood in special burning areas belonging to the smelting works. The piles were 1.5 – 2 m wide and tall, and up to 30 m long, enabling some 50 – 200 tonnes of shale to be burned. The piles were ignited on the side facing away from the wind. The fire then spread to the shale and a smouldering fire developed which lasted for between two and four months, depending on the quality of the ore and the weather conditions. This burning process led to pyrolytic decomposition within the ore particles.

The reactor most commonly used in the metallurgical industry for smelting metals and to remove a large proportion of impurity elements is the blast furnace. Using the principle of a two- or three-phase moving grate reactor, it comes in a wide variety of different designs depending on the material to be smelted. The principle of the blast furnace was developed back in the Bronze Age (3300–1800 BC) for copper and tin production. The fuels used were mainly wood, charcoal or coke; nowadays blast furnaces can also be fired by oil and gas.

For smelting copper matte, over the centuries a blast furnace with continuous smelting proved most suitable. In contrast to blast furnaces used in the iron and steel industry where the molten metal is removed discontinuously (crucible melting), copper smelting involves the continuous movement of a mixture of matte, slag and sows from the melting pot into a settler, where separation takes place due to the different solubilities.

Most copper deposits (including those occurring in the Mansfeld syncline and the Sangerhausen district) are in the form of sulphide ores. Direct smelting to copper is unprofitable and entails high losses. As the ore usually contains low levels of copper, preceding the actual process of copper production by enrichment smelting has proved expedient. In this stage, a sulphide product known as matte is made which contains all the copper fractions. In the majority of copper deposits, iron is also contained in the sulphidic minerals. Other elements include lead, tin, zinc and antimony. The ratio between copper and sulphur is important in the enrichment process. A high proportion of sulphur in the melt enables the complete sulphidising of the copper to form Cu_2S, and hence to the reduced slagging of the copper.

When mining ore at greater depths became possible in the late sixties of the 19th century, new smelting capacities had to be built. In 1870, a blast furnace with a diameter of 1.9 m and a height of 9.5 m went into operation for the first time in Eisleben at the Krug smelter. Its daily ore capacity of 120 – 130 tonnes was about seven times greater than that of the smelting works near Leimbach opened in 1856.

In 1900 the Krug smelter consisted of 5 furnaces, which were subsequently expanded to a diameter of 2.2 m and converted to continuous smelting, increasing the throughput of ore and fluxes to 200 t/d. These technological modifications had a number of consequences. One was the increasing accumulation of blast furnace gas.

This oxygen-free gas contains chemically equal amounts of carbon monoxide and carbon dioxide plus the carbonate-CO_2 and nitrogen introduced. The volume produced is about 1.15 times the amount of air blasted in. Previously the blast furnace gas had been blown directly from the furnace top (sometimes it was burnt off) into the atmosphere. However, the quantities of waste gas now accumulating, which owing to the higher quantities were partly burned immediately above the charge column in the furnace, made working on the furnace top impossible. This development led to the gases being discharged beneath the furnace top from the upper section of the shaft.

In 1874, the blast furnace gases were burned in the steam boilers for the first time. In 1876, they also began to be used to pre-heat the air. The high percentage of carbon monoxide in the blast furnace gases as well as the experience gathered in using energy in the waste gas led in 1904 to the construction of the "blast furnace gas centre" at Krug smelter in Eisleben.

Gas washing at Krug smelter was carried out with two gas washers with a capacity of 6,500 m^3/h using the Theisen system. One year later in 1905, the gas-washing capacity was increased by retrofitting two scrubbers manufactured by Zschocke (LORENZ, 1994).

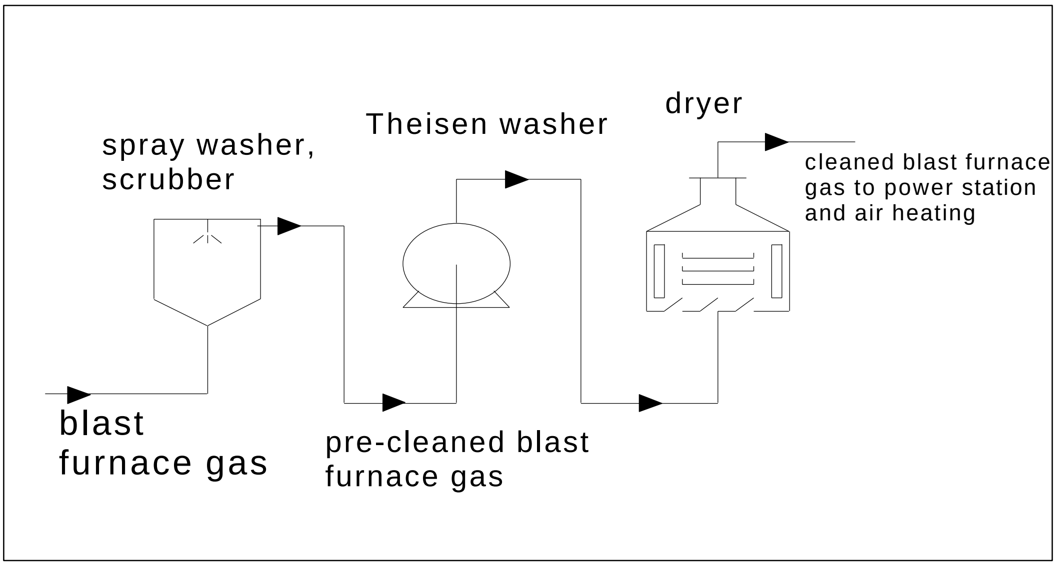


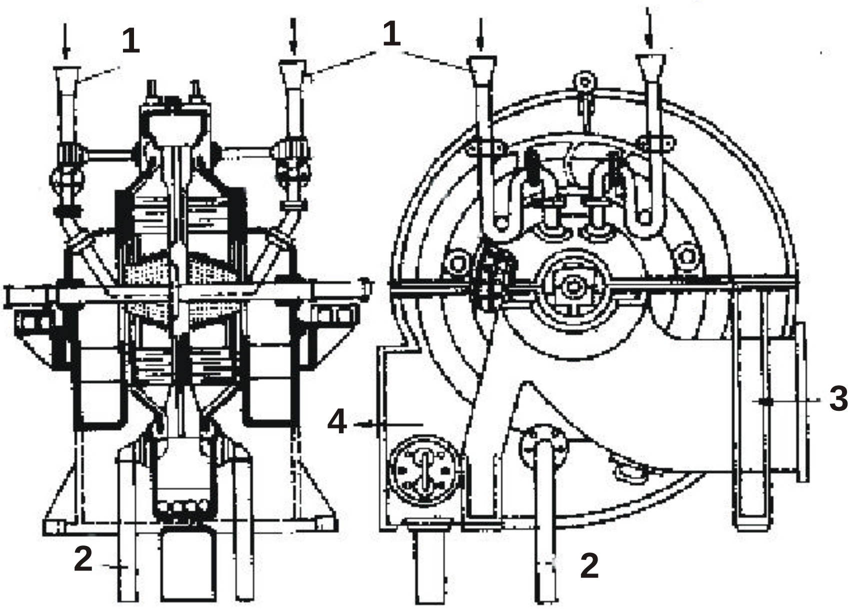
Figure 2: *Flow diagram of waste gas scrubbing*

The large amount of air blasted into the furnaces increased the proportion of flue dust proportionately. In order to achieve optimum combustion for both steam generation and to pre-heat the air, the blast furnace gas needed to be treated.

During the first phase of development when relatively little air was blasted into the furnace, the horizontal separation and the washing effect of the Theisen washer purified the gas sufficiently for further usage. However, the drastic increase in the amount of air used naturally caused more flue dust to be ejected with a greater particle size. The need to treat this broad grain-size range in the flue dust soon prompted the decision to install a scrubber between the gas pipeline for horizontal separation and the washer. This also had the advantage of inducing a quenching effect in the gas, causing the temperature to drop by more than 100°. This gas-purification technology introduced back in 1906/1907 was mainly used at the Koch and Krug smelting works until they were closed down.

Whereas the (primary) flue dust in the funnels of the classifiers could be immediately returned to the production process (e.g. by means of briquetting, sintering, mixing it with the ground ore, etc.), the sludge from the scrubber and the washer first had to be thickened.

The Theisen washer worked by producing a low pressure in the waste gas area while simultaneously spraying and scrubbing the gas. The low pressure was created by a system of blades on five rings. Owing to the angular arrangement of the blades, the necessary low pressure was generated when the rings were rotated. Two blade systems positioned laterally on the shaft created the necessary turbulence in the spray water (cf. Figure 3).



Desintegrator: 1 water inlet; 2 water drain-off
3 gas inlet; 4 gas outlet

Figure 3: *Theisen washer*

The gas emerging from the primary washer was conducted through two right-angled pipes (regulated using butterfly valves) to the small external blade rings which were located on the rotor shaft and powered by motors. Water was injected through openings in the casing lid. Upon hitting the blade ring, the jet created an powerful veil of water with a cleaning effect exceeding 99 percent. In the washer itself, the flow of gas was centred from the two lateral intake openings towards the central outlet.

The cleaning water flowed through the conical outlets into the wastewater channels below the gas washer. The channels converged into the main channel, which transported the sludgy water into the conical tank system for separation. The conical tank system reduced the flow speed by increasing the volume. For this purpose, part of the stream was diverted out of the channel by a flap valve and conducted through a downpipe into a stilling chamber of the conical steel tank. The stilling chamber had an opening to allow the water to flow out.

The flue dust precipitated in the cone was regularly pumped off and transferred to a sedimentation tank, where the water content was reduced to about 30%. The compacted sludge was named Theisenschlamm after the inventor of the dust washer.

Theisenschlamm

Melting matte of copper using the Mansfeld blast furnace process resulted in the following products:

Matte of copper Cu_2S*FeS – target product		3.5%
Slag		73.0%
Sows		1.0%
Flue dust →	Primary flue dust	1.5%
→	Secondary flue dust → Theisenschlamm	
Blast furnace gas		21.0%

Theisenschlamm is in fact a by-product which only accounts for a small fraction of the total production quantity. In its heyday, for example, smelting performance in Mansfeld was as high as 3,800 tonnes per day, whereas only a few tonnes of Theisenschlamm were produced daily. The proportion accounted for by flue gas and hence Theisenschlamm varied over the years and depended on a number of factors such as:

- Furnace construction
- Air quantity
- Air temperature
- Quality of ores (share of fine fraction)
- Composition of ores

Consequently, analyses of Theisenschlamm over the years have substantially differed. In line with the technological processes listed above, Theisenschlamm is a mixture of very fine-grained bituminous particles which can be precipitated and washed out of the untreated gas by chemical reactions, condensation, crystallisation and moistening with scrubbing water.

Since the Theisen washer first went into operation in 1904 at the Krug smelter in Eisleben, the Krug and Koch smelters were successively upgraded. This process continued until 1956, when the number of gas washers at the Koch smelter was increased from three to five. At the same time, ways of using Theisenschlamm were also sought. Although lead and zinc are the main components of Theisenschlamm, it also contains other valuable metals. Its complex composition makes the economic extraction of its high-quality products a tough challenge for metallurgy.

After the new gas washer was completed in 1922 at the Krug smelter in Eisleben, it was followed in 1923 by the erection of first one low-temperature carbonisation drum at the lead works, and then another in 1926 at the Krug smelter. In the following years, Theisenschlamm was pre-treated in low-temperature carbonisation drums before being sintered. In 1934, after the experiments into lead sulphide evaporation from Theisenschlamm and low-temperature carbonisation residue in a rotary furnace had shown positive results, the entire process of Theisenschlamm treatment was switched to the differential evaporation of lead and zinc. However, this approach was abandoned in 1936.

The new technique for smelting Theisenschlamm and low-temperature carbonisation residue comprised phased pelleting, mixing the zinc clinker with lead blast furnace slag granules, and the fractionation of the flue dust to form various lead oxides (LORENZ, 1994). Until rolling operation was discontinued at the lead works in Hettstedt in 1978 for environmental reasons, rhenium, cadmium, raw lead, white vitriol, zinc oxide and sludge containing lead, zinc and germanium were all obtained from Theisenschlamm. Some of these products in turn served as raw material for the production of zinc and germanium.

Storage since 1978

The production of matte at the Koch works in Helbra continued undiminished after rolling operation had been shut down at the lead works in Hettstedt. In fact ore mining and treatment reached their highest level ever in the first quarter of the 1980s. Air quantities of up to 15,000 m³/h and furnaces with daily capacities exceeding 400 tonnes each were common.

In 1978, despite the shutdown of the rolling furnace line in Hettstedt, the dried Theisenschlamm continued to be carbonised for one year. Some 60,000 tonnes of low-temperature carbonisation residue had been dumped on the waste heaps. This quantity still remains at the Koch smelter at the time of writing (July 2001); in 1992 it was secured by covering it with geo-textile.

After low-temperature carbonisation had been shut down, sludge basins 1 – 6 were filled with Theisenschlamm suspension. This was followed by two basins set up on the slag as Ponds VII and VIII as well as Pond IX. All in all, some 104,500 m³ of Theisenschlamm was deposited in the basins, which was then transferred to the unsecured Pond X (BISANTECH, 1996). Parallel to Ponds VII – IX being filled, a Theisenschlamm basin was planned and built on the dump at Walter Schneider shaft, which with a volume of 350,000 m³ had a sufficient storage capacity.

At this time, both selling the Theisenschlamm and erecting a new lead and zinc works were discussed. However, the proposed new plant was not built after all, owing to technical and financial reasons.

Processing Theisenschlamm

Up until 1978 and beyond, there was no lack of activities and attempts to use the metals contained in the dumped Theisenschlamm, especially when some of these metals rose exponentially in price. However, in addition to the fundamental possibility of treating Theisenschlamm, a number of environmental, safety and economic aspects argue against its treatment. This was extensively highlighted by STEINKAMM (1994), whose findings are dealt with below.

Until production ceased at the lead works in Hettstedt, raw lead, cadmium, zinc oxide, white vitriol, rhenium, raw selenium and germanium concentrate were all produced here. In the period from 1978 until the plant in Helbra was shut down 12 years later, 220,000 tonnes of sludge accumulated.

Numerous elements and compounds, some of which must be classified as hazardous substances, hamper treatment, as aspects such as purity/substance quality, labour safety and environmental protection cause disproportionately high demands. The hazardous substances concerned include dioxin, sulphur compounds, bitumen and its cleavage products, halogens, thallium, cadmium, arsenic, mercury and bismuth, as well as radio nuclides.

Total monetary valuation is only possible for limited periods owing to the sharp price fluctuations of the main metals zinc and lead. For example, the price of rhenium per gram was DM 2.50 in 1993, but by 2000 had risen to DM 10–15.

Despite the many factors which argue against treating Theisenschlamm, there are numerous proposals for how it can and should be processed. Table 3 contains a survey of the various methods developed in recent decades.

Table 3: *Proposed methods for Theisenschlamm (internal documents of the Mansfeld Kombinat and references in the literature)*

Method	**Institution**	**Period**	**Results**
Flotation treatment	Forschungsinstitut für Aufbereitung, Freiberg	1980–85	Negative overall balance
Sulphuric acid pressure leaching	Berzelius-Metallhütten GmbH Duisburg	1983	Negative overall balance
Roasting in a fluidised bed	Forschungsinstut für Nichteisenmetalle, Freiberg; Mansfeld Kombinat Eisleben	1982	Technically suitable but uneconomic
Roasting in a circulating fluidised bed	LURGI – Frankfurt / Main	1990	Technically suitable but uneconomic
Flash smelting	Bergakademie Freiberg Institut für Metallhüttenwesen	1958/59	Technically suitable, stringent environ. conditions
Kaldo process	Boliden AB, Mannesmann-Demag	1984	Technically suitable but uneconomic
Smelting in a fluid trough	Research department of Mansfeld Kombinat Eisleben	1986	Technically possible
Oxidising acidic pressure leaching followed by extraction (GOCK & SÖTEMANN, 1993)	Institut für Aubereitung der TU Clausthal, Sanierungsverbund e.V. Mansfeld	1993	Technically possible
Modified base-catalysed detoxification (AK Mansfeld, 1994)	ASG GmbH, Australia	1993	Technically possible
Theisenschlamm oxidation process (MORENCY et al., 1998)	UFZ-Umweltforschungszentrum Leipzig-Halle GmbH, Université de Québec à Montréal	1998	Technically possible

Irrespective of whether there is an economic way of treating Theisenschlamm, the environmental impact persists to both the air and water by the dump in Pond X as well as the risk of scraps of mixed material surrounding the site. Consequently, action still urgently needs to be taken.

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3. Chemical Characterization of Theisenschlamm

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Abstract

The predominant elements in Theisenschlamm are Pb, Zn, and S, typically surpassing 10 % w/w each. The content of highly toxic elements such as As, Sb, Cd, and Hg are remarkable as well as those of economical interest, e.g. Re and Ag. A four-step extraction procedure of the Theisenschlamm shows that most of the elements have a high mobilization potential under natural conditions.

The organic constituents of the Theisenschlamm are mainly higher boiling polyaromatics, biphenyls, and dibenzofurane derivatives. The dioxine (PCDD/PCDF) concentration is not alarming. Some relative ratios of individual polyaromatic hydrocarbons in Theisenschlamm are distinctly different from those in the initial ore, the Kupferschiefer, and can be used as indicators for uncontrolled release of Theisenschlamm into the (aqueous) environment.

Element contents

Theisenschlamm contains various heavy metals in high concentrations. Table 1 shows the values for each element as well as the analytical technique used for its determination (experimental details see WEISS et al., 1997). Standard deviations in all cases do not exceed 10% of the reported value using 3 samples taken at one site.

Compared with the reported concentration values in the original Kupferschiefer samples (HAMMER et al., 1990) of 87 – 12,100 µg/g zinc, 90 – 21,000 µg/g lead and 2.5 – 2,000 µg/g arsenic, the enrichments of these elements are considerable in the Theisenschlamm.

The most striking feature of the analysis is that Pb, Zn and S are the predominant elements in the Theisenschlamm, typically surpassing 10%(w/w) each. Those elements which are usually included in silicate phases, such as Si, K, Ca, Al etc. are present in much smaller quantities. The content of highly toxic elements such as As, Sb, Cd and Hg is remarkable, (Table 1). Elements of a potential economic interest are also present, particularly the elevated content of Re or Ag with 63 µg/g and 510 µg/g respectively.

Table 1: *Chemical analyses for a representative sample of the Theisenschlamm Methods: 1 = XRF pellet; 2 = ICP-AES after aqua regia elution; 3 = XRF fusion; 4 = LECO technique*

Element	Conc. (µg/g)	Method	Element	Conc. (µg/g)	Method
Ag	510	2	Mn	930	3
Al	13,380	3	Mo	590	3
As	3,800	2	Na	1,100	2
B	230	2	Ni	130	1
Ba	580	1	Pb	143,000	3
Bi	165	2	Re	63	2
Ca	7,200	1	Sb	1,470	2
Cd	435	1	Se	720	2
Co	137	1	Si	79,500	3
Cr	130	3	Sn	11,600	1
Cu	13,200	3	Ti	840	1
Fe	12,700	1	V	220	1
Ge	31	2	Zn	193,000	3
Hg	100	1	Zr	810	1
K	9,380	1	C_{total}	82,000	4
Mg	6,030	3	S_{total}	113,000	4

However there are significant differences in the composition of the materials taken from different sampling points. As shown in Table 2 the concentration of elements of interest could be varied between few and more that 100% analysing samples taken from three different sites.

Table 2 : *Variation of the elemental composition of Theisenschlamm samples after aqua regia elution of three different samples (mean ± SD; ICP-AES and ICP-MS* data)*

Element	Concentration [µg/g]	Element	Concentration [µg/g]	Element	Concentration [µg/g]
As	5,060 ± 1,100	Cd*	340 ± 14	Cr	320 ± 495
Cu	10,900 ± 1,420	Mn	440 ± 46	Ni	230 ± 240
Pb	35,200 ± 4,800	Mo*	530 ± 105	U*	22 ± 7
Zn	208,000 ± 33,400	S	143,500 ± 27,400		

Traditionally, in most studies dealing with the heavy metal analysis total contents of elements in the sample were considered. However, the mobility and bioavailability of metals depend strongly on their chemical form and type of binding. Consequently, the data on total contents of elements are quite insufficient to estimate the possible risk of remobilization of heavy metals under changing environmental conditions and potential uptake of liberated metals by biota. Thus, procedures for distinguishing different forms of heavy metals are required. In recent years a great number of papers have been published on various analytical techniques proposed for the fractionation analysis of trace elements in various environmental samples (soils, sediments, etc.). An approach that has been found to be preferable is the fractionation of trace metals into operationally defined forms under the sequential action of different extractants *(*TESSIER et al*.,* 1979*)*. Selective extractants, used in the sequential extraction procedures, are aimed at the simulation of natural conditions whereby metals associated with certain soil (sediment) components can be released. For example, changes in the ionic strength affecting adsorption-desorption reactions or a decrease in pH may lead to the release of metals, retained on a matrix by weak electrostatic interactions or co-precipitated with carbonates ("exchangeable" and "acid soluble" forms). Decreasing the redox potential can result in dissolution of oxides, unstable under reducing conditions, and liberation of scavenged metals ("reducible" forms). Changes in oxidizing conditions may cause the degradation of organic matter and release of complexed metals ("oxidizable" form). Finally, the destruction of primary and secondary mineral lattice releases heavy metals retained within the crystal structure e.g. due to isomorphous substitution ("residual" form) .The sequential extraction provides more detailed information on the origin, biological and physicochemical bioavailability, mobilization and transport of heavy metals. The nominal "forms" determined by operational fractionation can help to estimate the amounts of heavy metals in different reservoirs which could be mobilized under changes in chemical properties of soil *(*DAVIDSON et al., 1998*)*.

For estimation of long-term impact on groundwater from Theisenschlamm the established four stage sequential extraction by SCHOER and FOERSTNER (1987) was used. Briefly, the scheme was used to differentiate between the exchangeable fraction (S1: soluble in 1M NH_4COOH) the reducible fraction (S2: soluble in 0.4 M $(NH_4)_2C_2O_2$, the oxidable fraction (S3: soluble in 30% v/v H_2O_2 at pH=2) and the residual fraction (S4: soluble in hot $HNO_{3\ conc.}$).

As shown in Figure1 (log scale) comparing the sum (S1-S4) of concentration leached in the different steps and the total concentration in the solid material (XRF data) most of the tested elements (with exception of V) are mobilizable higher than 70 % within this procedure. In the exchangeable fraction relatively high amounts of sulfur (11%), nickel (12%), manganese (14%) and lead (9%) are soluble. After step S3 are 81% of sulfur, 84% of lead and 93% of cadmium removed from the original material. That means there is a high risk to mobilize these elements under natural conditions. On the other hand the mobilization of As (20%), V (14%), Cu (4%), and Mo (3%) is relatively low. These elements are mainly soluble by nitric acid only (S4).

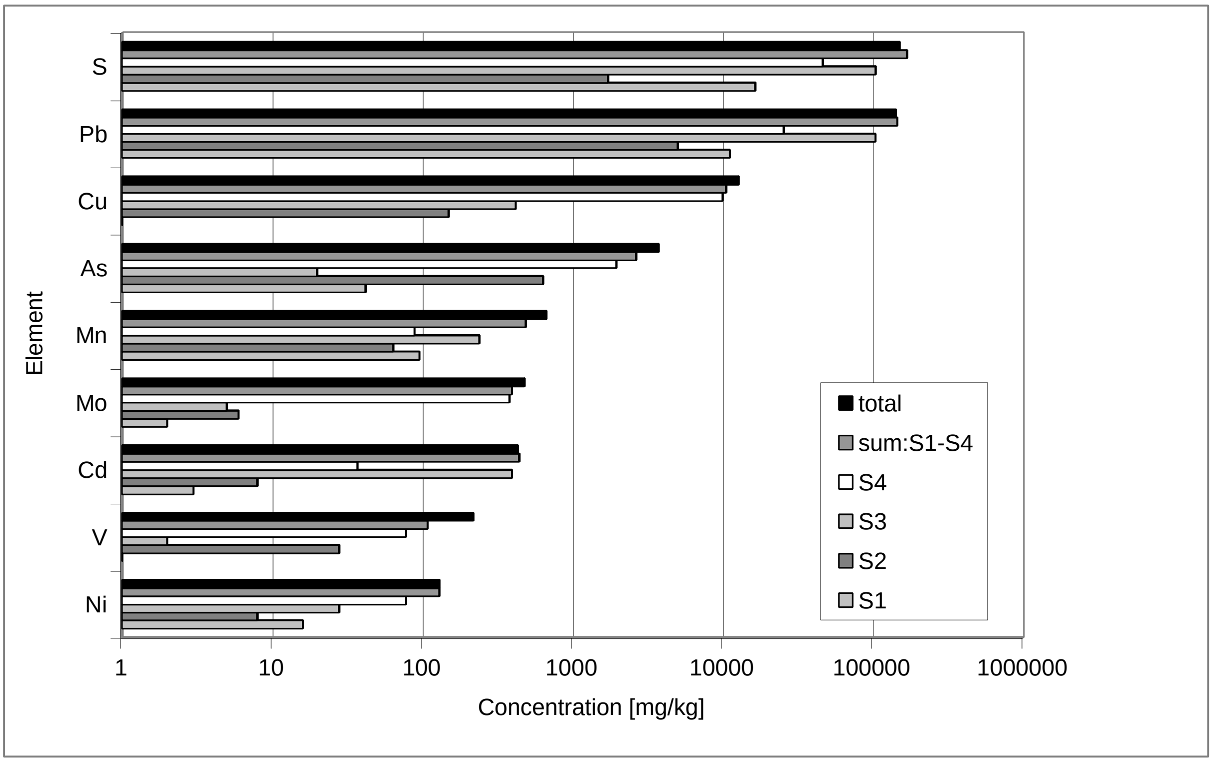

Figure 1: Comparison of extraction yields from different leaching steps (see text for explanation)

Although the Theisenschlamm is quite properly viewed as an environmental hazard, it should also be viewed as a metal resource, especially when the contents of elements like Ag, Ge and Re are taken into account.

Concentrations of selected organic priority pollutants

Investigations on individual organic substance classes in Theisenschlamm are not available from literature. However, the initial mineral, Kupferschiefer, contains a bituminous fraction of 5 – 15%(w/w), which mainly consists of asphalathenes, polyaromatic hydrocarbons and resins (HAMMER et al. 1988). It is clear that the major part of this organic matter undergoes pyrolytic decomposition and rearrangement during the smelting process, followed by volatilisation and condensation of conversion products in the scrubber dust.

Using gas chromatography/mass spectrometry the organic substances present in a Soxhlet extract of Theisenschlamm were classified into groups of compounds (see WEISS et al., 1997 for more details). Table 3 summarises the semi-quantitative results as peak area counts per gram sample.

The Theisenschlamm contains only a few volatile organic compounds, such as the methyl- and dimethylbenzene, remain in the matrix despite ageing and weathering due to strong adsorption. The main part of the hydrocarbons is a mixture of polyaromatic compounds with a higher boiling point, however additional alkylated homologues and partially hydrogenated aromatics were also detected, as were some hydroxy-aromatics and O-heterocyclic compounds, quinoline and/or isoquinoline as well as dibenzothiophene derivatives.

Table 3: *Results of GC/MS identifications of organic compounds in the Theisenschlamm*

Compound (class)	Relative concentrations, area/g sample
Alkanes	4,927,739
Polycyclic aromatics	21,691,242
Benzene derivatives	415,116
Naphthaline derivatives	1,860,532
Biphenyles and/or dibenzofuranes	20,674,225
Diphenylethanes	traces
Quinoline and/or Isoquinoline derivatives	24,969
Aromatic amines	n.d.
Dibenzothiophene derivatives	5,672,415
Fluorenone-9	431,204
Benzenemethanol	43,781
Stryene	34,166

n.d.: not detectable to a limit of approx. 5 - 10 ng/component (full scan mode)

Results of the determination of the concentrations of polycyclic aromatic hydrocarbons (PAH) according to EPA 610 (experimental details see WEISS et al., 1997) are presented in Table 4. The total of the 15 analysed PAHs is 469 mg/kg. This confirms other findings (POPP et al., 1997) in both concentration level and pattern of individual compounds.

Table 4: *PAH concentrations in the Theisenschlamm [µg/g]*

Compound (Abbrev.)	Concentrations, µg/g
Naphtalene	1.9
Acenaphtene	0.3
Fluorene	2.9
Phenanthrene (Phe)	111.7
Anthracene (Ant)	10.7
Fluoranthene (Flu)	71.0
Pyrene (Py)	74.5
Benzo(a)anthracene (BaA)	21.2
Chrysene (Chry)	62.3
Benzo(b)fluoranthene	45.6
Benzo(k)fluoranthene	4.7
Benzo(a)pyrene	18.0
Dibenzo(a,h)anthracene	1.2
Benzo(g,h,i)perylene	31.7
Indo(1,2,3)pyrene	11.2

The PAHs found at high levels in the Theisenschlamm are ubiquitous contaminants. Ratios of individual PAHs found in the samples can be compared with the fingerprints of PAHs from pyrolytic or petrogenic origin to identify the most likely contamination source of specific environmental compartments, e.g. surface water or sediments (BLUMMER & YOUNGBLOOD, 1975; SPORSTOL et al., 1983; SOCLO et al., 2000). The usual index of anthropogenic input (mainly from fuel combustion, here from a specific smelting process) is an increase in the proportion of the thermodynamic less stable parent PAH isomers relative to the more stable isomers (e.g. anthracene relative to phenanthrene, fluoranthene relative to pyrene etc. The PAH ratios in Theisenschlamm (calculated from Table 4) are compared with those derived from Kupferschiefer analyses (POPP & PASCHKE, 2000). Kupferschiefer is characterized by extremely low Ant/Phe ratio of 0.003, low Flt/Py ratio (0.31) and low BaA/Chry ratio (0.1), which allow for clear differentiation of this natural (petrogenic) PAH source from other potential PAH sources. Theisenschlamm exhibits characteristic ratios distinct from those. The Ant/Phe ratio in Theisenschlamm samples is higher (0.096), typical for matter with pyrolytic origin. However, in contrast to such pyrogenic matter, Theisenschlamm is characterized by a BaA/Chry value smaller than one, i.e. 0.34.

A preliminary study (ARBEITSGEMEINSCHAFT TÜV BAYERN/L.U.B., 1991) has revealed the presence of polychlorinated dibenzo-dioxins (PCDD) and -furans (PCDF) in samples of Theisenschlamm. The results of the PCDD/PCDF analysis of an aliquot of the above mentioned Soxhlet extract is listed in Table 5. The sum concentration of each group is shown in µg/kg.

Table 5: *Concentrations of PCDD/PCDF (T=Tetra-, Pe=Penta-, Hx=Hexa-, Hp=Hepta-) in the Theisenschlamm [µg/kg]*

Compound	Concentrations, µg/kg
Sum TCDF	86.0
Sum PeCDF	40.3
Sum HxCDF	10.5
Sum HpCDF	8.4
OCDF	1.4
Sum PCDF	146.6
Sum TCDD	5.9
Sum PeCDD	0.8
Sum HxCDD	1.8
Sum HpCDD	1.9
OCDD	5.5
Sum PCDD	15.8
Sum PCDD/PCDF	**162.4**

The PCDD/PCDF concentration in the Theisenschlamm is 162 µg/kg, corresponding to 171 iTE (International Toxicity Equivalents) per kilogram (KUTZ et al., 1990). This value is considerably lower than that reported by HARNLY et al. (1995), who studied fly ash from copper recovering facilities in California which have PCDD/PCDF concentrations of approximately 510 mg/kg. According to recommendations of the German Federal Minister of Environment (BUNDESMINISTER FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT (ed), 1992) for contaminated soils the Theisenschlamm is not considered hazardous with respect to the PCDD/PCDF content.

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4. Mineralogical and Physical Characterization of Theisenschlamm

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Abstract

A physical and mineralogical description of Theisenschlamm is presented. This material was generated as a by-product during extraction of copper from the Kupferschiefer formation a mineralized Permian black shale in Sachsen-Anhalt, Germany. The Theisenschlamm consists of sulphide grains which are a complex solid solution of Pb, Zn, Cu and Fe. The crystal structures are modified forms of galena and sphalerite/ wurtzite. Variations in the X-ray diffraction peak positions of these minerals reflect the intensive ionic substitution that underwent the lattice structures of these phases. Anglesite is a secondary phase associated with the alteration through oxidation of the lead sulphides in the slurry. The original particles have a median diameter of 1.25 µm, however these particles are themselves aggregates of still smaller particles, typically of sub-micron in size. In this chapter we describe the physical properties of the Theisenschlamm, including the mineralogy, radioactivity and grain size as well as the micro-chemical composition and variation.

X-Ray Diffraction

All inorganic compounds discussed in this chapter are referred to as "minerals", however it is recognized that those which formed rapidly during the smelting process are more properly termed "chemical compounds" since they did not form in a "natural" manner. In particular, zinc sulphides (ZnS) is used here to refer to both naturally occurring sphalerite or wurtzite, as distinguished by X-ray diffraction as well as zinc rich sulphides with a sphalerite-type structure that were produced in the smelter. Similarly galena refers to the naturally occurring mineral lead sulphide (PbS) as well as to the artifically produced Pb rich sulphides, containing other elements such as Zn, Cu and others, in its structure. Anglesite ($PbSO_4$) is similarly employed to describe any lead sulphates.

X-ray diffraction (WEISS et al., 1997) is used to obtain the main mineral phases of the Theisenschlamm. Figure 1 is a diffractogram scan for a Theisenschlamm sample for which the background noise was substracted, otherwise a "camel hump" is present between 2θ = 25° and 2θ = 45° indicating the amorphous fraction for the sample. In other figures, a smoothing of the curve is made for a better presentation of the data. The peak index lines are indicative of the presence of those associated chemical or mineralogical phases given in the captions of the diagram. The predominant phases identified on the diffractogram are a sulphate ($PbSO_4$) as well as the sulphides PbS and ZnS.

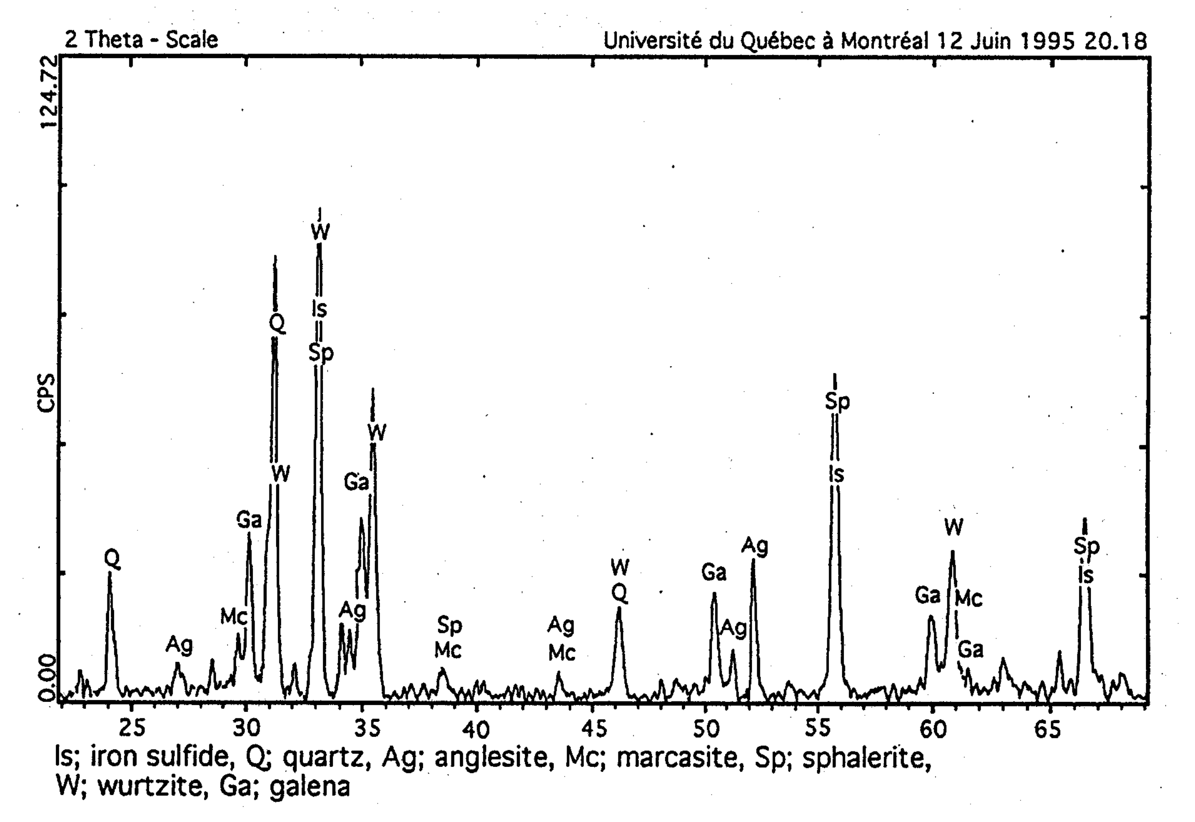

Figure 1: *2q diffractogram scan for Theisenschlamm (Weiss, 1997). The peaks have been indexed using the following code: Is = iron sulphide; Q = quartz; Ag = anglesite; Mc = marcasite; Sp = sphalerite; W = wurtzite; Ga = galena*

Figure 2 is a comparaison between two diffractograms of representative samples of Theisenschlamm. Two features are immediately apparent:

1. The diffractograms are not identical despite the fact that they are splits of the same material. Not only are the positions of the peaks different from one another, but the relative heights also differ. The differences are significant and even the disappearance of some peaks was noted in some diffraction patterns. A similar effect was noted when the powder used to produce the XRD pattern was removed by washing and then remounted.
2. The position of the peaks has been offset with respect to the standard ASTM values for these natural minerals.

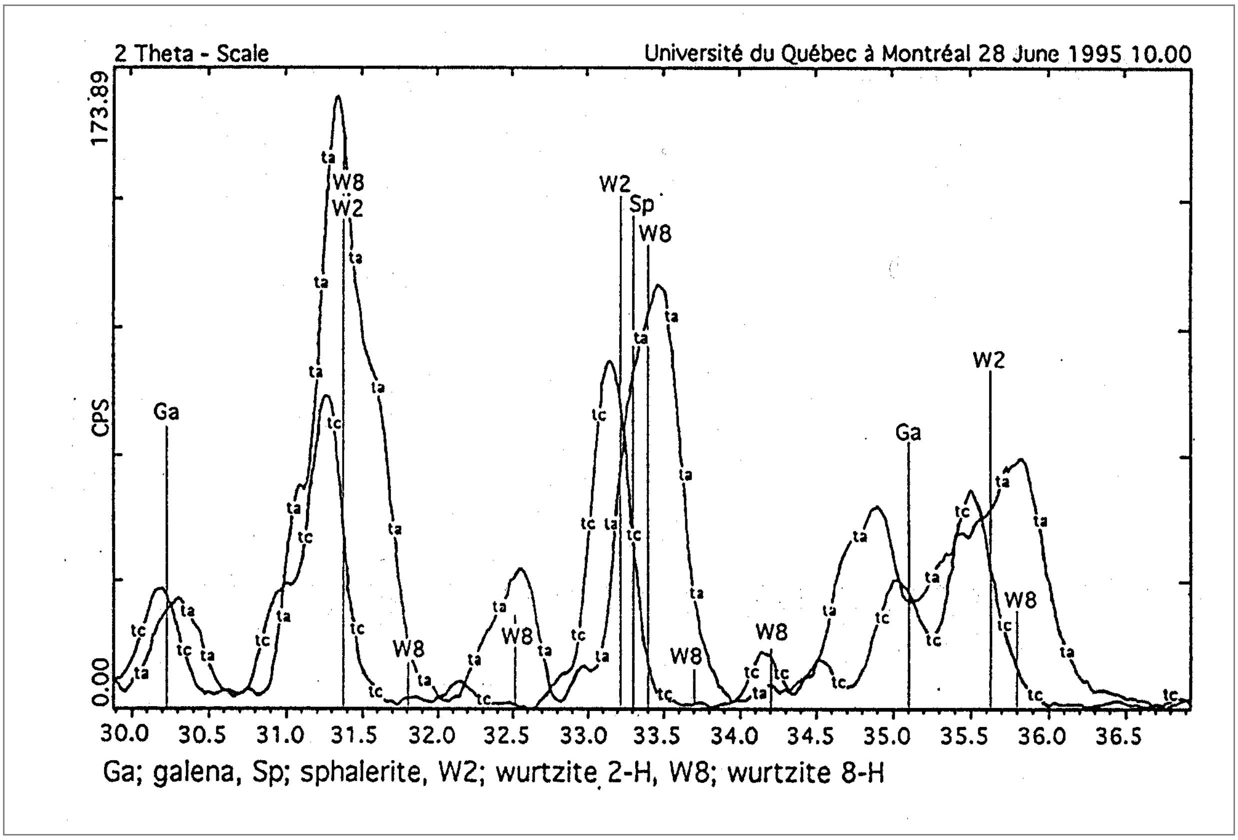

Figure 2: *Enlargement of a portion of a diffractogram for two samples of Theisenschlamm. Legend: Ga = galena; Sp = sphalerite; W2 = wurtzite 2-H; W8 = wurtzite 8-H*

Variation in peak heights can be caused by preferential orientation of particles during the mounting process (DAVIS, 1987; MANIAR & COOKE, 1987), but mounting cannot explain the shift in position of the various peaks. This feature indicates that the Theisenschlamm is an heterogeneous material and must be variable even on the scale of the individual sub-micron sized particle.

In spite of the complexity shown by the individual minor phases, examination of numerous X-ray diffraction patterns of different samples indicated that the mineral abundance calculated for the Theisenschlamm vary within narrow limits. Table 5 gives the approximate concentrations of the major phases in the powder and clearly shows an abundance of sulphides and sulphates. The percentages were determined by calculation of the area under the curve for selected peaks for each mineral and because the peak height variations these values are only semi-quantitative.

Table 5: *Approximate concentration of mineral phases in the Theisenschlamm [vol-%]*

Mineral	Volume %
Wurtzite	19.5
Sphalerite	17.5
Galena	6.9
Anglesite	6.3
Quartz	2.5
Amorphous	38
Others	8

Scanning electron microscopy (SEM) results

The Scanning Electron Microscopy **(**SEM**)** was used to determine the micro-chemical composition and element distribution as well as the texture and size of the different chemical phases. Samples of a dried slurry powder were embedded in a polymer from which a polished section was obtained and coated with either gold or carbon. This sample preparation technique gives a cross section of the component particles and enhances the textural and morphological characteristics of the grain.

Two populations of fragments can be observed on Figure 3a which is an image at low magnification (100x) (WEISS et al., 1997). A bright (white) fraction of variable size consisting of large agglomerates of 100 µm, less frequent spheres of 10 µm and a large population of needle-like grains, typically 5 µm in length by 1 µm wide, which appear on the image as little white spots. The other, darker population consists of gray large irregular shaped agglomerates several hundred microns in size. The texture of the fragments aggregates and/or agglomerates are porous and no uniformly solid grains are evident.

The analytical spectrum for the bright fraction is represented on Figure 3b and shows the presence of significant Pb with lesser amounts of Zn and Si and minor amounts of other elements. This is interpreted to be indicative of the presence of lead sulphide, which has also incorporated some Zn. The remaining elements of the spectrum could either originate from the filled interstices of the fragment or from the a signal coming from below the thin analyzing surface.

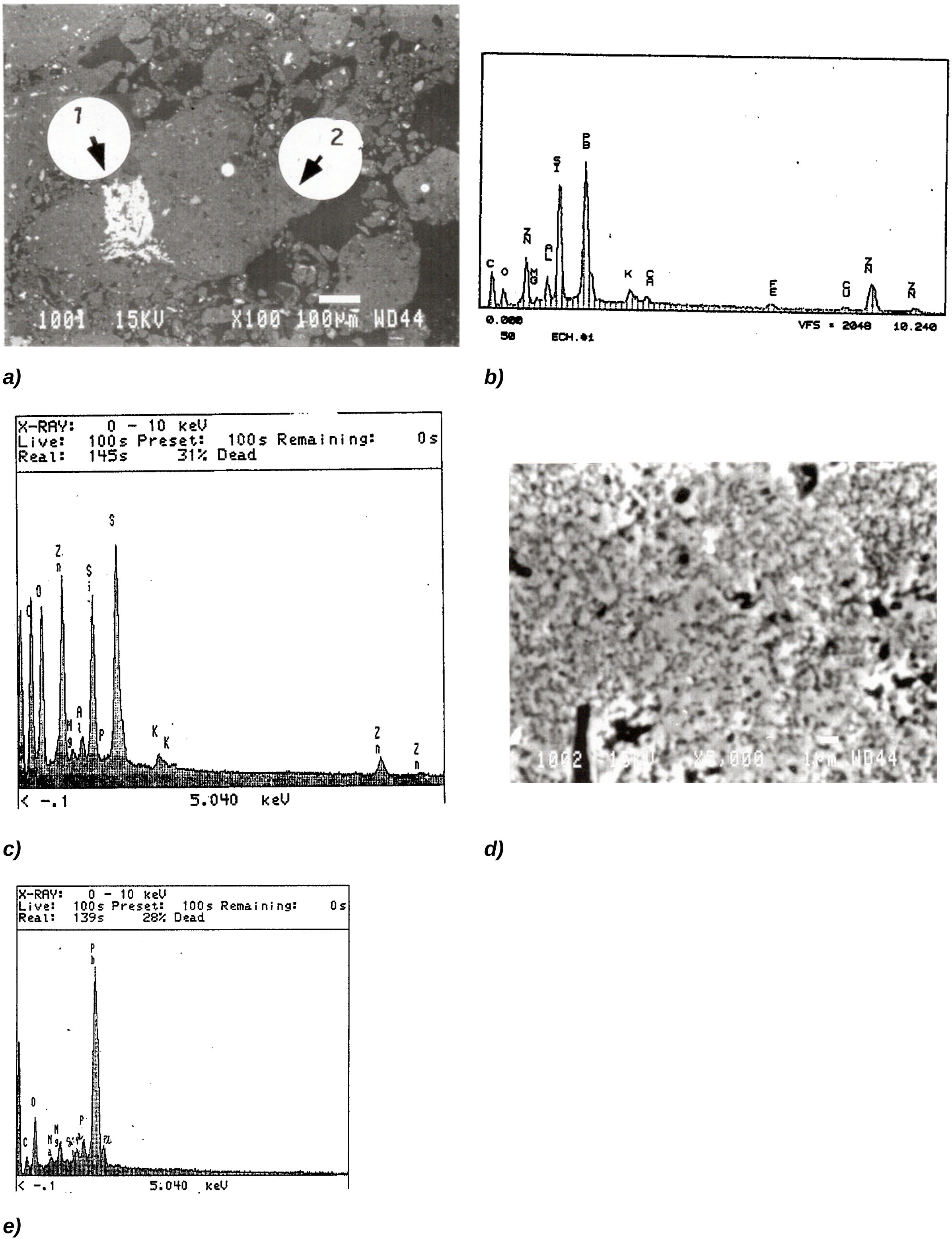

Figure 3: a) SEM image at low magnification (100x) showing two populations of fragments
b) analytical spectrum for the bright fragment seen in Fig 3a (arrow 1)
c) analytical spectrum for a grey agglomerate seen in Fig 3a (arrow 2)
d) image of a large bright fragment of 100 µm seen in Fig 3a (arrow 1), enlarged to 5000x
e) analysis of the fragment shown in Fig 3d

The gray agglomerates yield a spectrum given by Figure 3c which is characterized by a predominance of zinc with sulphur (ZnS sphalerite or wurtzite). Quartz (SiO_2) is often present in small solid grains, but amorphous silica appears to be scattered throughout the sample. Small concentrations of Al, Mg and K were also detected. In this particular instance, the apparent absence of lead is related to the low voltage used for the analysis and the gold plating used on the polished sections. Lead is very abundant in the powder as demonstrated by element mapping (see Figure 5).

An image of a large (100 µm) bright fragment, enlarged to 5,000x, is illustrated in Figure 3d with the matching analyses on Figure 3e. The fragment is porous and/or constituted by an agglomeration of irregular sub-micron size particles. The particle has elevated values for both lead and oxygen, indicating the presence of anglesite.

A needle-like fragment embedded in a gray agglomerate was enlarged to 20,000x and is illustrated on the photomicrograph of Figure 4. On closer examination it is seen that the needle is not a homogeneous solid but rather seems to be made of even finer particles which combine to form a needle-shaped agglomeration. The finer particles, which have diameters < 0.1 µm are disperse into the gray material adjacent to the needle. This texture, grain size and compositional variation could explain the reflection shifts in the diffraction pattern mentioned above and the diffuse nature of the mapping images (Figure 5).

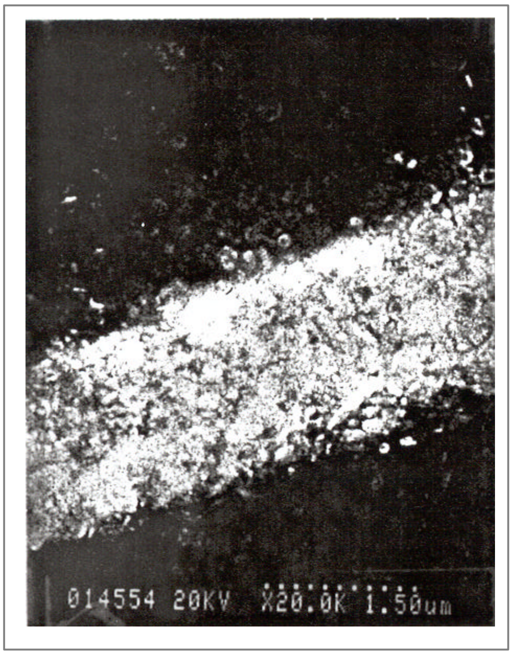

Figure 4: *SEM photomicrograph of a needle-like fragment embedded in a grey agglomerate, enlarged to 20,000x*

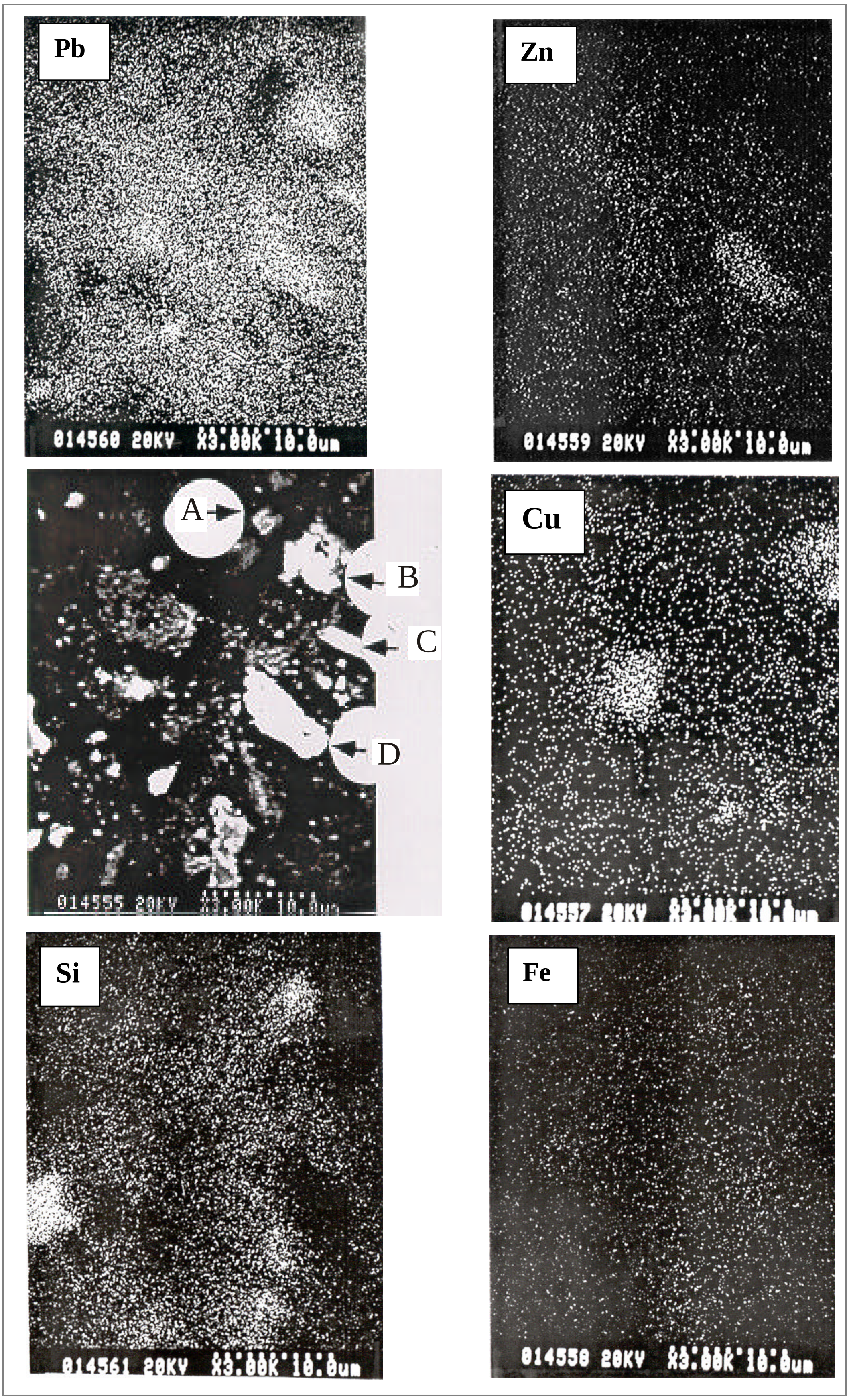

Figure 5: *Element mapping as indicated by back-scatter electron imagery*

The element mapping of Figure 5 associates the element with individual grains and illustrates the distribution and association for a selected area. Lead displays a strong signal throughout the analyzed area, often more concentrated on particular fragments (grains), but never defining a sharp outline. In all cases the grains boundaries are fuzzy. Zinc is not as abundant and its distribution is more uniform over the area considered. In general zinc is associated with the smallest fractions and is therefore more evenly distributed in other spots its absence or concentration can be associated with specific grains or fragments. Iron is also distributed throughout with very little variation.

The identified fragments on the photomicrograph (Figure 5, middle, left) have the following element associations:

B = Pb, Cu**;**

D = Pb, Zn, Fe**;**

A and C = Si, Pb**.**

It should be noted that the samples moved slightly during the mapping procedure, as a result the overlap is not exactly matching.

In conclusion the SEM evaluation indicates that the Theisenschlamm material contains fragments which are aggregates and/or agglomerates of extremely fine grained particles. In some cases these agglomerations are rich in lead and in other cases they are a mixture of Pb, Zn, Cu and Fe. The bright agglomerations generally have a lead sulphide or sulphate composition. The zinc sulphides do not form large fragments and as a result the zinc is more uniformly disseminated throughout the powder and forms the gray matrix in most sections. The multi-element composition of some of the sulphides indicates that they have undergone extensive substitution, a fact already alluded to in association with the X-ray peak shifts on the diffractograms.

Density and Grain Size

The density values of 2.92 g/cm^3 for the Theisenschlamm is low when compared with the known values of the individual identified phases. Sphalerite (ZnS), anglesite ($PbSO_4$) and galena (PbS) have densities of approximately 4.1, 6.4 and 7.6 g/cm^3 respectively and, according to X-Ray data these minerals constitute approximately 50% of the samples. The low density figures are almost certainly related to the porous nature of the fragments and agglomerates in the Theisenschlamm and also to the 40% of amorphous material present in the slurry. Figure 6 illustrates the grain size distribution for the Theisenschlamm - the median and mean diameters of the component particles are 1.25 µm and 1.55 µm respectively. It should be remembered that the laser instrument measures the diameter of the agglomerations of particles and not necessarily that of the particles themselves.

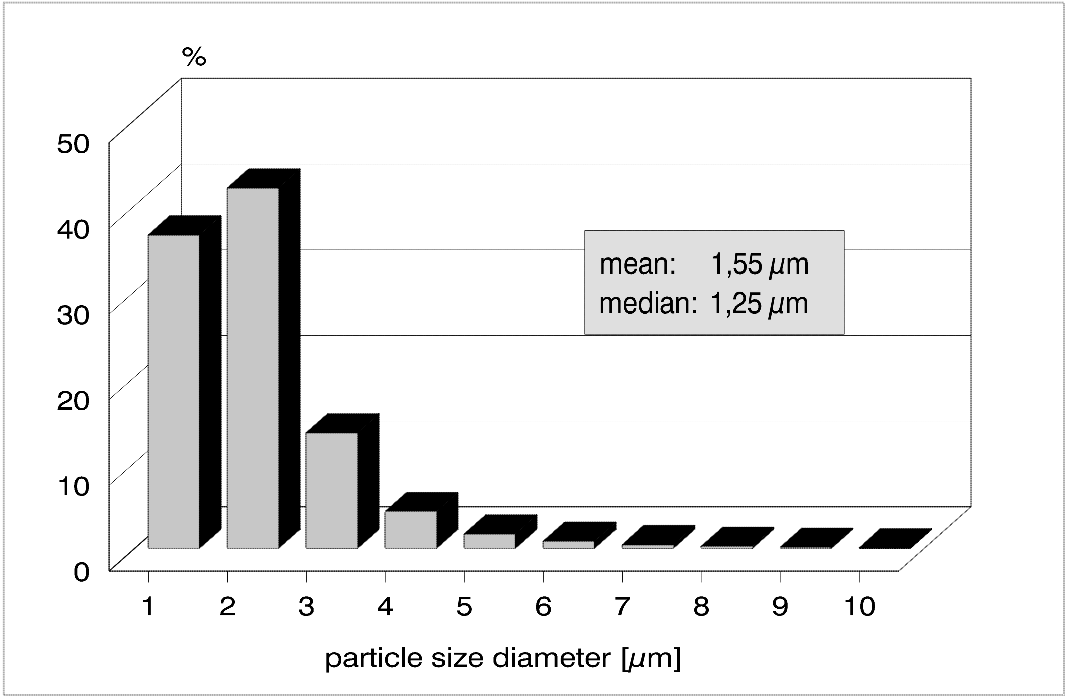

Figure 6: *Particle size distribution for a representative sample of the Theisenschlamm*

The risk of particle deposition of such small particles in the human respiration system should be mentioned Particles with diameters of 1 to 5 µm corresponding to the bulk size distribution of the Theisenschlamm can make its way and settle down in the peripheral bronchial tree (Table 6). Therefore the management of this residue should include these health factors.

Table 6: *Aerosole, relation between particle diameter, deposition place and mechanism of deposition*

particel diameter	place of deposition	mechanism of deposition
< 1 µm	expiration	gaseous phase
1 - 5 µm	periphereal bronchial tree	sedimentation
5 - 10 µm	upper respiration system and central bronchial tree	inert impact
> 10 µm	upper respiration system	

Radioactivity

The alpha spectrometry technique yielded concentrations of 32.9 µg/g ± 0.9 of ^{238}U and 2.1 µg/g ± 0.8 of ^{232}Th.

Alpha spectrometry measurements yielded a ^{210}Po activity of 16.6 kBq/kg; measurements by high resolution gamma spectrometry for ^{210}Pb yielded a value of 22.1 kBq/kg.

But as can be seen in the Figure 7 the risk based on the lead concentration is more critical with respect to the ADI-values (Annual Limit of Intake). The Theisenschlamm is not only a dangerous residue based on its heavy metal content and organic toxic compounds but also because of the associated radioactivity of the substance.

^{210}Pb / ^{210}Po in equlibrium: 1250 Bq

Þ **22 g Theisenschlamm / a**

respiration volume: 1,3 m^3 / h

working time: 2000 h / a

Þ **8,5 mg Theisenschlamm / m^3 air**

MAK-value for lead: 0,1 mg / m^3 air

Þ **0,85 mg Theisenschlamm / m^3 air**

Figure 7: *Theisenschlamm - Inhalation (Annual Limit of Intake (ALI) for adults without professional radiation exposure)*

Discussion

The X-ray diffraction study indicates that sphalerite, wurtzite and galena are the dominant phases present in the Theisenschlamm. Amorphous material is also an important fraction of the material. The X-ray peaks of the mineral phases present in the Theisenschlamm, with the exception of anglesite, are difficult to index properly. This fact is believed to be caused by extensive ionic substitution. The SEM study identified two main populations of particles consisting of PbS or $PbSO_4$ and the other of ZnS, the Zn-bearing particles being smaller. The $PbSO_4$ is believed to be of secondary origin.

The Theisenschlamm consists of particles which have a much lower density than would be expected, considering the minerals identified and their abundance. This is attributed to the porous nature of the grains and agglomerates as well as the amorphous nature of the substances. The SEM results show that the grain size of the particles for the Theisenschlamm is variable. Particles ranging in size up to 100 µm were observed, however the measured median diameter is 1.25 µm. The SEM data also reveal that the particles, whatever their size, are themselves agglomerates consisting of a collage of sub-micron-size particles.

The results of both alpha and gamma spectrometry confirmed the previously reported values for the radioactivity. This high radioactivity is due to the presence of ^{210}Pb in the slurry. This ^{210}Pb in turn decays to ^{210}Po; an equilibrium is reached after approximately 2 years. Due to the presence of these nuclides, the Theisenschlamm represents an additional radio-ecological risk (BUNDESAMT FÜR STRAHLENSCHUTZ, 1992; BUNDESAMT FÜR STRAHLENSCHUTZ 1994; LEHMANN, 1994; MINISTERIUM FÜR FÜR UMWELT UND NATURSCHUTZ DES LANDES SACHSEN-ANHALT, 1994).

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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.

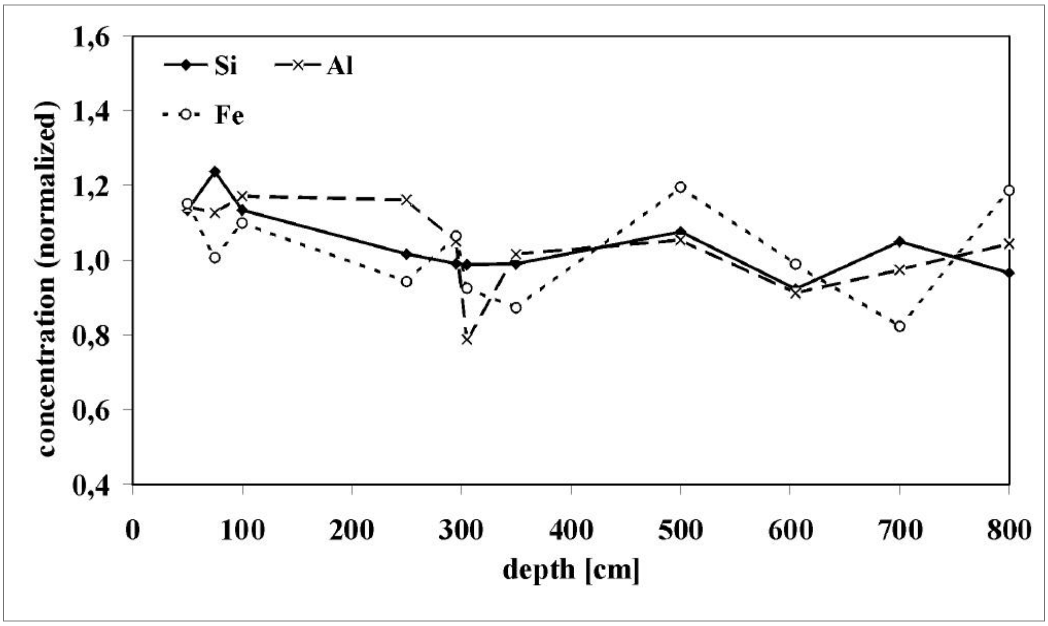

Figure 1: *Normalized concentrations of silica, aluminum, and iron in a Theisenschlamm drill core*

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.

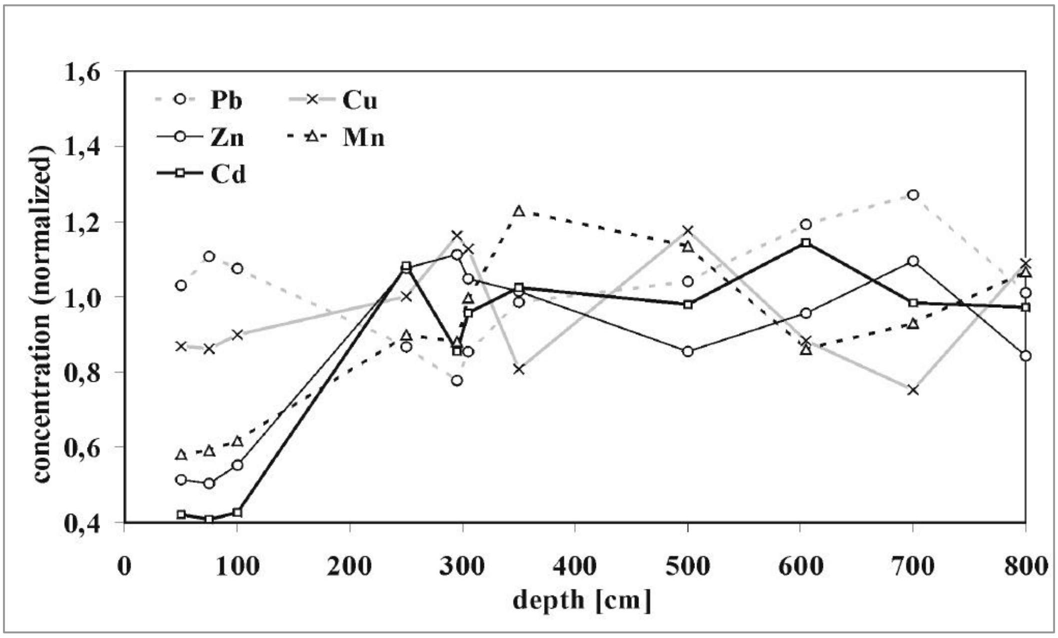

Figure 2: *Normalized concentrations of heavy metals in a Theisenschlamm drill core*

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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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.

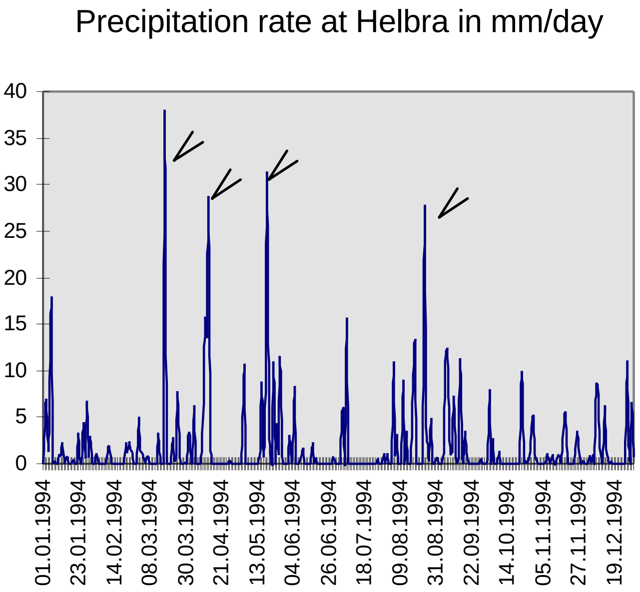

Figure 1: *Diurnal precipitation record at Helbra in 1994. Data from Mansfeld Rohhütten GmbH i.L, Helbra*

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

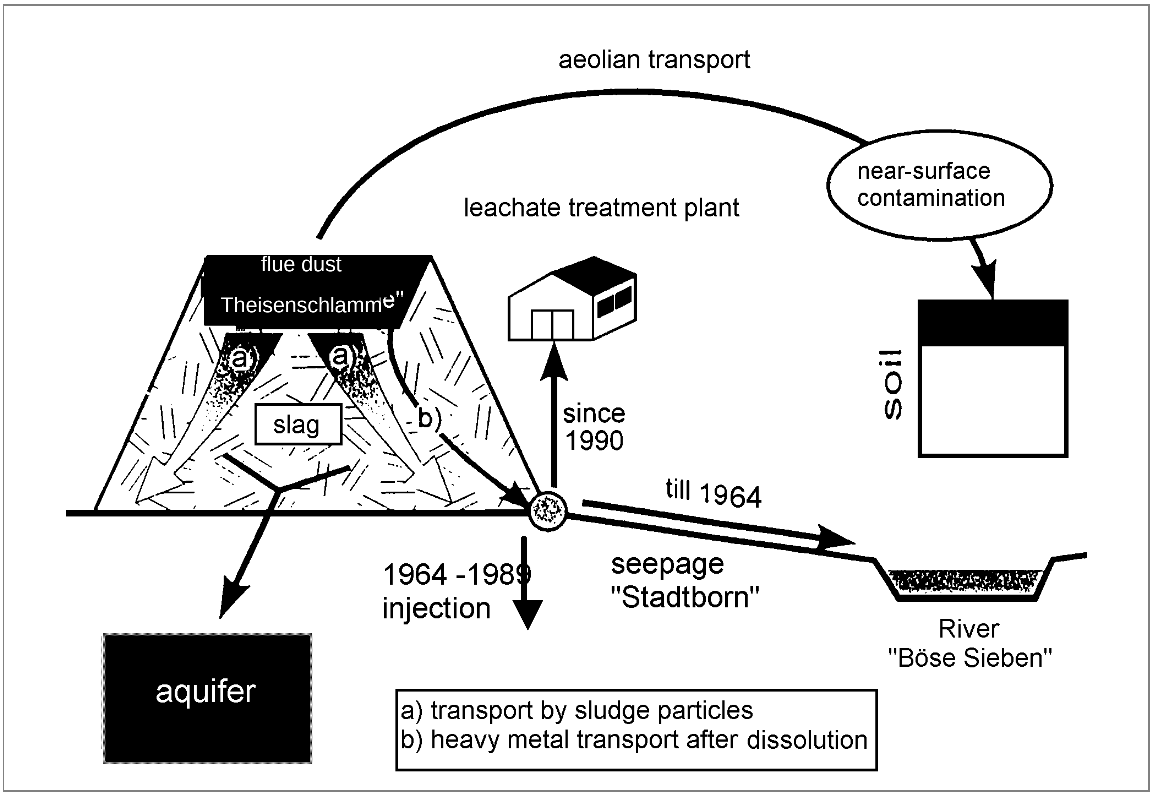

Figure 2: *Paths of pollutant migration by the weathering of Theisenschlamm. Modified after Jahn et al. (1997)*

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* S*CHRECK (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.

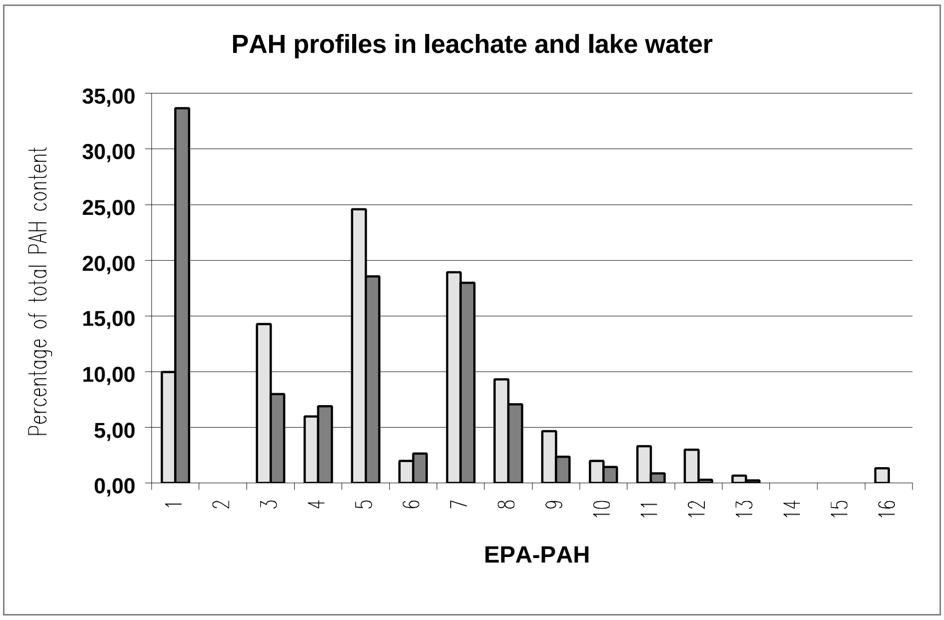

Figure 4: *PAH profiles in seepage from Theisenschlamm (Stadtborn, dark grey, total PAH = 1,736 ng/l) and in lake water (light grey, total PAH = 301 ng/l).*
Numbers 1-16: EPA-PAH from naphthalene (1) to indeno(1,2,3-cd)pyrene (16).

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.

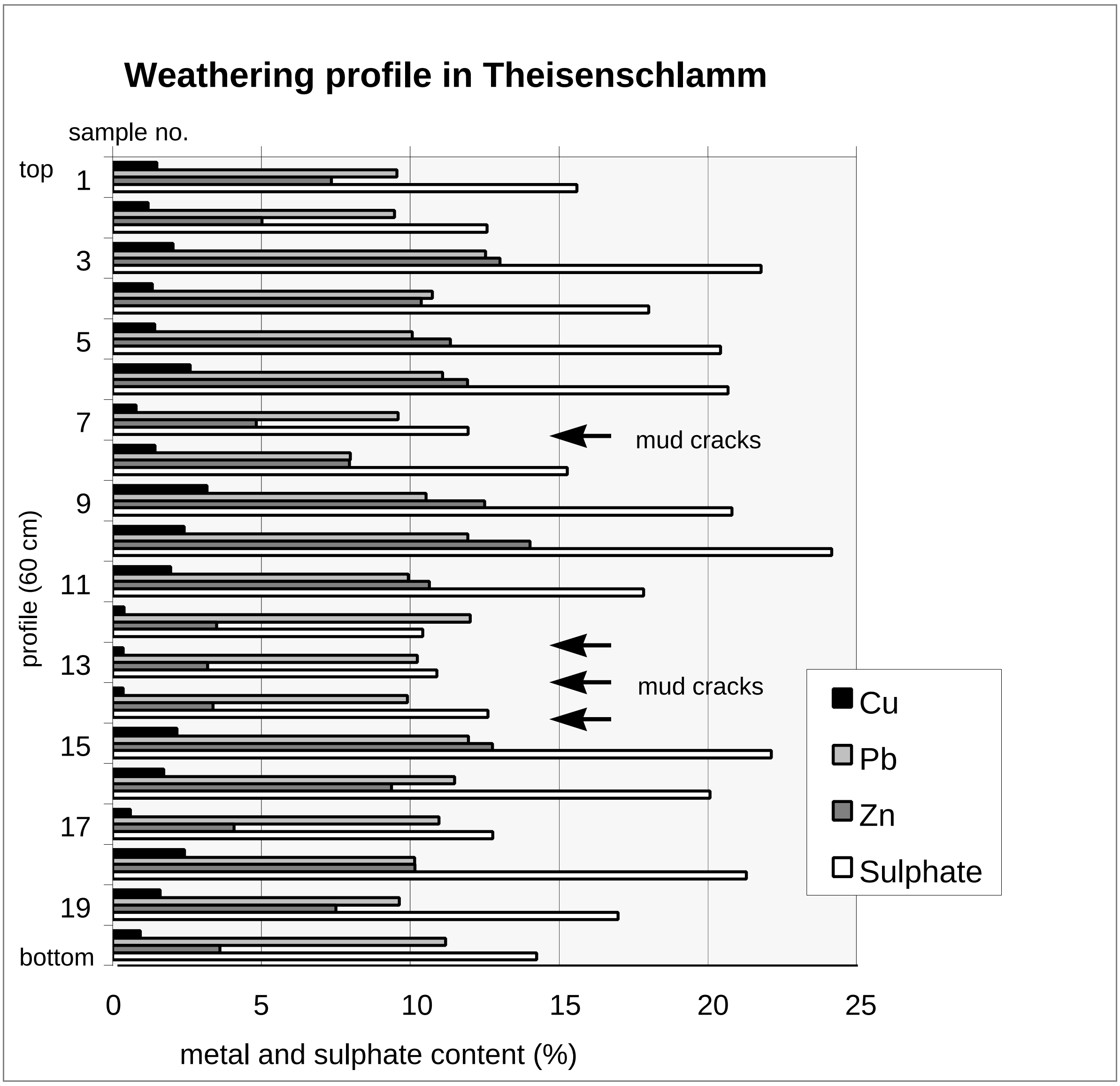

Figure 5: Vertical profile in consolidated Theisenschlamm, Pond 9. From MARQUARDT *(1997).*

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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7. Ecotoxicity Characterization of Seepage Waters from a Theisenschlamm Pond Discharging into a Riverine System

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Abstract

An ecotoxicological analysis of a scrubber dust slurry known as Theisenschlamm was performed. Seepage water from a Theisenschlamm pond and water samples from the receiving riverine system Böse Sieben were investigated. The toxic potential of the samples was assessed by using a bacterial luminescence test, the pollen tube growth assay, and in vitro determinations of cytotoxicity and 7-ethoxyresorufin-O-deethylase as a marker of the PAH-inducible cytochrome P4501A system. With all test systems, the seepage water showed massive toxicity. As indicated from EDTA complexation experiments, this effect was at least partly caused by the high Zn contents of the seepage water. In the water samples of the Böse Sieben, only moderate levels of acute toxicity were observed. However, all samples clearly induced the activity of 7-ethoxyresorufin-O-deethylase. This result points to the presence of substantial levels of bioavailable PAHs in the seepage water and the receiving riverine system.

Introduction

Theisenschlamm slurry is a complex contaminated scrubber dust which is generated as a byproduct of copper smelting (LORENZ, 1994). It contains high amounts of heavy metals, particularly Zn, as well as numerous organic contaminants, particularly poly aromatic hydrocarbons (PAHs*)* (WEISS et al., 1997). In the Mansfelder Land in Saxony-Anhalt, which is an area traditionally characterized by intensive mining activities, large quantities of Theisenschlamm slurry have been deposited. Seepage waters from these slurries represent a potential toxicological hazard for ground- and freshwaters in the Mansfeld area.

The objective of the present work was to provide initial data for an ecotoxicity assessment of seepage waters from Theisenschlamm deposits. The area which has been selected for the investigation is located close to the village of Eisleben in the Mansfeld area. Hydrogeological analyses have shown that the volume of seepage water from this Theisenschlamm deposit accounts for approximately 295 m^3 per day. This volume is at least partly released into the riverine system of the Böse Sieben.

We have analysed the toxic potential of the seepage water from the Theisenschlamm deposit at the former copper state smelter in Helbra, Saxony-Anhalt. In order to learn about the propagation of seepage water toxicity in the Böse Sieben, we have additionally investigated samples of creek water at various distances from the contamination source.

For toxicity characterization, a battery of biotests was utilized. The test battery approach is considered to improve predictability of adverse pollutant effects in ecosystems from toxicity data obtained in the laboratory. Conventionally, a tiered hazard assessment strategy is applied, using test organisms which represent different trophic levels of an ecosystem. In the present study, we have adopted an alternative approach incorporating assays and testing systems that assess phylogenetically conserved mechanisms of toxicity, such as depression of cellular energy metabolism, cytotoxicity, and induction of xenobiotic metabolism (cf. TWERDOK et al., 1997). Metabolic inhibition was measured in luminescent bacteria, cytotoxicity was determined in both plant (pollen tube) and animal (fish) cells, and xenobiotic metabolism was estimated from the activity of the cytochrome P4501A-dependent 7-ethoxyresorufin-O-deethylase (EROD) enzyme activity which catalyzes the monooxygenation of dioxin- and PAH-like substances.

Material and Methods

Sampling sites (see Chapter 6 and Figure 1 of Chapter 1):

Samples were taken

(1) directly from the seepage water of the Theisenschlamm deposit above the well at Stadtborn; the pH of the sample was 6.4;

(2) from creek water of the Böse Sieben at the village of Hergisdorf (approximately 0.5 km distance to Stadtborn); pH 7.7;

(3) from creek water of the Böse Sieben at the city of Eisleben (approximately 4 km distance to Stadtborn); pH 7.6

(4) from creek water of the Böse Sieben at Wormsleben, 1 km west of the entrance into the Süßer See (approximately 13 km distance to Stadtborn); pH 7.8;

(5) from lake water at the outlet of the Süßer See (approximately 18 km distance to Stadtborn; total lake area approximately 246 ha, 8.6 x 10^6 m^3 water); pH 8.1.

Sampling was done during January 1996. The samples were stored in dark flasks at 4°C and were tested immediately or the day after arrival in the laboratory. Adjustment of the pH values of the samples for testing was not performed.

Biotests

Inhibition of bacterial luminescence: This assay measures the toxicant-induced inhibition of energy-dependent luminescence of the bacterium *Vibrio fischeri*. The test was carried out according to DIN 38412, Part 34. An acute exposure time of 30 minutes at a temperature of 15°C was used for effect determination. For conducting the bioluminescence test, commercially available kits containing lyophilized bacteria were purchased from Dr. Lange GmbH, Düsseldorf. Bacterial luminescence was read in a luminometer (Lumistox, Dr. Lange GmbH, Düsseldorf). The bacteria were rehydrated prior to testing and mixed in a 1:1 ratio with a dilution series of the water sample. In order to meet the osmotic requirements of *Vibrio fischeri*, 2 % NaCl had to be added to the samples. Controls were treated with NaCl only. The inhibition of bioluminescence by the samples was calculated in relation to the alterations of lumenscence in the control incubations (BACKHAUS et al., 1997).

Pollen tube growth test: This assay determines inhibitory effects of samples on the growth of pollen tubes from the tobacco species *Nicotiana sylvestris* (KRISTEN and KAPPLER, 1995). The suitability of the pollen tube growth test for toxicity analysis of complex environmental samples has been recently demonstrated by JUNG et al. (1997). For testing, tobacco pollen were suspended in mixtures of growth medium and environmental sample. After an 18 h-incubation period, growth of pollen was quantified by staining with Alcian Blue and subsequent measurement of optical density in a photometer. Sample-induced inhibition of pollen tube growth was calculated in relation to controls maintained in pure growth medium.

Cytotoxicity assay with fish cell lines: Lethal effects of samples on cells can be measured using in vitro cytotoxicity tests (SEGNER and LENZ, 1993). The cell line used in the present study was the continuous cell line, RTG-2, originally derived from gonadal tissue of rainbow trout, *Oncorhynchus mykiss* (WOLF and QUIMBY, 1962). For the test, individual wells of a 96-well tissue culture microplate were inoculated with 30 000 - 40 000 cells in 0.2 ml of cell culture medium (MEM, Minimum Essential Medium). The cells were allowed for 4 hours to attach firmly to the culture substrate. Afterwards, the medium was removed, and 0.2 ml of pure medium (controls) or medium amended with different concentrations of the test sample were added to each well. The wells were tightly covered with sterile plastic foil and the cells were incubated for another 20 h at 19°C. Then the decrease of cell viability was measured using the neutral red uptake inhibition assay (BORENFREUND and PUERNER, 1984). For this, the exposure medium was removed from the wells, and 0.2 ml of culture medium supplemented with 50 µg neutral red/ml was added. The microplate was re-incubated for another 3 h to allow for the uptake of the vital dye neutral red into the lysosomes of viable, uninjured cells. Thereafter, the medium was removed and the cells were fixed for 1 min with a 1 % formaldehyde/Ca solution. Finally, 0.2 ml of 1 % acetic acid/ 50 % ethanol was added for 30 min to extract the dye accumulated by viable cells. The plate was transferred to a microplate reader equiped with 540/690 nm filters to measure absorbance of the extracted neutral red. Toxicant effects were quantified as percent decrease of neutral red staining in relation to the controls.

Induction of 7-ethoxyresorufin-O-deethylase (EROD): The cytochrome P450-dependent EROD enzyme is induced by dioxin-like chemicals via the aryl-hydrocarbon receptor (cf. SEGNER and BRAUNBECK, 1998). The measurement of EROD induction is an established biomarker for exposure to halogenated hydrocarbons and polyaromatic hydrocarbons (SAFE, 1990). In the present study, EROD induction by the test samples was measured using an in vitro assay with the fish cell line RTL-W1 (LEE et al., 1993). Approximately 60 000 cells in LEIBOVITZ-15 medium were seeded into individual wells of 48 well tissue culture plates and were grown at 19°C for 3 days. Then, the medium was removed and the cells were exposed for another 24 h to culture medium amended with various concentrations of the samples. At the end of the exposure period, EROD activity was measured using a live cell assay (CLEMONS et al., 1996, BEHRENS et al., 1997). Briefly, the exposure medium was removed, the cells were washed with phosphate buffered saline, and DULBECCO´S medium containing 8 µm 7-ethoyresorufin was added. Production of resorufin by the intact cells was followed in a fluorescence plate reader over 20 minutes at an excitation wavelength of 544 nm and an emission wavelength of 590 nm. Afterwards, cell protein was determined by using the fluorescent dye fluorescamine.

Ecotoxicological assessment

Seepage water of Theisenschlamm led to a 100% inhibition of energy-dependent bacterial luminescence (Figure1). In contrast, the water samples taken from the creek Böse Sieben and from the Süßer See resulted in only minor effects on bacterial energy metabolism (less than 20 % inhibition of luminescence; Figure1).

The high toxic potential of the seepage water from the Theisenschlamm, as indicated from the results of the bacterial bioassay, is confirmed by the findings of the RTG-2 cytotoxicity test (Figure1). Almost 100% cytotoxic activity was observed for this sample, whereas water samples of the Böse Sieben and the Süßer See showed no cytotoxicity. The results obtained with RTG-2 cells were confirmed by cytotoxicity measurents using a different fish cell line (Figure 5), the RTL-W1 cell line originating from rainbow trout liver (LEE et al., 1993).

Chemicals with prooxidant activity can be a major source of toxicity in environmental samples. In order to estimate the contribution of prooxidants to the observed toxic responses of the bioassays, we performed a cytotoxicity test using glutathione-depleted RTG-2 cells. The tripeptide glutathione acts as intracellular antioxidant and protects against the toxic action of oxidative stress. Intracellular glutathione levels of

RTG-2 cells can be decreased to 20% or less of the normal cell concentration by culturing the cells in the presence of the glutathione synthesis- inhibitor buthionine sulfoxime (BSO) (MARACINE and SEGNER, 1998). When performing the cytotoxicity assay with glutathione-depleted cells, only the sample from Eisleben showed enhanced toxicity compared to untreated cells (Figure 1). This indicates that prooxidants are not critical toxicity factor in the investigated water samples.

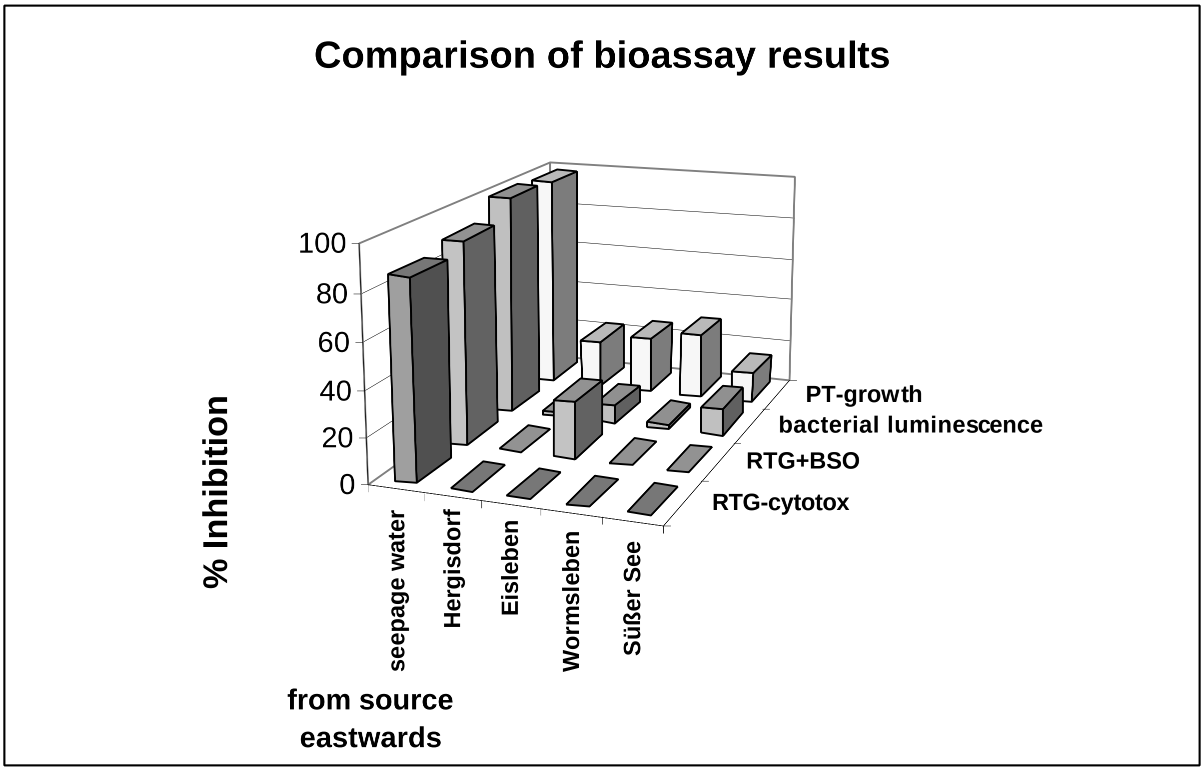

Figure 1: *Toxicity test results as obtained for the 1:2 diluted samples in the various bioassays: Neutral red assay with RTG-2 cells for measurement of acute cytotoxicity („RTG-Cytotox“), neutral red cytotoxicity assay with glutathione-depleted RTG cells for detection of prooxidant toxicity („RTG+BSO“), analysis of toxicant-induced inhibition of bacterial luminescence with Vibrio fischeri („bacterial luminescence“), and toxicant-induced inhibition of the growth of tobacco pollen tubes („PT growth“).*

The findings of the pollen tube test confirmed the findings of the bacterial luminescence or cytotoxicity assays. The seepage water from the Theisenschlamm showed 100 % toxicity, whereas for the water samples of the Böse Sieben and the Süsser See only minor or moderate toxic potentials were observed.

Likely candidates possibly responsible for the high acute toxicity of the seepage water sample are metal contaminants, particularly Zn. The seepage water contains massive amounts of Zn, going up to concentrations of more than 50 mM. These concentrations are far above the EC50 values of Zn in the biotests used in this study. EC50 values for Zn were determined to be 0.35 mM in the bacterial luminescence assay and 0.44 mM in the RTG-2 neutral red cytotoxicity assay (unpublished data).

In order to estimate the contribution of Zn to overall toxicity of the seepage water, an EDTA complexation assay was performed (Figs. 2 and 3; HOCKETT and MOUNT, 1996). This approach is based on the assumption that the „free“ metal ion is the toxic species whereas complexed metals are not toxic. Through complexation of the free metal ions in the sample by addition of EDTA concentrations which are at least equimolar to the metal levels in the sample, the toxic metal ions will become non-toxic for the biological target system (Figure 2).

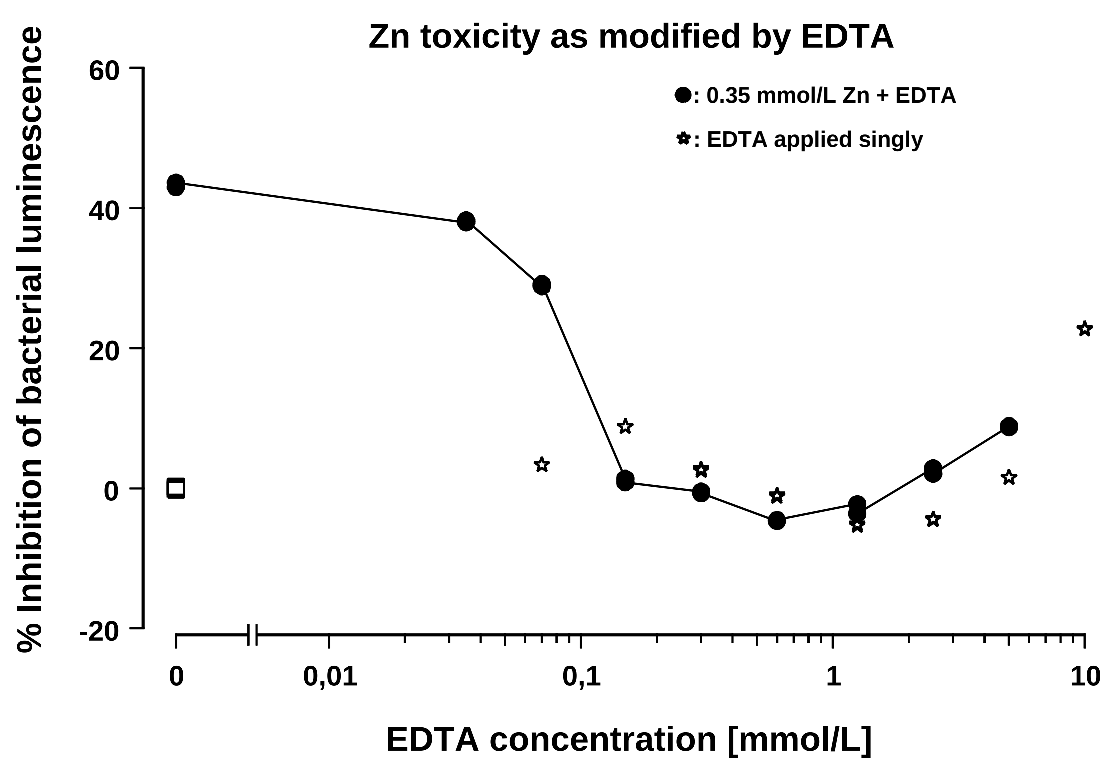

***Figure 2**: Principle of EDTA testing: Through EDTA complexation, metals can be removed from a solution. By comparing the toxicity before and after EDTA treatment, the contribution of metals to the overall toxicity of the sample can be estimated. For this purpose, a series of dilutions of an EDTA stock solution were added to the sample (here: pure Zn solution), incubated under constant stirring overnight, and toxicity to luminescent bacteria was recorded the next day, in comparison to pure EDTA dilutions and the pure seepage water. When approaching equimolar concentrations to Zn, EDTA effectively removed Zn toxicity from the sample.*

The results of the EDTA complexation experiment with RTG-2 cells are shown in Figure 3: EDTA was added up to concentrations of 50 mM; at concentrations higher than 25 mM, EDTA itself became cytotoxic. Cytotoxicity of the seepage water from Theisenschlamm was partly reduced by EDTA, with the maximum effect at the highest non-toxic EDTA concentration (25 mM). Complete removal of toxicity could be not achieved since Zn concentrations in the sample (52 mM) were higher than the highest non-toxic EDTA concentrations (25 mM).

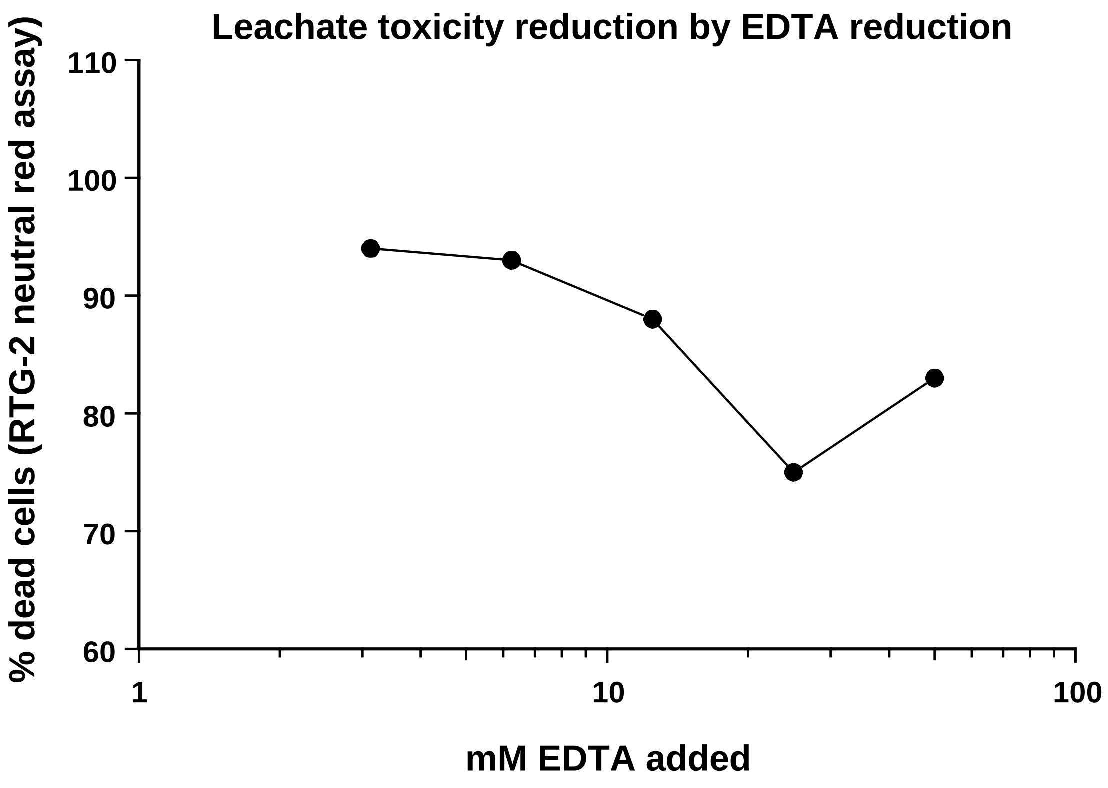

Figure 3: *EDTA complexation of the seepage water from Theisenschlamm (method as described for Figure2).*

Apart from heavy metals, Theisenschlamm slurry contains high concentrations of polycyclic aromatic hydrocarbons. As shown by chemical analyses, the PAHs are leached from the slurry and are released into the water. However, due to their hydrophobicity, the PAHs may attach to DOM (dissolved organic matter) and/or may be transferred into the sediment , leading to their removal from the water phase. To detect the presence of bioavailable PAHs in the water samples, we used the EROD induction bioassay with RTL-W 1 cells (Clemons et al. 1996). This assay indicates the presence of dioxin-like substances, including dioxins, furanes, PCBs and PAHs, in a sample (Brack et al., 2000). The results, as shown in Figure 4, demonstrate a significant induction of EROD in all samples analysed, except for the seepage water itself. Importantly, there is no significant decrease of EROD activity with increasing distance to the entry site of the seepage water into the riverine system. This indicates that substantial levels of bioavailable PAHs stay in the water phase of the Böse Sieben and are not removed into the sediments.

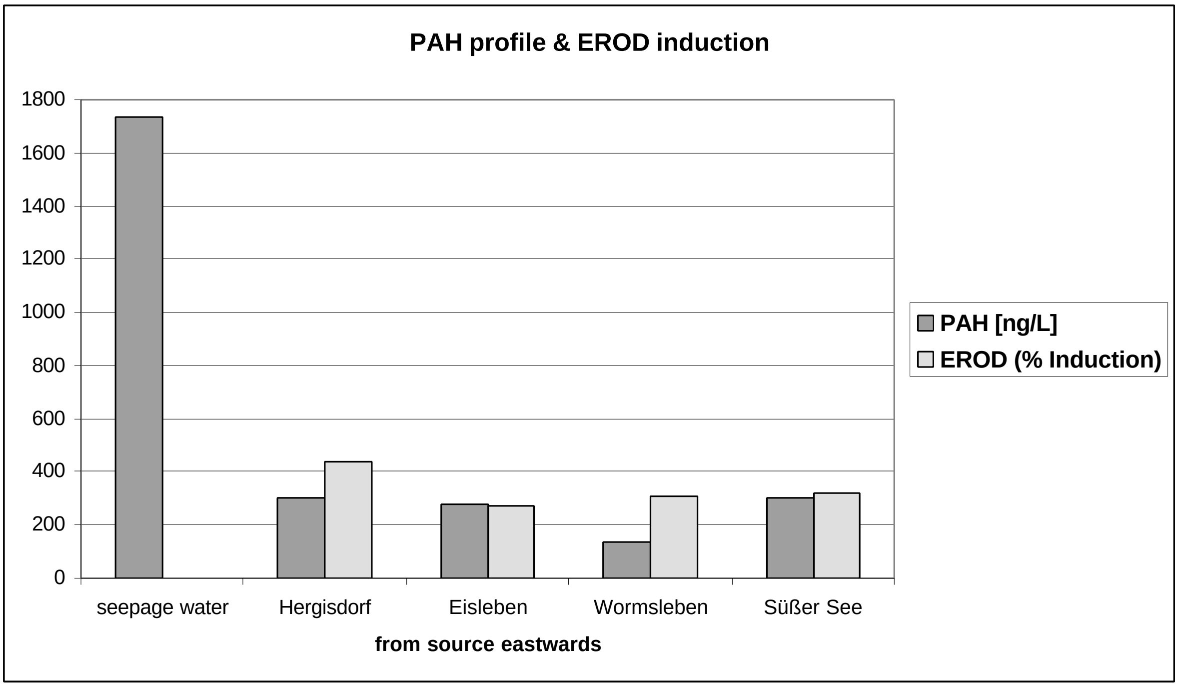

Figure 4: *Total PAH levels in the samples and the corresponding EROD response. The measurement was done in RTL-W1 cells which were exposed for 24 h to 1:2 diluted samples of the seepage water and from the Böse Sieben.*

The lack of EROD induction by the seepage water from Theisenschlamm (Figure 4) is explainable by the extreme acute cytotoxicity of this sample, which hides any sublethal effect such as the EROD response. When diluting the seepage water, an increasing EROD induction with decreasing cytotoxicity is evident (Figure 5).

The bioassay findings on EROD induction are well in line with the findings from chemical analyses on total PAH levels in the water samples (Figure 4). The bulk constituents of the PAH fraction are compounds such naphtalene, fluoranthene, phenanthrene or pyrene (SCHRECK et al., 1998, WEISS et al., 1997) These compounds, however, are non-inducing PAHs, i.e. they lack the ability to induce the cytochrome P450-dependent EROD activity (BEHRENS et al., 2001). The fact that we observe clear-cut EROD induction in the assay with RTL cells indicates that the seepage water from Theisenschlamm, in addition to the quantitatively dominating non-inducing PAH congeners, contains toxicologically relevant amounts of inducing PAHs. This response is of particular relevance since cytochrome P4501A-mediated metabolism of PAHs leads to the generation of mutagenic and, ultimately, carcinogenic metabolites.

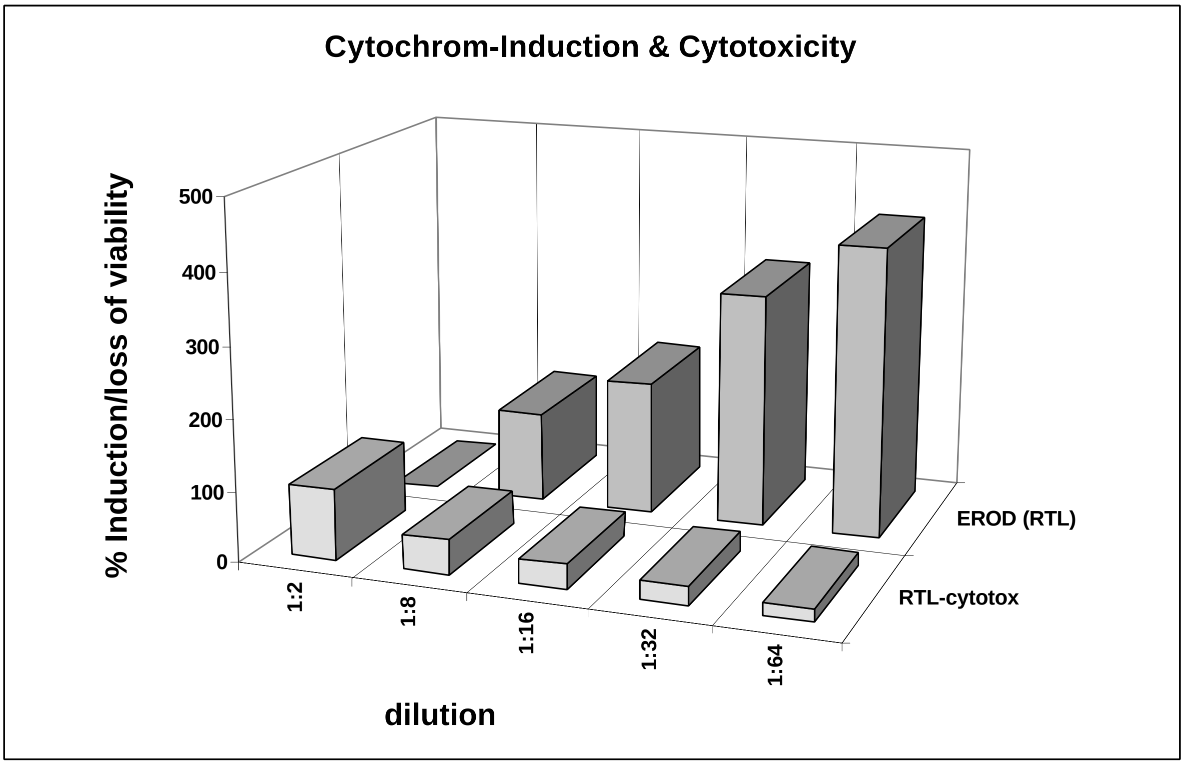

Figure 5: *The 1:2 diluted seepage water from Theisenschlamm is 100% cytotoxic to RTL-W1 cells and, therefore, does not allow the detection of EROD activity. Enzyme induction represents a sublethal response to toxicants and requires the functioning of differentiated cellular functions. Only in sepage water samples diluted 1:8 or more, when cytotoxicity is lower than 50%, EROD induction could be detected.*

Conclusions

The seepage water from Theisenschlamm shows a drastic acute toxicity which appears to be mainly caused by its very high Zn levels. Removal of Zn from this sample lead to a (partial) reduction of the acute toxicity. The high, metal-associated acute toxicity of the seepage water is not detectable in the water samples from the riverine system of the Böse Sieben and the Süsser See. Obviously, Zn ions are sedimented within a short distance after the entry site of the seepage water, and the toxic ions are no longer bioavailable. However, high levels of Zn could be expected in the river sediments close to the seepage water entry site.

Contrary to Zn, PAHs obviously are not quantitatively trapped into sediments but can be found at all sample stations analysed. Accordingly, all investigated stations show a clear-cut induction of EROD activity which is responsive to PAH exposure. The PAHs do not give rise to acute toxicity, however, via EROD-mediated metabolism they may cause mutagenic and carcinogenic effects. This toxic potential must not be overlooked in the hazard assessment of the riverine system of the Böse Sieben. Future studies should address in more detail the presence of genotoxic potentials, the distribution of chemical toxicity between water and sediment, and their spatial distribution along the river system.

Acknowledgements

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8. Assessment of Theisenschlamm Leaching Behaviour

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Abstract

The aim of this laboratory study was to obtain basic information on the leachability of the priority pollutants in the Theisenschlamm. Beside the German standard leaching test applying distilled water, a serial concentration buildup test (a five-step shaking cascade) for the simulation of drainage water from sludge ponds was used. In addition, a special aspect of Theisenschlamm weathering, the influence of acid rain deposition, was investigated by using the pH_{stat} shaking test. The leachate analyses have been focused on heavy metals, arsenic and on polycyclic aromatic hydrocarbons (PAH), but we have also performed a screening on other leachable organic substance classes with gas chromatography/mass spectrometry (GC-MS). None of the Theisenschlamm leachates provide any cause for radiological concern. Chemical analyses of leachates show that relevant regulatory criteria for surface dumping are exceeded for Zn, Pb, Ni and Cd and for selected PAHs. The much greater mobilization of these elements and of arsenic at $pH_{stat} = 4$ than under neutral conditions has to be considered in a worst case scenario because the tests showed also that Theisenschlamm has an acid neutralization capacity of only 900 mmol H^+/kg.

Introduction

The Theisenschlamm can have a considerable environmental impact due to its content of inorganic and organic pollutants in large quantities (WEISS et al., 1997; cf. also Chapter 3). After prevention of dust emissions, primary concern is directed towards whether and to what extent pollutants are washed out by the rain or surface water, and whether drainage into the groundwater is to be expected.

Theoretical prediction of the leaching behaviour of polluted solids and sludges is virtually impossible owing to the many different combination effects between the substances, such as complexation of heavy metals and the different sorption phenomena occurring on the solid matrix. Experimental techniques must therefore be applied to estimate the maximum pollutant concentration which can occur in the aqueous phase under the specific milieu conditions, what parameters mainly affect the mobilization of individual pollutants, and how they develop over time. Moreover, the entire release potential of a polluted material in a worst case scenario must be determined.

Numerous leaching tests exist for waste, industrial residue, contaminated soil and sediment (cf. for instance HAM et al., 1980; RUMP & SCHOLZ, 1988; Fachgruppe Wasserchemie, 1997). They are used for different purposes (FRIGGE, 1991; Fachgruppe Wasserchemie, 1997) and can be performed under unsteady or steady-state conditions. In the former case, the solid is either mixed with a defined quantity of elution agent (batch tests) or placed in contact with the eluent in a continuous flow (semi-batch tests). Batch tests include one-step shaking and stirring tests, jar tests and sequential extractions. Semi-batch tests include shaking cascades and recirculation or continuous flow tests. Steady-state conditions (implemented via the continuous or cascade-type counter-current flow of solid and liquid phase) is more suitable for technological leaching processes.

In Germany, the environmental sustainability of residues and waste is still mainly assessed using the DEV S4 shaking test („Determining elution properties with water"; DIN 38 414-S4) and the DEV S7 extraction technique („Dissolution with aqua regia for the subsequent determination of the acid-soluble portion of metals", DIN 38 414-S7) or Soxhlet extraction (of organic pollutants using very different solvents). However, these investigations reflect the long-term mobility of pollutant components insufficiently.

One interesting development among the laboratory test methods for studying how the pH and redox potential affect heavy metal remobilization (ECKHARDT & HABERER, 1986; CALMANO et al., 1992) and which in particular has been designed to increase the practical relevance of the results is the pH_{stat} shaking test developed by OBERMANN & CREMER (1992). The solid sample (at a ratio of 1:10 with the solution phase) is eluted with an aqueous solution, while pH constantly maintained at either 4 or 11 (reflecting the limits of the pH milieu under actual landfill conditions). The determination of the maximum acid and base neutralization capacity of the material in combination with the above-mentioned tests DEV S4 and S7 enables information to be obtained concerning the worst case scenario (HAASE & FÖRSTNER, 1995; SOMMERFELD & SCHWEDT, 1995; PASCHKE et al., 1997; GÄBLER, 1997; WUNSCH et al., 1997).

In consideration of various authors' findings (e.g. HAM et al., 1980; GOUNARIS et al., 1993, MATTHIESEN, 1994; PENNELL et al., 1993), the pH_{stat} shaking test can also be used if a suitable elution agent is chosen (synthetic drainage water, artificial rainwater, solution with synthetic humic acids or surfactants) to determine the leaching behavior of hydrophobic organic compounds. In both cases, however, the test parameters need to be optimized. Tests adopting this approach have been carried out by HIRNER and co-workers (PESTKE et al., 1997 and BUSCHE & HIRNER, 1997). However, our own pH_{stat} shaking tests on contaminated waste (PASCHKE et al., 1996) showed that the mobilisation of polycyclic aromatic compounds increases even without the addition of solubilizer at pH 4.

During the actual study, further determination of the total heavy metal content of Theisenschlamm was unnecessary (see Chapter 3 of this report). The level of selected polycyclic aromatic hydrocarbons (PAH) was determined by Soxhlet extraction with toluene, the solvent which according to POPP et al. (1997) is particularly suitable for this substance class. The leaching tests used were:

1. The DEV S4 shaking test in its standardized procedure to describe the initial contact of the material with water (e.g. upon the resuspension of sedimented particles in a large volume of water);
2. A five-step shaking cascade to simulate drainage water for comparative purposes with real leachates;
3. The pH_{stat} shaking test for the long-term prediction of pollutant mobilisation under acid deposition.

Materials and methods

Theisenschlamm was taken from a representative sample (WEISS et al., 1997). Using a pycnometer, the material (which with the exception of Soxhlet extraction was not dried before usage) was found to have the following density (in kg/m^3): 1780 (at 5°C), 1770 (15°C), 1766 (25°C), 1730 (35°C). By drying a small amount at 105°C, the material was found to have a moisture content of 25%(w/w). All leaching tests were carried out twice each, the eluates of the parallel tests subsequently being combined prior to analysis.

The DEV S4 shaking test (DIN 38 414-S4) and the pH_{stat} test (OBERMANN & CREMER, 1992) were perfomed as described elsewhere (PASCHKE et al., 1997). In the first step of the shaking cascade, about 200 g solid and 1000 ml water were agitated in a 2-liter polyethylene vessel at room temperature (about 25°C) in the overhead shaker as in the DEV S4 test. After the leached material had been removed by centrifugation (see below), an aliquot of eluate was stored for the analyses and the greater part of eluate was shaken again for 24 h with a fresh solid sample. This procedure is repeated four times (always at a liquid/solid ratio of 5:1).

Eluate/solid separation by centrifugation, electrochemical measurements on the eluates and conservation or solvent extraction of the leachates prior analysis are also described in detail in PASCHKE et al. (1997).

Gamma spectrometry of eluates was carried out using an HPGe coaxial low-level detector (n-type; crystal diameter: 53.2 mm; crystal length: 55.4 mm; beryllium window: 0.5 mm; resolution at 122 keV (Co57): 720 eV and at 1.33 MeV (Co60): 78.8 keV; TARGET ISA plug-in card; passive screening with low-level lead) in 450-ml Marinelli beakers. Spectral analysis was aided by the special software GAMMAW. To calibrate the set-up of measuring instruments, Physikalisch-Technische Bundesanstalt (PTB) Germany radionuclide mixtures NG1 and NG4 were used (NG 1 for the range > 80 keV, NG 4 for the range < 140 keV). The following gamma energies were used for analysis:

Pb-214[1]	241.9 keV	(7.12 %)	Bi-214[1]	609.3 keV	(46.10 %)
	295.2 keV	(18.15 %)		1120.4 keV	(15.00 %)
	351.8 keV	(35.10 %)	Pb-210	46.5 keV	(4.05 %)

The detection limit for the above-described measuring set-up for both radionuclides was about 1 Bq/l.

The elements As, Cd, Cr, Cu, Ni, Pb and Zn in the eluates were determined as stated in DIN 38 406-E22 using an ICP-AES unit (Spectorflame P/M, Spectro A.I.) with cross-flow nebulization. Calibration was performed with ICP standard solutions (Merck) over two to three orders of magnitude and the standard addition technique, respectively. The limits of detection were about 10 – 20 µg/l for Cu, Ni, Cr and Zn, about 50 µg/l for As, about 100 µg/l for Cd, and about 250 µg/l for Pb.

Mercury determination was performed using cold vapour AAS (FIMS, Perkin-Elmer) pursuant to DIN 38 405-E12. The limit of detection was around 0.1 µg/L.

After changing the solvent of the extracts from toluene to acetonitrile, the PAH analyses were carried out with an HPLC system (Gold, Beckmann) with a fluorescence detector (RF-551, Shimadzu) using a 250 × 3 mm separation column (Bakerbond-PAH-16-Plus, Baker) and gradient elution (acetonitrile/water) at 25°C. Acenaphthylene, one of the 16 PAHs according to EPA 610, is not fluorescence-active and so cannot be determined with this method. The limits of determination were about 0.5 ng/ml extract, or in terms of the initial eluate 6.25 ng/l.

Concentrated samples of the toluene extracts of the eluates were separated in a GC HP 5890 II (Hewlett Packard) via a capillary column HB-5 (30 m × 0.25 mm I.D. with 0.25 µm film thickness) using a temperature program and identified in a directly linked mass spectrometer (MSD, Hewlett Packard). Full-scan mode was used in order to perform substance classification with the help of a spectrum library.

Results

In addition to the main characteristics of the shaking tests, Table 1 also lists the concentrations of selected heavy metals.

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[1] Ra-226 activity was determined assuming radioactive equilibrium with its decay products (Pb-214, Bi-214).

***Table 1**: Liquid-to-Solid Ratio (L/S), leachate pH-value. conductivity (c), redox potential ($U_H^{25°C}$) and heavy metal concentration of different leaching tests. (The underlined values exceed the relevant criteria for disposal options of hazardous wastes, see text for details.)*

	L/S	pH	χ [mS/cm]	$U_H^{25°C}$ [mV]	As [mg/L]	Cd [mg/L]	Cr [mg/L]	Cu [mg/L]	Hg [mg/L]	Ni [mg/L]	Pb [mg/L]	Zn [mg/L]
pH_{stat}4/24 h	10.61	4.0[a]	6.63	434	$\underline{4.849}$	$\underline{1.02}$	<0.05	0.028	0.0004	$\underline{2.360}$	$\underline{30.43}$	$\underline{2056}$
pH_{stat}4/336 h	10.18	4.0[b]	9.32	442	1.542	3.92	<0.05	0.056	0.0002	2.450	23.4	2710
DEV S4/24 h	10.00	6.80	1.92	393	0.129	0.29	<0.05	0.025	<0.0001	1.046	$\underline{4.30}$	$\underline{639}$
Cascade/24 h	5.40	6.72	3.48	401	0.253	0.44	<0.05	0.028	<0.0001	1.634	3.78	1206
Cascade/48 h	2.68	6.71	5.78	393	0.333	0.75	<0.05	0.030	<0.0001	3.102	6.34	2338
Cascade/72 h	1.82	6.50	7.72	368	0.396	1.16	<0.05	0.038	0.0001	4.708	9.32	3180
Cascade/96 h	1.40	6.41	9.56	370	0.482	1.48	<0.05	0.028	0.0003	6.320	9.37	4278
Cascade/120 h	1.16	6.54	9.80	367	0.483	1.68	<0.05	0.127	0.0001	7.100	8.89	4923
„Elution box“[c]	0.05[d]	4.3	12.76	n.d.[e]	n.d.	11.80	n.d.	0.200	n.d.	n.d.	5.80	6370

[a] $ANC_{24\,h}$ = 602 / 631 mmol H^+/kg.

[b] $ANC_{336\,h}$ = 884 mmol H^+/kg.

[c] data taken from (Jahn et al., 1997) - second leaching sequence.

[d] calculated under the realistic assumption that 30 L earth-moist material (with a density of 1.75 kg/L and a water content of 25 mass-%) were leached by 2 L water.

[e] n.d. = not determined.

Despite having the same liquid/solid ratio, the pH_{stat} test at pH = 4 resulted in much higher eluate concentrations in the 24 h test than the DEV S4. This effect was intensified in the 14-day pH_{stat} test. The concentration determined under field conditions in an „elution box" (JAHN et al., 1997) is exceeded in the pH_{stat} eluates only for lead. The shaking cascade successively approaches the „elution box" value for zinc and possibly for copper. Nickel seems to show also the same leaching behaviour. The lead concentration exceeds the field measure already in the second step of the shaking cascade. Only one seventh of the „elution box" value is is reached for cadmium. Interestingly, the eluate from the "elution box" is acidic, whereas all cascade eluates are neutral.

Gamma-spectrometry studies of the various shaking test eluates resulted in no radiation values above the limit of determination of 1 Bq/L.

Table 2 lists the findings of PAH determination in the Soxhlet extract and in the various eluates.

***Table 2**: Concentration of indiviual PAH compounds (according to EPA 610) in the Soxhlet extract (=„total content") and in different leachates.*

PAH compound	Soxhlet extract mg/kg	DEV S4/24 h µg/L	Cascade/120 h µg/L	pH_{stat}4/24 h µg/L	pH_{stat}4/336 h µg/L
Naphthalene	n.d.[a]	n.d.	n.d.	n.d.	0.82
Acenaphthene	n.d.	n.q.[b]	1.28	n.q.	n.q.
Fluorene	11.9	0.61	4.78	4.14	0.88
Phenanthrene	154.2	1.63	14.58	9.68	1.32
Anthracene	28.3	0.16	2.56	1.89	0.26
Fluoranthene*	56.6	0.31	3.30	1.21	0.20
Pyrene	84.0	0.18	5.91	1.30	0.22
Benzo(a)anthracene	29.6	n.q.	1.10	0.33	0.15
Chrysene	59.7	n.q.	2.63	0.49	0.15
Benzo(b)fluoranthene*	17.0	0.16	1.76	0.30	0.04
Benzo(k)fluoranthene*	6.9	0.04	0.44	0.08	0.01
Benzo(a)pyrene*	19.2	0.14	1.46	0.23	0.06
Dibenz(a.h)anthracene	n.d.	n.d.	n.d.	n.d.	n.d.
Benzo(g.h.i)perylene*	11.9	n.d.	0.40	n.d.	n.d.
Indeno(1.2.3)pyrene*	7.4	n.d.	0.74	n.d.	0.02
Sum (EPA 610)	486.6	3.23	40.93	19.63	4.13
Sum* (TVO)[c]	119.1	0.65	8.10	1.81	0.33

[a] n.d. = not detectable.
[b] n.q. = not to quantify.
[c] sum of starred PAH compounds according to the German Drinking Water Standard (TVO).

All shaking tests displayed a similar distribution spectrum for the 15 PAH representatives analysed. Surprising differences arose between the 24 h and the 14-day pH_{stat} shaking test. A successive PAH photodegradation during the long-term test can be supposed.

Table 3 gives the results of GC-MS summary analysis of the various eluates. The partly considerable differences cannot be due to inhomogenities in the solid material used since the investigated samples (100 – 400 g) were taken from a single homogenized whole sample weighing about 2 kg. The very high fraction of nitrogenated compounds in both pH_{stat} eluates could however be attributable to the addition of nitric acid required in this test.

***Table 3**: Percentage of substance classes in relation to the overall sum of identified organic compounds in the different leachates via GC-MS (full scan mode).*

Substance class	DEV S4/24 h	Cascade/120 h	pH_{stat}4/24 h	pH_{stat}4/336 h
	%	%	%	%
Alkylbenzenes & derivatives	8.4	5.4	4.2	14
Phenols	10.8	15.8	5.9	2
PAHs	33	36.2	19.8	23
Partial hydrogenated aromatics	9.2	10.7	4.6	15
Cyclic- & ketonic compounds	2.8	5.2	2.3	1
Nitrogen-containing compounds	17.6	13	39.8	36
Sulfur-containing compounds	4.4	8.4	6.3	5
Carboxylic acids & esters	1	2.7	3.7	2
Benzofuranes & derivatives	12.6	1.9	13.2	-
Chlorinated Compounds	-	0.6	-	-
Alkanes	-	-	-	2

Figure 1 shows the development over time of the acid neutralization capacity (ANC) of the Theisenschlamm as calculated from HNO_3 consumption required to maintain the pH at 4 during the pH_{stat} test. It can be seen that while after 24h the material was only two thirds titrated, with the test continued for a longer period it asymptotically approached an ANC of about 900 mmol H^+/kg.

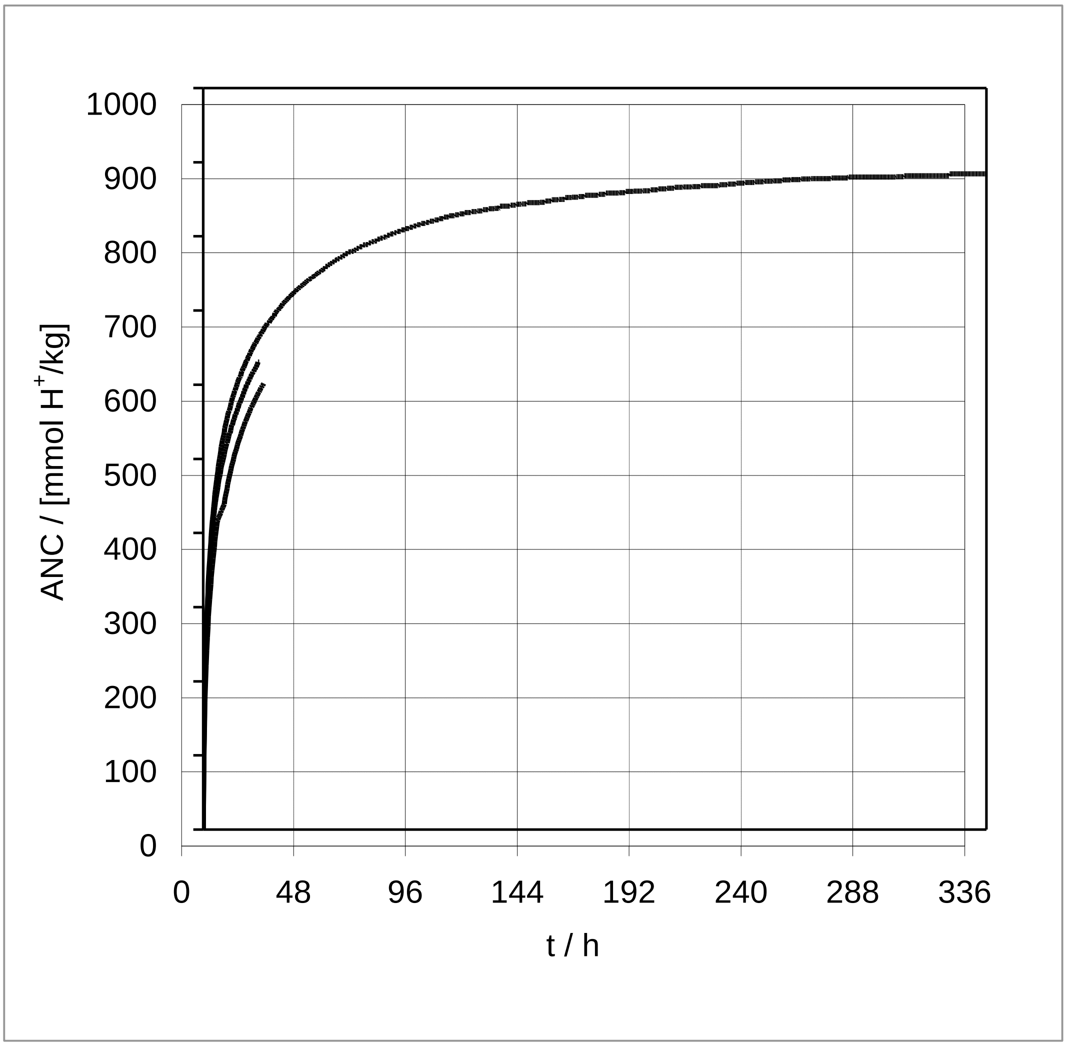

***Figure 1**: Time dependence of acid neutralization capacity (ANC) of Theisenschlamm in the pH_{stat} leaching test (at pH = 4) – In addition to the long-term experiment, two runs over 24 h are shown.*

Discussion

When the eluate concentration of the heavy metals analysed (Tab. 1) are compared with the criteria for surface dumping in the Swiss Technical Waste Regulations (the only published limiting values nearly relevant for the pH_{stat} test at pH= 4) or with the German Technical Instructions for Hazardous Waste (prescribing the DEV S4 test)[2], the limits for Zn, Pb, Ni, and Cd are exceeded. The concentration of arsenic is above the limit only in the pH_{stat} leachates. It has already been pointed out that none of the Theisenschlamm eluates provide any cause for radiological concern.

A comparison of the heavy metal elution yields normalised to the total content of a Theisenschlamm sub-sample of the same origin (WEISS et al., 1997) shows a clear difference in the mobilisation behaviour between Cd, Ni and Zn on the one hand, and

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[2] The criteria are listed for example in FÖRSTNER (1996).

Cu and Pb on the other. Nickel has the largest leachability of the investigated elements under both neutral and acidic conditions with 6-8% and around 19%, respectively. Also zinc (with 11-14% / 3%) and cadmium (with 2-8% / 0.5%) are relatively leachable. The elution yield of lead is less than 0.05% (apart from in the pH_{stat} test, where it amounts to about 0.2%), while that of copper is even one order of magnitude lower. This coincides with the findings from the "elution box" (JAHN et al., 1997). Furthermore it clearly seen that the elements As, Cd, Ni and Zn at pH = 4 are mobilized to a much greater extent than under neutral conditions.

The total levels of PAH determined after 24h Soxhlet extraction with toluene (Table 2, 1st column) are comparable with values from previous studies (WEISS et al., 1997; POPP et al., 1997). After passing through the shaking cascade, the eluate concentration of the PAHs (pursuant to EPA 610) exceeds the intervention level for contaminated plateau locations of 20 µg/l according to the *"Berliner Liste"* (HEIN et al., 1997), and also nearly reaches it during the 24h pH_{stat} test.

With the exception of fluorene, all PAHs are less than 10% mobilized. There is no significant difference between the leaching techniques used. If the different findings of the GC-MS summary analysis of the eluates (see Table 3) are also taken into account, it is obvious that further investigation is still required to correctly predict the mobilisation behaviour of the hydrophobic organic compounds in Theisenschlamm.

Information on the buffering potential of Theisenschlamm to acid inputs and thus on the heavy metals mobilization ratios (under "worst case" conditions) is provided by the acid neutralization capacity (ANC) at pH = 4. The pH_{stat} tests show Theisenschlamm to be a material with an average ANC, a view reinforced by the long-term experiment. Nevertheless, a comprehensive scale of comparison of similar hazardous waste and residues is still lacking (PASCHKE et al. (1997) does however contain an initial guide.) Moreover, it should be pointed out that a conclusive assessment of the buffering capacity of Theisenschlamm can only be made after its internal acid formation capacity has been determined. Corresponding investigations (pH_{stat}11) have yet to be carried out.

During the comprehensive characterization of the leaching behavior of Theisenschlamm, attention must also be paid to the pollutants bonded to the fine-grain fraction in terms of both its nature and its sorption characteristics. This has so far not been possible during eluate treatment. Moreover, future chemical analyses (including heavy metal speciation) should be combined with biological effect tests on the eluates/extracts (cf. e.g. CLEMENT et al., 1996; SOMMERFELD & SCHWEDT, 1996; SALLENAVE & FOMIN, 1997; FOMIN et al., 1999; BRACK et al., 2000) so that additional conclusions concerning bioavailability and (eco)toxic effects of priority pollutants in their various forms can be drawn. This would in turn enable a link to be established with ecotoxicological investigations on water samples from the Mansfeld region (cf. chapter 7 of this report and KLUMPP et al., 2000).

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9. Oxidation Treatment of Theisenschlamm

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Abstract

A low temperature oxidation process has been developed to separate lead from zinc in a complexly contaminated scrubber dust. The two-stage process consists of a grinding stage followed by contacting this material with a hydrogen peroxide solution. The resultant oxidation reaction is violently exothermic - the temperature rises spontaneously to approximately 96°C. The amount of solid phases remaining after completion of the reaction was reduced by approximately 40% and consisted largely of insoluble lead sulphate which retained the bulk of the radiation. Almost all of the zinc was placed into solution by this process as was the Cd, Re and Cu. The total PAH content of the original Theisenschlamm (468 µg/g) was reduced to 11.25 µg/g in the residual sediment and the PCDD/PCDF concentrations were reduced by approximately 40%. The radioactivity is almost completely concentrated in the solid phase. The method shows considerable promise for treatment of very fine-grained sulphide-bearing residues.

Introduction

Several attempts have been made to develop an hydrometallurgical or pyrometallurgical process to treat by extracting the valuable metal content of the Theisenschlamm residue, however none were found to be appropriate (LORENZ et al., 1992; LORENZ, 1994; WEILANDT, 1994). The treatment of this heterogeneous material requires a flexible technique that can deal with the complex characteristics of the material and at the same time minimize the cost of treatment and minimize the environmental impact. Conventional separation techniques cannot be readily applicable to this material due to its agglomerated state and its small grain size.

A series of experiments were carried out with a view to develop a low-temperature oxidation process in which the sulphide phases would be converted to sulphates, making it possible to separate the soluble zinc sulphate from the more stable lead sulphate. This possibility only exists if an oxidizing agent can act efficiently on the variety of complex phases present in the Theisenschlamm. The advantage of such an approach is that the zinc in solution could be recovered by standard metallurgical methods whereas the lead sulphate, including the radioactivity, could be processed by lead smelting (LEIPNER et al., 1994; WEILANDT, 1994).

In addition, several other characteristics of the oxidation process had to be monitored:

1. The partitioning of As, Cd, Tl (hazardous elements) and Ag, Ge,Re (valuable elements) between the soluble and solid fraction.
2. Any changes in the nature and concentrations of the organic compounds during the process.
3. The partitioning of the radionuclides between the reaction products.

The sample preparation techniques, the results of various oxidation experiments, the partitioning data and the evaluation of the reaction involving the organic compounds of the Theisenschlamm are presented in this chapter**.**

Oxidation Experiments

Samples of the Theisenschlamm were ground in an attritor and dried prior to treatment with hydrogen peroxide. The grinding was done to create fresh surfaces on the constituent particles which would be more reactive. Also, the reduction of the grain size would help to make the reaction more complete and more exothermic. Figure 1 is a flow sheet of the grinding and oxidation processes that were adopted as our standardized procedure.

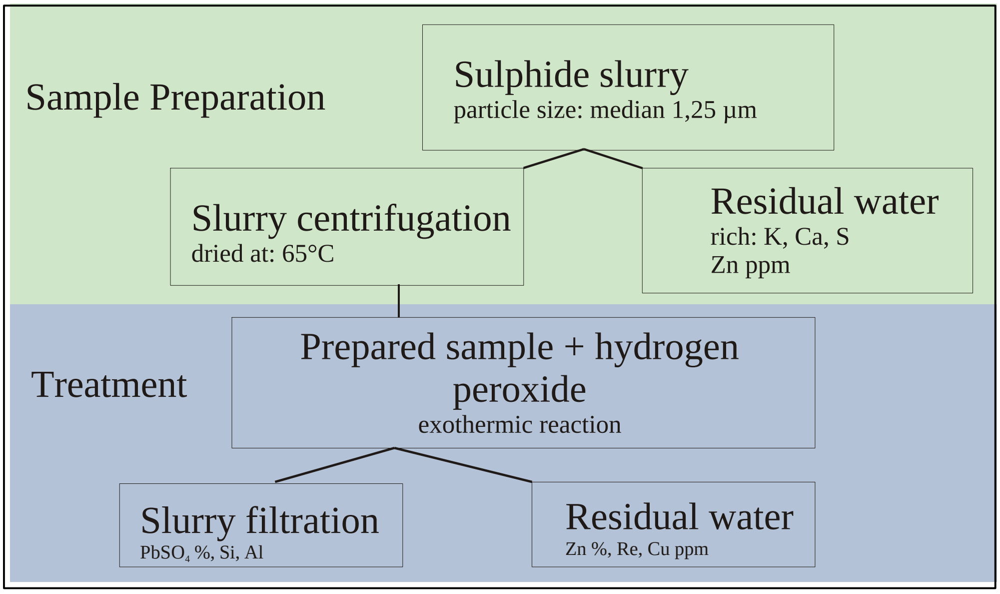

Figure 1 *Schematic illustration of the grinding and oxidation procedure developed for TSOP*

The flow process consists of two separate steps - a mechanical pre-treatment phase (grinding) and the oxidizing reaction *per se*. The whole process is referred to as the Theisenschlamm-Oxidation-Process (TSOP). The flow diagram also gives the conditions under which each step of the process was conducted.

Grinding Procedure and associated Chemical Changes

For the grinding procedure, 37 grams of the Theisenschlamm were placed in an attritor along with 300 ml of distilled water. The grinding medium consisted of roughly 2 kg of steel balls with a diameter of 2 mm. Mechanical erosion of the steel balls caused an iron contamination of the ground Theisenschlamm. The grinding time was standardized at one hour, after which the sample was dried. This procedure was used to produce the standard starting material for subsequent experiments. A substantial weight lost in excess of 14% was measured during the grinding step. Table 1 presents the chemical evaluation of the grinding process.

Table 1: *Chemical evaluation of the grinding process*

Parameter	Ground Theisenschlamm [mg/kg]	Concentration in the grinding liquid [mg/l]	Proportion in solution [%]
Al	23,600	0.7	0.03
B	111	2	17.21
Ca	8,800	540	41.45
Cd	360	0.04	0.13
Co	80	0.51	6.85
Cr	890	0.51	0.66
Cu	14,100	0.12	0.01
Fe	30,850	0.84	0.03
K	6,700	290	33.31
Mg	2,500	98	31.14
Mn	670	12	17.13
Ni	510	2.2	4.74
Pb	122,000	3.6	0.03
Tl	320	0.7	2.46
Zn	163,000	830	5.55
S_{total}	113,000	1,500	13.28
Oil & grease	8,700		0

Shown is the concentration for a limited number of elements for the Theisenschlamm after grinding as well as the composition of the recovered liquid which can contain elements in solution as well as matter in suspension. The proportion of each element that was found in the water phase is also presented in Table 1. This proportion varies from roughly 40% for Ca to almost 0 for Pb and Cu. It is clear that the composition of the Theisenschlamm before and after grinding differ considerably, however only the concentrations of the most easily water-soluble elements are affected - the concentrations of the elements of economic interest (e.g. Pb, Zn) or of environmental interest (e.g. Cd, Tl) are not significantly modified.

The Peroxide Reaction

A mass of 5 grams of the ground Theisenschlamm was then treated with 350 ml of 30% hydrogen peroxide solution. The slurry was continuously stirred magnetically and the temperature was monitored during the process. The resultant reaction was violent and strongly exothermic. At the peak of the reaction a temperature of 96ºC was measured and the slurry began to fume and froth which required vigorous stirring to prevent the slurry from boiling over. After leaving the solution overnight, the slurry was filtered and the solid residue examined by diffraction and with scanning electron microscope (SEM). The chemical composition of the liquid was determined by ICP (experimental details MORENCY et al., 1998). The radioactive elements, as detected by alpha counting, and the Pb are preferentially concentrated in the sediment at the bottom of the beaker (solid product), whereas the zinc is found in solution.

Aging of the ground Theisenschlamm.

As mentioned, the reaction between the ground Theisenschlamm powder and the hydrogen peroxide is strongly exothermic. To check for the possible influence of aging on the ground material that could be related to an oxidation process, three groups of samples (10 samples total) were prepared as described above, and the dried powders were stored in an oven at 65°C for periods of one, two and three weeks respectively prior to reaction with the peroxide. The temperature-time relationships during reaction of these ten powders are illustrated on Figure 2.

The behaviour of all three groups of samples was the same except that the time for the reaction to occur is different for the three groups. The results seems to relate to an oxidation process with the static air environment for the ground Theisenschlamm when the sample is stored at 66°C for several weeks.

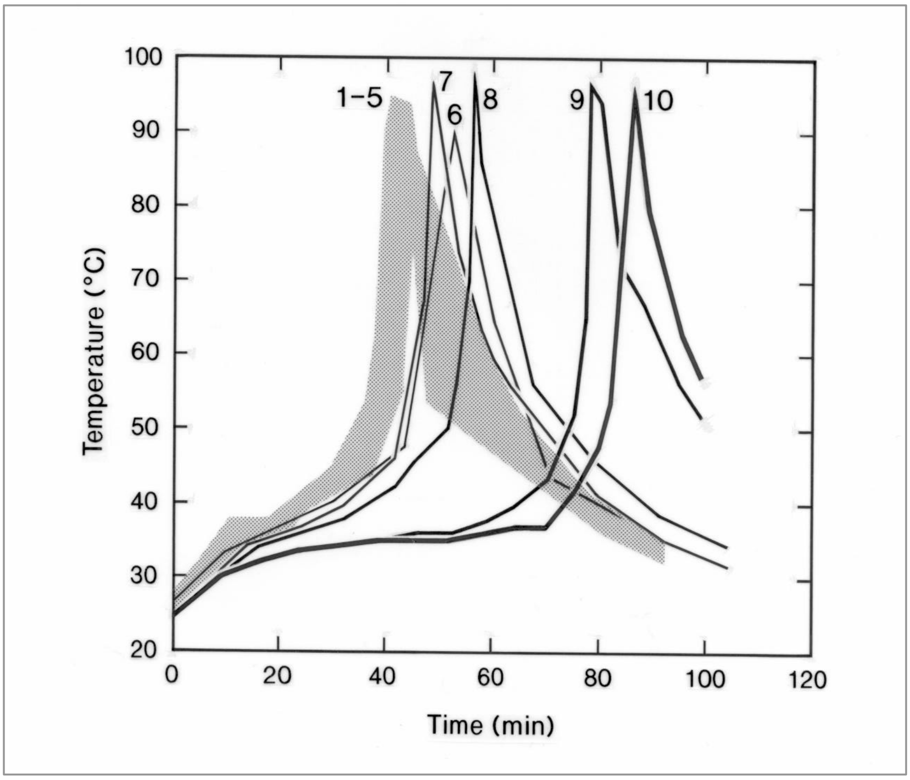

Figure 2: *Time-temperature relationship during TSOP reaction for samples of different drying ages (65°C)*

Results

Mineralogical changes resulting from the peroxide reaction

Figure 3 is a composite diffractogram showing the profile for the starting material prior to reaction, the residual solid after reaction, as well as a diffraction profile for the solid obtained by total evaporation of the liquid phase. The Theisenschlamm is shown to be a mixture of phases, predominantly galena, sphalerite/wurtzite (sulphides) and anglesite (sulphate), whereas the diffractogram of the solid product of the TSOP reaction indicates the presence of anglesite only. In particular, two peaks for the sulphides ZnS, (at $2\theta = 33.2°$ and $35.7°$), are visible on the ground Theisenschlamm curve whereas they are absent from the middle curve. The diffraction pattern for the liquid product is dominated by boyleite (zinc sulphate) since the liquid phase was almost completely clear after the reaction.

These results indicate that the zinc and lead sulphides are oxidized and the zinc is found in solution. It was determined that the lead sulphide is converted to lead sulphate which is a stable phase under surface conditions. It is probable that the negligible residual zinc in the solid is associated with a more stable phase and is not readily available for reaction with the hydrogen peroxide It has been shown that some grains in the Theisenschlamm residue are complete solid solution mixtures of Pb and Zn. It is therefore possible that an anglesite coating forms around the larger grains during reaction, thereby shielding the Zn from further dissolution.

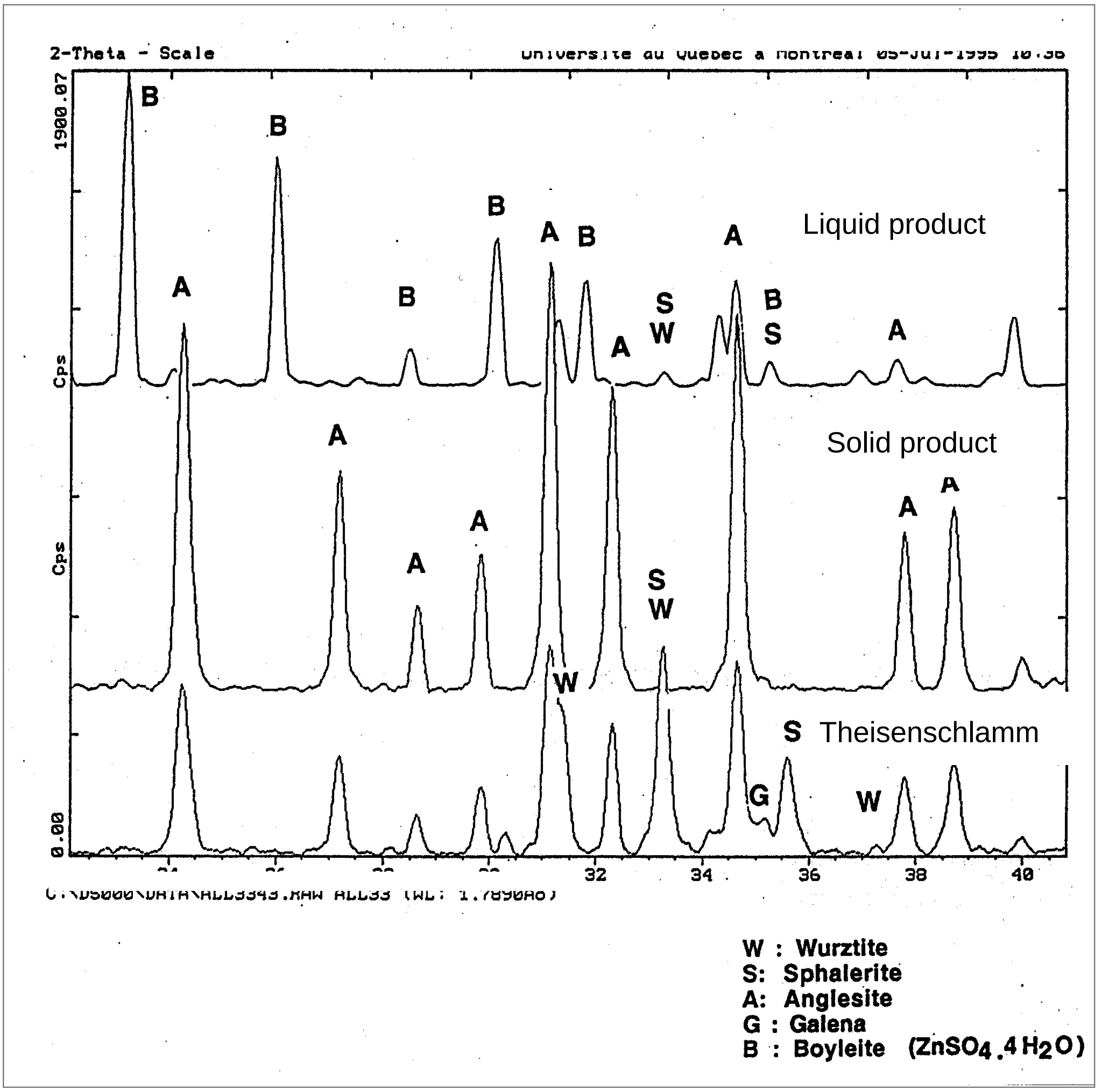

Figure 3: *Composite diffractogram showing the profile for the starting material prior to reaction (Theisenschlamm),the solid product of the reaction, as well as a diffraction profile for the sediment obtained by total evaporation of the peroxide solution.*

Effect of Peroxide Treatment on Particle Size

Figure 4 is a relative frequency distribution diagram for a sample of Theisenschlamm and the solid product of the reaction. The ground sample had a median diameter of 3.98 µm for the volume calculated results compared with a median value for the solid after TSOP treatment of 3.20 µm.

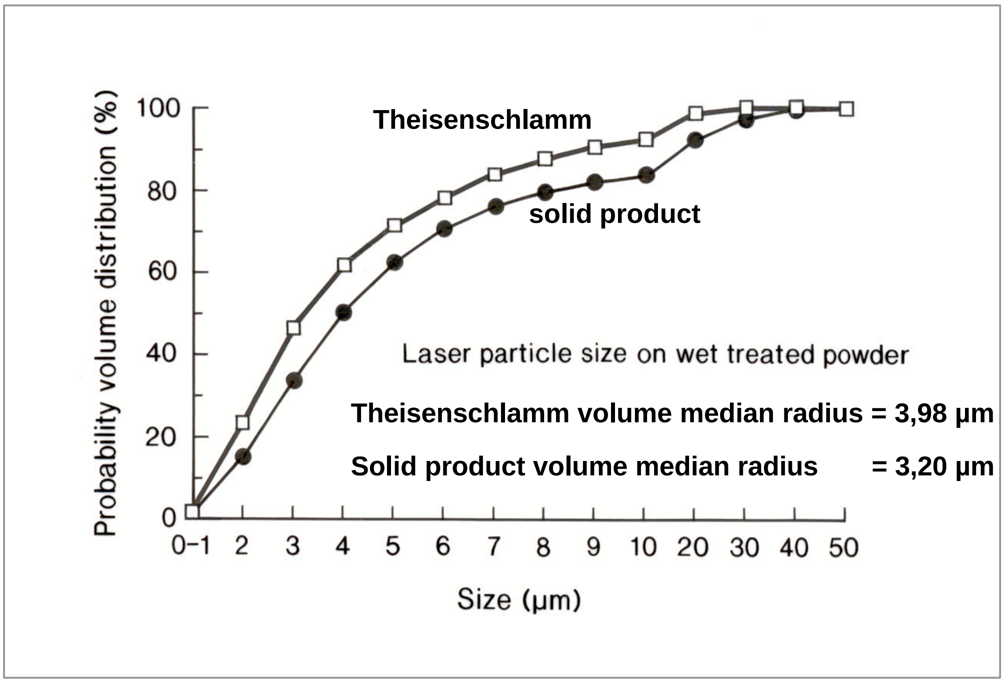

Figure 4: *Relative grain size distribution for ground Theisenschlamm and the remaining solid product of TSOP treatment*

Impact of the Peroxide Treatment on the Inorganic Chemistry

Table 2 presents results of analyses of solid products after treatment as well as the composition of ground Theisenschlamm and the composition of the residual liquid.

The most important feature of the results is seen by comparing the Pb:Zn ratio for the ground Theisenschlamm prior to treatment with that of the solid remaining after treatment, in the former the ratio is 0.75:1 whereas in the latter it is approximately 12:1 while the same ratio for the liquid phase is 1:700.

The percentage of the original mass in solution for each element was calculated by assuming 3 grams of solid remaining for 280 ml of liquid after the reaction. These values are shown graphically in Figure 6 in relationship to their concentrations in the Theisenschlamm. Results show that 93.7% of the zinc originally present was found in solution whereas the comparable figure for Pb is about 0.2%. In other words, the separation of Pb from Zn is almost complete. Pb, S, Si and Fe are the most important elements in the residual sediment, whereas in the liquid phase, the total of Zn + S is 92% of the total amount present, with Re and Cu being important associated elements.

Table 2: *Composition of a typical sample of ground Theisenschlamm and the composition of the remains of the hydrogen peroxide solution after cessation of the reaction*

	Ground Theisenshlamm	Products after TSOP Reaction	
Element	[µg/g]	Solid [µg/g]	Liquid [mg/l]
Ag	520	810	n.d.
As	4,080	7,600	0.19
Cd	360	30	5.10
Cr	890	1,160	1.56
Cu	14,100	1,215	183.50
Fe	30,850	43,700	1.45
Hg	110	130	n.d.
Mn	670	580	5.82
Ni	510	360	4.57
Pb	122,000	182,000	3.75
Re	63	9	1.00
Sb	1,470	2,400	0.06
Se	720	320	8.40
Sn	17,200	26,500	n.d.
Th	2	3	n.d.
Ti	5,000	5,580	n.d.
Tl	320	290	2.18
U	30	32	0.12
Zn	163,000	15,800	2,500
S_{total}	113,000	39,900	1,680

n.d.: not detectable

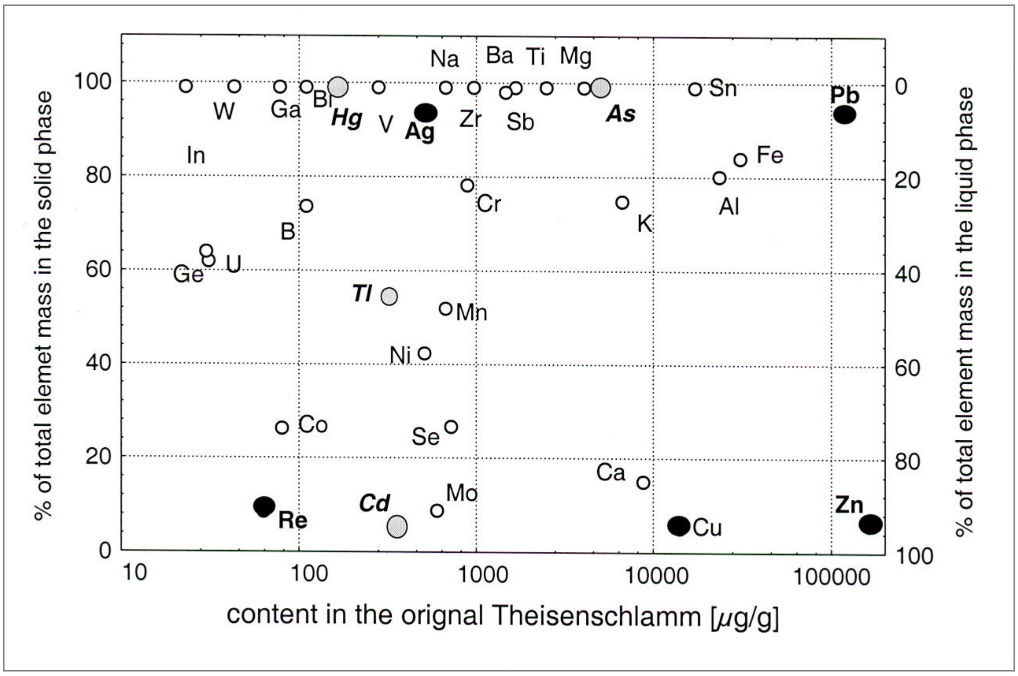

Figure 5: *Element distribution pattern between the solid and the liquid phases after the TSOP treatment*

Impact of the Peroxide Treatment on the Organic Chemistry

Results of the determination of the PAH concentrations (Morency et al., 1998) are presented in Table 3. The data show that the concentrations in the original material are much higher than in the solid residue of the oxydation process. Total PAH concentration (see Table 3) in the untreated material is 468.9 mg/kg, whereas in the residual sediment it is 11.25 mg/kg giving a reduction of almost 98%.

Table 3: *Results of PAH measurements on ground Theisenschlamm and TSOP reaction products*

Compound	Ground Theisenschlamm [µg/g]	Solid reaction product [µg/g]	Liquid product [µg/ml]
Naphtalene	1.9	0.20	0.0140
Acenaphtalene	0.3	0.03	0.0012
Fluorene	2.9	0.12	0.0033
Phenanthrene	111.7	0.04	0.0100
Anthracene	10.7	n.d.	0.0009
Fluoranthene	71.0	1.90	0.0070
Pyrene	74.5	2.31	0.0014
Benzo(a)antracene	21.2	1.16	n.d.
Chrysene	62.3	2.20	n.d.
Benzo(b)fluoranthene	45.6	1.64	n.d.
Benzo(k)fluoranthene	4.7	0.27	n.d.
Benzo(a)pyrene	18.0	0.57	n.d.
Dibenzo(a,h)antracene	1.2	n.d.	n.d.
Benzo(g,h,i)perylene	31.7	0.63	n.d.
Indo(1,2,3)pyrene	11.2	0.18	n.d.

n.d.: not detectable

The results of the identification of several categories of compounds by GC/MS analysis (Morency et al., 1998) were classified into groups and are presented in Table 4. The solid product has a chromatogramm which is dominated by the paraffines.

The high boiling temperature of the mixture has been reduced. The values in Table 4 clearly show the decrease in the concentration of aromatic compounds. Specifically, the quinoline/isoquinoline derivatives are absent and their alteration products, the aromatic amino compounds are present.

Table 4: *Results of GC/MS analyses of ground Theisenschlamm and TSOP reaction products*

Compound	Ground Theisen-schlamm [area/g sample]	Solid product [area/g sample]	Liquid product [area/148 ml water]
Alkanes	4,927,739	1,689,739	51,504
Polycyclic aromates	21,691,242	617,529	17,612
Benzenederivates	415,116	495,526	411,736
Naphthalinederivates	1,860,532	399,127	1,776
Biphenyles and/or dibenzofuranes	20,674,225	4,618	traces
Diphenylethanes	traces	9,607	57,720
Quinoline- and/or Isoquinolinederivatives	24,969	n.d.	n.d.
Aromatic amines	n.d.	12,787	n.d.
Dibenzothiophene-derivatives	5,672,415	69,959	n.d.
Fluorenone-9	431,204	4,729	traces
Benzenemethanol	43,781	40,865	38,776
Stryene	34,166	35,134	14,060

n.d.: not detectable to a limit of approx. 5-10 ng/component (full scan mode)

The analysis of the extract from the liquid residue indicates a low concentration of hydrocarbons. Water soluble substances, such as benzenemethanol and benzene-dicarbonyl acids are predominant with volatile compounds such as the xylenes also present. The concentration of the toxicologically relevant N- and S-heterocyclic compounds has been significantly reduced in the solid while the liquid product contains insignificant quantities of hydrocarbons, predominantly alkanes, some low boiling aromatics and water soluble compounds such as phthalates.

The results of the PCDD/PCDF analyses of the original material and the solid product are listed in Table 5. The sum total concentration of each group is shown in ng/g of dried material. A decrease in PCDD/PCDF concentration after peroxide treatment is observed, particularily in the smaller chlorosubstituted isomer range. It is possible that some of the more volatile (tetrachloro-substituted) isomers might have been overlooked during the analysis - this is because an open beaker was used during the exothermic oxidation reaction.

Table 5: *Results of PCDD/PCDF analyses on ground Theisenschlamm and the sediment remaining after TSOP treatment. Also shown are the International Toxicity Equivalents (ITE) expressed in ng/g.*

	Ground Theisenschlamm [ng/g];	Solid product [ng/g]
Sum TCDF	86,0	47,1
Sum PeCDF	40,3	30,1
Sum HxCDF	10,5	14,7
Sum HpCDF	8,4	6,2
OCDF	1,4	2,5
Sum PCDF	146,6	100,6
Sum TCDD	5,9	0,7
Sum PeCDD	0,8	1,1
Sum HxCDD	1,8	0,3
Sum HpCDD	1,9	n.d.
OCDD	5,5	n.d.
Sum PCDD	15,8	2,1
Sum PCDD/PCDF	162,4	102,7
Toxicity Equivalents [ng iTE/kg]		
Sum PCDD/PCDF	**171,0**	**140,1**

n.d: not detectable lower than approximatly 50 pg.

A chemical change, involving the degradation or transformation of the dioxins and furans would produce changes in the isomeric pattern. However, when compared with Theisenschlamm sample, the relative proportion of the PCDD/PCDF compounds in the product was the same - only the total amount varies.

Radioactivity

Alpha and gamma spectroscopy (Morency et al., 1998) was carried out on the ground Theisenschlamm as well as on both TSOP reaction products to determine the activity of ^{210}Po and ^{210}Pb respectively. The radioactivity value associated with ^{210}Po in the Theisenschlamm sample prior to reaction was determined to be 16.6 kBq/kg. After the peroxide treatment, the value in the residual solid increased to 19.9 kBq/kg whereas the value for the liquid phase was 0.2 kBq/l. The radioactivity value associated with ^{210}Pb in the starting material prior to reaction was determined to be 22.1 kBq/kg, whereas in the solid and the liquid phase the values were 27.1 kBq/kg and 0.004 kBq/l respectively.

Both techniques yielded comparable results, indicating that the radioactivity is concentrated with the solid and in particular in the lead sulphate phase, after the peroxide treatment. The concentration level in the liquid phase is very low and thus the treatment can be considered to have been successful.

Discussion

Peroxide oxidation has occasionally been used as a technique for conditioning the surface of sulphide-bearing mine waste prior to application of coatings or other treatments (MAKI et al., 1995; GEORGOPOULOU et al., 1995). The mine waste samples were also ground prior to treatment but no details were given on the characteristics related to the size distribution, mean or median. On the other hand the median particle diameter of Theisenschlamm aggregates is approximately 1 µm and the particles which constitute the aggregates are smaller still. Thus it is likely that the mine waste, even after grinding, is still coarser than the Theisenschlamm. An additional difference in the process is related to the concentration of the hydrogen peroxide used (9%) and the solid:liquid ratio in which 30 mg of powder in 200 ml of peroxide Maki et al. (1995). In our process 5 g of powder in 350 ml of peroxide at 30% concentration was used**.** These significant differences, when combined with the finer particle size of the Theisenchlamm and the poorly crystalline nature of the sulphides of the scrubber dust, resulted in an exothermic reaction as described above which was not noted in the other two studies.

A peroxide treatment as described here has considerable remediation potential, particularily for very fine-grained material. Lead, zinc and sulphur are the most important components of the Theisenschlamm. The separation of the Zn from the Pb not only reduces the mass of the waste it also generates an economically useful product which can be used as input feedstock to other industrial processes. Hydrometallurgical and pyrometallurgical methods require significant capital investment which would not be economically feasible considering the relatively small amount of material to be treated (LEIPNER et al., 1991; LORENZ et al., 1992).

Conclusions

- Hydrogen peroxide is an excellent oxiding agent for the Theisenschlamm. It caused the near complete separation of the Zn from the Pb. This yields an hydrated zinc sulphate that can be used in an electrolytic process for zinc recovery and products with an added value. In addition, lead sulphate can be used in lead smelting for products with added values.
- The small amount of Zn remaining in the solid residue after treatment does not appear to be accessible at the grain size at which the experiments were conducted.
- The radioactivity is associated with the solid phase (i.e. lead sulphate).

- The peroxide treatment reduces the concentration of PAH in the solid residue by almost 98% and the PCDD/PCDF concentrations by approximately 40%.
- After peroxide treatment, the liquid phase contains insignificantly small quantities of hydrocarbons, predominantly alkanes, some low boiling aromatics and water soluble compounds such as phthalates.

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10. Feasibility Study of the Treatment for Theisenschlamm with Hydrogen Peroxide

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Abstract

The treatment of Theisenschlamm with hydrogen peroxide, was developed in the laboratory as a batch process and at this stage, no attempt was made to upscale the process. The technique has produced excellent results regarding the elimination of organic compounds, separating and recovering the main components lead and zinc. In so doing, the associated radiation is now concentrated with the lead phase. The phase transformation and the resulting separation allow for the recycling of zinc, lead and other valuable metals and at the same time eliminates the environmental problems inherent with the Theisenschlamm. Unlike disposal, this procedure could be a final solution to the problem. The cost associated with the treatment is offset by the value associated with the recoverable metals. The feasibility study presented in this paper considered the process as an industrial continuous treatment process. The process can also be designed to be applied to other environmental problems in particular those related with suphide residues from mining activities.

Options considered for solving the Theisenschlamm problems

Due to market globalisation and a greater accessibility to raw materials markets, Theisenschlamm is only of limited interest as a source of raw material (Steinkamm 1994). This explains why disposal is being considered as the main option.

In addition, the amount of chemical elements which are banned or restricted like thallium and mercury is small, less than 100 tonnes which means that expenditure for proper storage would be low. However other more serious problems would arise in connection with cell storage owing to the amount of arsenic (some 1,430 t) in the sludge. Also, depending on the method used, other residues will result which would in turn require storage or management of these residues.

According to KRAMM (1994), there are three viable options for the safe storage of Theisenschlamm:

- Local safeguarding

- Disposal elsewhere above ground
- Underground storage in mine galleries

Option 1 is associated with the risk of sink holes. Option 2 would be subject to constant aftercare costs. The drawback of Option 3, the safest approach, is that it impedes subsequent treatment and the associated cost is high. These options do not offer a permanent solution and no return or cost reduction from added value from recycling is possible.

When it originally arose, the Theisenschlamm problem was less serious, but with time alterations throught oxidation with the help of microorganisms brought about the generation of acid water with the resulting metal dispersion in the environment. These microorganisms, including those which could very well carry out the conversion of sulphides and organic compounds (STOLL, 1994) are presently at work except that this process is not controlled and will take several decades or centuries for complete restoration.

Hence dumping will not solve the problem in the long term, but will simply pass on the responsibility to subsequent generations. Dumping should only be regarded as an emergency solution in the absence of proper treatment or recycling methods for the Theisenschlamm.

The following possibilities were suggested for treatment:

- Physical separation
    - Colloidal separation (MORENCY, 1994)
    - Wet magnetic separation (MORENCY, 1994)
- Hydrometallurgical separation techniques, e.g.
    - VITROKELE methods with prior extraction of the organic components (Gesellschaft für Beseitigung und Sanierung von Altlasten mbH, 1994)
    - Sulphuric acid oxidising pressure leaching (GOCK *& SÖTEMANN*, 1994)
- Pyrometallic separation techniques, e.g. calcination (LURGI method) with post-combustion and purification of the calcination gas (WEILANDT, 1994)
- Microbiological techniques, e.g. using ‘chemolithotrophic’ bacteria (STOLL, 1994)

Other processes are described and assessed in LORENZ (1994), STEINKAMM (1994) and LEIPNER (1994). However, none of these methods provide a satisfactory solution to the Theisenschlamm problems.

The proposed oxidation process using peroxide treatment is a possible permanent solution which recovers valuable metals from the Theisenschlamm for further processing. This approach is in stride with the concept of industrial ecology.

Description of the reaction process

The method comprises directly mixing the Theisenschlamm with an H_2O_2 solution. The laboratory-scale experiments are described in Chapter 9. An exothermic reaction with a sharp rise in temperature occurs, which must be taken into account when designing the industrial plant.

A liquid and a solid phase are produced, which are separated by filtration. The sulphation (oxidation of the sulphidic components) results in the very good separation of lead and zinc. The organic substances are almost completely destroyed in the solid residue and only small amounts are present in the liquid phase (see also Chapter 9). For our purpose the initial and final state of these organic substances will not be considered any further in this paper.

The results of the laboratory batch experiment displayed an abrupt transition from the normal, slow oxidation reactions to spontaneous reactions that cannot be controlled on a batch industrial scale. In the laboratory, it was also established that the reaction could be initiated and would still result in a non-controlled exothermic reaction for concentration of H_2O_2 as low as 3%. Therefore one of the goal of this feasibility study was to evaluate if the process can be converted to a continuous process.

Description of the thre phases involved with the reaction

- *Gas phase*

During the reaction, carbon dioxide is released by the destruction of organic substances resulting from the oxidation of carbon, this is also accompanied by the emanation of steam. Since these experiments were carried in open vessels, and the gas phase was not collected for detailed quantitative analysis, undoubtedly, other decomposition products such as carbon monoxide, oxygen and hydrogen are certainly present. However, the process can be designed such that the amount of steam is minimised in order to avoid large heat lost. Moreover, process management must also take into account the fact that this gas development is accompanied by the formation of foam, and therefore a sprinkling system combined with cooling are required.

- *Liquid phase*

The liquid phase turns out, after filtration, to be a clear liquid mainly containing zinc sulphate. However, the zinc concentration is not very high, owing to the process involving high excess H_2O_2. The dilution lowers the zinc content from an average of 18% in the original solid to about 7.5% in solution, nevertheless a local electro-chemical treatment and metal extraction could be feasible.

- *Solid phase*

In the solid phase, the lead sulphate is enriched which in turns increases the radioactivity of the material. Although ^{210}Pb is dangerous in the form of very fine distributed particulate as it can penetrate the respiratory system of the human body, causing radioactive harm. The same material is harmless once process into lead products like bricks or batteries for motor vehicles. The type of radiation associated with ^{210}Pb only travels a few centimetres in air. Therefore this type of lead can be used safely with industrial products. The lead concentrate could be used at a smelting plant (Gesellschaft für Beseitigung und Sanierung von Altlasten mbH, 1994). Moreover, LEHMANN (1994) draws attention to the fact that the radioactive hazard of the lead present is outweighed by its chemical hazard. Therefore, when treating Theisenschlamm, special radiation protection measures are not required but the dust from a dried slurry can be a serious problem if inhaled.

Reaction parameters

This type of reaction responds to different kind of parameters and in our laboratory study, these parameters have hardly been studied in particular with respect to continuous process control. Therefore, only general remarks can be made at this time. Grain size, ratio of solid:liquid, pH-Eh and residence time for a complete reaction are required for the upscaling to a full-scale industrial plant.

- Temperature influence

Any increase in temperature has a positive effect, for example by significantly reducing the reaction times.

The course of the reaction indicates that if the components are pre-heated (e.g. to 55°C), the long initial waiting phase can be reduce considerably and the oxidation process should begin shortly thereafter with the oxidation and destruction of the organic compounds. The subsequent sulphide oxidation could take place earlier and attain a higher temperature if prior destruction of bituminous particles and organic coating of the feedstock has been accomplished.

This temperature pre-treatment is limited by the dissociation possibility of the H_2O_2 and the greater steam generation in the gas phase. Evaporation/sublimation from the Theisenschlamm is not expected below 100°C.

- Pressure influence

Increasing the pressure is not expected to change the reactions in the liquid phase and so the process can be carried out in the atmospheric range. This is convenient for the plant design.

- Treating other substances

The high energy gain would allow other substances to be treated simultaneously, as long as this does not impair the reaction mechanism. At the moment, suitable substances include neutral or sulphurous wastewater (as sulphide, sulphite or sulphate), sludge containing heavy metals, organic impurities (anode sludge), fly ash and residual materials from smelting plants in the region (WEILANDT, 1994). On the other hand, processing waste containing NO_x or halogens depends on the quality of the subsequent waste gas scrubbing system and this may render the material selection difficult.

Principles related to an industrial process design

Theisenschlamm cannot be directly recycled regardless of the methods used, its complexity make it impossible to obtain directly recyclable products in a single stage process. Ultimately hydrogen peroxide treatment results in products (e.g. zinc as sulphate in the liquid phase, lead as sulphate in the solid phase), which can be easily processed in other useful products. The spontaneous reactions during the discontinuous process show that the method can only be controlled if conducted in a continuous process with the liquid phase.

Slurrying the Theisenschlamm is a stage which would also have to take into account the impurities mixed within the slurry. In addition a separation stage (filtration) for the solid–liquid recovery when the reaction is completed will also be required.

Post-treatment is essential for the gas, liquid and solid phases. Impurities or other rejects from the process have to be kept to a minimum. The estimate made by WEILANDT (1994) that 5–6% of the Theisenschlamm will need to diposed of may well prove to be excessive.

The main process flow should be carried out using an ‘online’ technology. Conducting the H_2O_2 reaction stage as a two-stage reaction appears suitable. The heat from the reaction (exothermic) should be dissipated via a closed cooling system (hot-water system) to which heat consumers are connected directly or indirectly assuming the heat can be sold. The system should contain emergency coolers and an emergency heating boiler. The heat exchangers could also, if necessary, function not only as coolers but also as pre-heaters during start-up processes and pre-treatment of the slurry.

In all other respects, the method is subject to the same principles and conditions that guides the operation of a standard chemical plant (i.e. safety, environmental protection, etc.).

Flow process for an industrial production plant

The industrial process is centered around the reactor and is characterised by the following associated stages:

- Pre-treatment of the starting materials**;**
- Introduction (dosing) of the starting materials**;**
- Reaction per se;
- Output of intermediate products**;**
- Output of final products**;**
- Separation of final products**.**

The Theisenschlamm must be kept in suspension while undergoing this wet oxidation treatment. This can be carried out with a hot process solution in a mixer (see Figure 1). The coarse natural components (coarse gravel, sand, and slag) must also be removed in this mixer otherwise they could disrupt the flow process and the re-circulation and cooling processes.

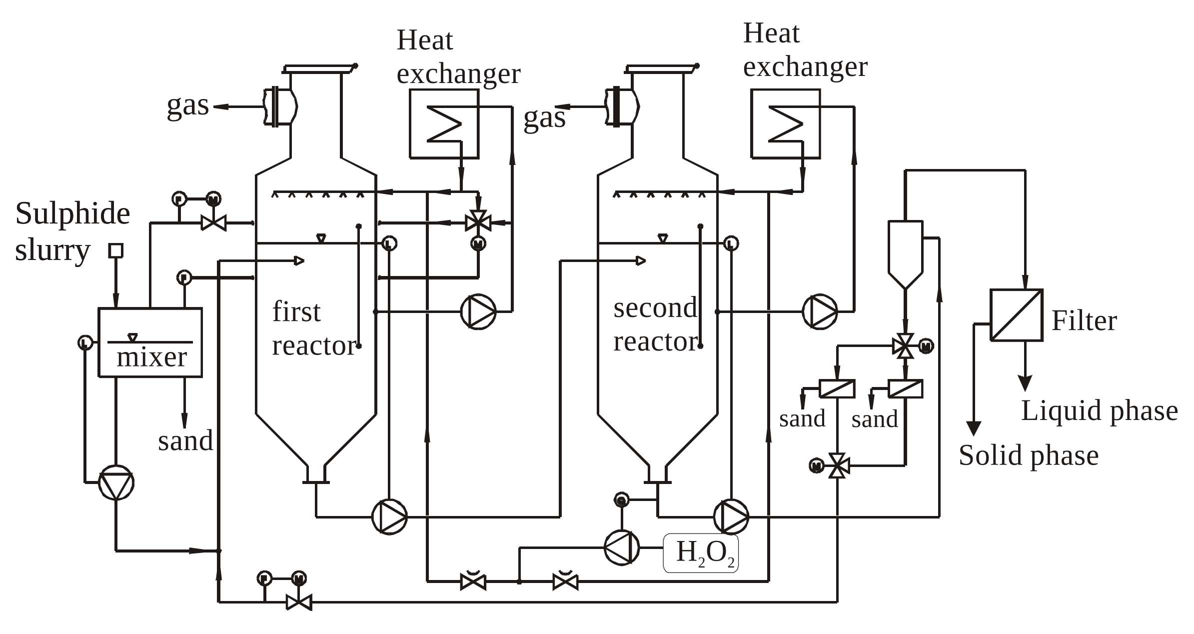

Figure 1: *Flowsheet of the process*

Of course, the Theisenschlamm must initially be collected, transported, placed in a silo for interim storage in a state suitable for a slurry preparation. The Theisenschlamm in a slurry form, will be pump and injected via a nozzle into the primary reactor, where already turbulence and mixing are ongoing due to the violent reaction.

The primary reactor should be cooled by an unregulated circulation pump with a subsequent hot-water cooler. Temperature control (not shown) will take place on the hot-water side depending on the amount of cooling water required. Shortly before entering the sprinkler system, the hydrogen peroxide solution is added. Sprinkling will destroy the foam created during gas development and will also cool the system.

As already mentioned above, the main purpose of the first reactor is for the breakdown and destruction of the organic substances. Therefore, considerable gas and steam formation will take place in this reactor, and the sprinkling capacity should be designed accordingly.

After a certain residence time in the first reactor and depending on the level of the material, the content is pumped into the second reactor. The procedure in this reactor is identical to the first one .

A cyclone is used after the second reactor to separate coarse material from the fine components. A partial flow is returned to the first reactor via the sand filters. Two sand filters are used in order to allow for cake recovery which can accumulate after several cycles of processing. The recovered sandy material is washed, flushed, and if necessary screened to provide a usable building or filling material. The fine-grained water–solid mixture from the cyclone is separated on the filter. Experiments must be conducted to select the type of filter most suited for the process. Although all the process stages need to be tested, they can all be controlled with the current engineering state of the art and the process can be implemented on an industrial plant. The reactor material would need to be enamelled in order to provide resistance against acid components and corrosion. Austenitic steels, e.g. V4A, or steels such as that employed in flue gas scrubbing plants containing SO_2 should be used for pipes, fittings and the heat exchangers (conventional plate exchangers). Stainless steel, ceramic materials (porcelain) or steel with mineral coating (enamel) would be suitable. Polytetrafluoroethylene (PTFE) could be used as a sealing material.

The control equipment for the plant comprises relatively simple temperature gauges, level monitoring and throughput controls. The pumps should preferably feature speed control using frequency converters. Hydrogen peroxide solution should be fed at a rate which depends on the residual concentration of H_2O_2 and free oxygen measured at the reactor output.

As far as safety is concerned, care should be taken that the amount of H_2O_2 added to the first reactor does not exceed the required amount which is actually consumed for the oxidation of the organic compounds. Otherwise additional reactions may take place during pumping and in the heat exchanger. Moreover, the process water not completely used up could release undesirable reactions in the mixture.

When adding hydrogen peroxide, a powerful exothermic reaction will always be triggered and it will require cooling. Optimising the amount of hydrogen peroxide required in the process without bringing the reaction to a halt would result in substantial cost savings measures.

Products and preliminary mass balance

The treatment plant should be geared towards treating the waste material to produce the maximum metal recovery that can immediately be sold to lower the cost of the treatment. In the case of the Theisenschlamm with its diverse chemical composition and compounds, some metals will not be able to be recovered economically.

Therefore, some of the residue will have to be managed. However, thanks to the good separation which can be achieved by treatment with hydrogen peroxide, the amount needing to be dumped will be less than 5%, corresponding to less than 11,000 t will need to be managed.

Based on total amount of 220,000 t of Theisenschlamm, the following yield will arise:

Gas phase:	106,600 t (of which 92,000 t CO_2, 14,600 t steam)
Liquid phase:	505,100 t (of which 398,300 t water, 106,800 t salts)
Solid-phase:	110,100 t

Processing will require 501,800 t 60% H_2O_2 solution. Hopefully the energy associated with the gas and liquid phase can be sold. Obviously, the liquid phase should be processed locally with an electrolytic process to get the valuable metals (Zn, Re, Cu) and sulphuric acid. Only relatively clean but salty water will remain, which if necessary can then undergo further treatment. Valuable metals and ballast materials would then have to be separated from the solid-phase, so that the lead concentrate can be used in a lead smelting plant.

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Annex

A 1: Tabular slag heap (southern part) of the Helbra copper shale smelter, deposited between 1960 and 1990. On the lower plateau of the slag heap (arrow) remains of a former Theisenschlamm storage basin. Ahead of the heaps the wetlands of the river Glume with Theisenschlamm-bearing sediments (dark grey). (Foto: P. Schreck)

A 2: Central part of the tabular slag heap of the Eisleben copper shale smelter, deposited by 1967. Molten slag was supplied by the “slag train” and dumped down the slope. In the foreground the embankment for the slag train (white arrow). (Foto: P. Schreck)

A 3: Wetlands of the river Glume next to the Helbra copper shale smelter. Theisenschlamm (black sediment) was flushed in from the former flue gas treatment plant, situated close to the chimney. (Foto: P. Schreck)

A 4: Theisenschlamm deposit Pond IX, a basin for the dewatering of metalliferous slurry from top gas scrubbing, constructed on the Helbra slag heap. The upper part of the up to 5 m thick Theisenschlamm dump is disturbed by mud cracks of several decimeters in depth. (Foto: P. Schreck)

A 5: Central Theisenschlamm dump Pond X, the final deposit for about 250,000 tons of Theisenschlamm and related smelting residues from the two smelters. The basin is embedded in a heap of mine dump material. Mud cracks, several decimeters deep, at the surface of the unprotected deposit. (Foto: P. Schreck)

A 6: Former smelter site Helbra, slag heaps with Theisenschlamm deposit Pond IX (Foto by courtesy of R. Lorenz)

A 7: Pond XI, deposit of seepage water neutralisation products, mainly Zn hydroxides and carbonates. (Foto: H. Weiss)

A 8: Pond IX, Theisenschlamm deposit on a tabular slag heap. (Foto: H. Weiss)

A 9: Decantation cells on Theisenschlamm deposits in the foreground, dolostone heap with Pond X (brown) and copper shale heap (black) in the background.
(Foto: H. Weiss)

A 10: Theisenschlamm decantation cells and partly demolished Helbra smelter in the background (1994). (Foto: H. Weiss)

A 11: Secondary copper minerals on the surface of weathered Theisenschlamm (Foto: H. Weiss)

A 12: Surface of weathered Theisenschlamm exposed about 10 years, white material is mostly Zn hydroxide. (Foto: H. Weiss)

A 13: The Stadtborn brook- a highly contaminated spring; green Glaucocerinite (a Zn-Cu-Al-Sulfate) precipitates spontaneously, a sampling system for water quality monitoring has been installed by UFZ (Foto: M. Schubert)