

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 than 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 $(\text{NH}_4)_2\text{C}_2\text{O}_2$, 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).

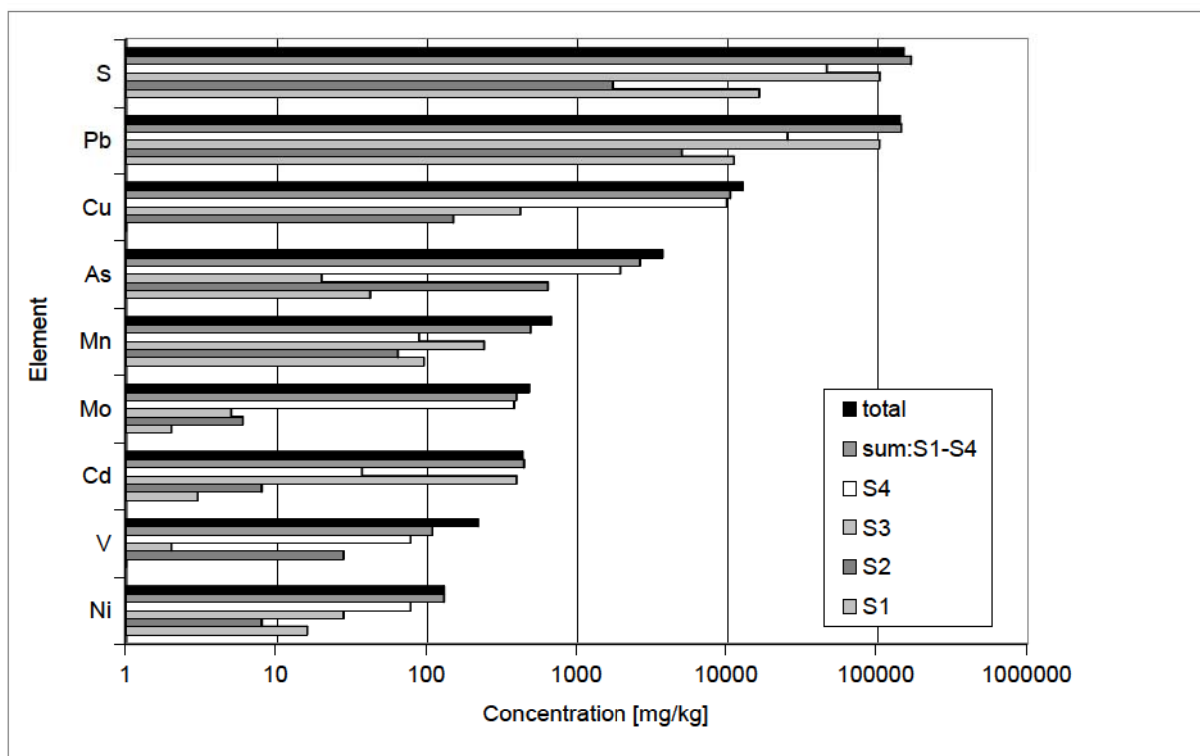


Figure 1: Comparison of extraction yields from different leaching steps (see text for explanation)

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, poly-aromatic 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 [$\mu\text{g/g}$]

Compound (Abbrev.)	Concentrations, $\mu\text{g/g}$
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 $\mu\text{g/kg}$.

Table 5: Concentrations of PCDD/PCDF (T=Tetra-, Pe=Penta-, Hx=Hexa-, Hp=Hepta-) in the Theisenschlamm [$\mu\text{g/kg}$]

Compound	Concentrations, $\mu\text{g/kg}$
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 $\mu\text{g/kg}$, 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.

References

- ARBEITSGEMEINSCHAFT TÜV BAYERN/L.U.B. LURGI-UMWELT-BETEILIGUNGSGESELLSCHAFT (1991): Abschlußbericht zum Forschungs- und Entwicklungsvorhaben "Umweltsanierung des Großraumes Mansfeld".- 1403 S. + Anlagen; Eisleben
- BLUMER, M. & YOUNGBLOOD, W. W. (1975): Polycyclic aromatic hydrocarbons in soils and recent sediments.- Science 188, 53-55.
- BUNDESMINISTER FÜR UMWELT, NATURSCHUTZ UND REAKTORSICHERHEIT (Ed.) (1992): Bericht der Bund/Länder-Arbeitsgruppe DIOXINE. Rechtsnormen, Richtwerte, Handlungsempfehlungen, Meßprogramme, Meßwerte und Forschungsprogramme.- Bonn.
- EPA (= U.S. Environmental Protection Agency, Ed.) 610 (1984): Polynuclear aromatic hydrocarbons. Federal register Part VIII, EPA, 40 CFR Part 136.
- DAVIDSON, C.M.M DUNCAN, A.L., LITTLEJOHN, D., URE, A.M. & GARDEN, L.M. (1998) A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land.- Anal. Chim. Acta 363, 45-55.
- HAMMER, J., JUNGE, F., RÖSLER, H.J., NIESE, S., GLEISBERG, B. & Stiehl, G. (1990): Element and isotopic geochemical investigations of the Kupferschiefer in the vicinity of "Rote

- Fäule", indicating copper mineralization (Sangerhausen basin, G.D.R.).- Chem. Geol. 85, 345-360.
- HAMMER, J., RÖSLER, H.J. & GLEISBERG, B. (1988): Neutronenaktivierungsenergie, säulen-chromatographische und IR-spektroskopische Untersuchung der Bitumensubstanz des Kupferschiefers der Sangerhäuser Mulde (DDR).- Chem. Erde. 48, 61-78.
- HARNLY, M., STEPHENS, R., MCLAUGHLIN, C., MARCOTTE, J., PETREAS, M. & GOLDMAN, L. (1995): Polychlorinated dibenzo-*p*-dioxin and dibenzofuran contamination at metal recovery facilities, open burn sites and a railroad car incineration facility.- Environ. Sci. Technol. 29, 677-684.
- KUTZ, F., BARNES, D.G., BOTTIMORE, D.P., GREIM, H & BRETTHAUER, E.W. (1990): The international toxicity equivalency factor (i-TEF) method of risk assessment for complex mixtures of dioxines and related compounds.- Chemosphere 20, 751-757.
- POPP, P. & PASCHKE, A. (2000) unpublished work.
- POPP, P., KEIL, P., MÖDER, M., PASCHKE, A., THUSS, U. (1997): Application of accelerated solvent extraction followed by GC, HPLC and GC-MS for the determination of polycyclic aromatic hydrocarbons, chlorinated pesticides and polychlorinated dibenzo-*p*-dioxins and dibenzofurans in solid wastes. J. Chromatogr. A, 774, 203-211.
- SCHOER, J. & FOERSTNER, U. (1987): Estimation of Long-Term Impact on Groundwater from Depositions of Metal-Bearing Solids.- Vom Wasser 69, 23-32.
- SOCLO, H.H., GARRIGUES, P.H. & EWALD, M. (2000): Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas.- Mar. Poll. Bull. 40, 387-396.
- SPORSTOL, S., GJOS, N., LICHTENTHALER, R. G., GUSTAVSEN, K. O., URDAL, K., ORELD, F. & SKEI, J. (1983): Source identification of aromatic hydrocarbon in sediments using GC/MS.- Environ. Sci. Tech. 17, 282-286.
- TESSIER, A., CAMPBELL, P.G.C. & BISSON, M. (1979): Sequential Extraction Procedure for the Speciation of Particulate Trace Metals.- Anal. Chem. 51, 844-851.
- WEISS, H., MORENCY, M., FREYER, K., BOURNE, J., FONTAINE, D., MÖDER, M., MORGENSTERN, P., POPP, P., TREUTLER, H.-CHR. & WENNRICH, R. (1997): Physical and Chemical Characterization of the Theisenschlamm Slurry, a Complexly Contaminated Scrubber Dust from Copper Smelting.- Sci. Tot. Environ. 203, 65 – 78

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edited by:

BIRGIT DAUS and HOLGER WEISS