

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 rain-water, 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 performed 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 Bundes-

anstalt (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 (Spectroflame 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.

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 (χ), redox potential ($U_H^{25^\circ\text{C}}$) 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]	$U_H^{25^\circ\text{C}}$ [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	<u>4.849</u>	<u>1.02</u>	<0.05	0.028	0.0004	<u>2.360</u>	<u>30.43</u>	<u>2056</u>
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	<u>4.30</u>	<u>639</u>
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 $\text{pH} = 4$ 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 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 individual 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 $\mu\text{g/L}$	Cascade/120 h $\mu\text{g/L}$	$\text{pH}_{\text{stat}}4/24 \text{ h}$ $\mu\text{g/L}$	$\text{pH}_{\text{stat}}4/336 \text{ h}$ $\mu\text{g/L}$
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 HNO₃ 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.

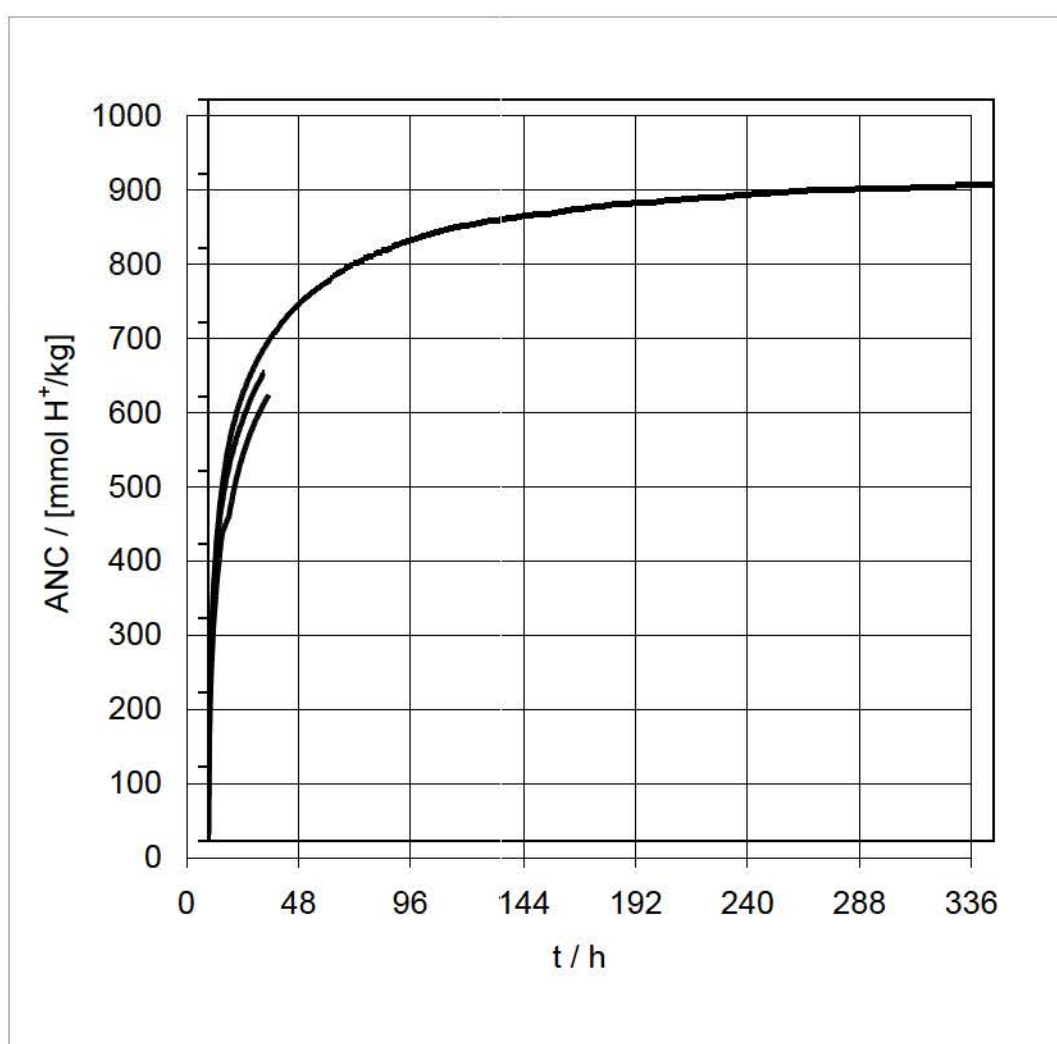


Figure 1: Time dependence of acid neutralization capacity (ANC) of Theisenschlamm in the pH_{stat} leaching test (at $pH = 4$) – In addition to the long-term experiment, two runs over 24 h are shown.

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

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 $\text{pH} = 4$ 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 $\mu\text{g/l}$ 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 $\text{pH} = 4$. 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 ($\text{pH}_{\text{stat}11}$) 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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