

SOLIDIFIKATION, STABILIZATION AND ENCAPSULATION OF ORGANIC COMPOUNDS FROM REMEDIAL ACTIONS USING INORGANIC AND ORGANIC FILLERS AND BINDING AGENTS

R. KHORASANI, R. WIENBERG, U. FÖRSTNER

Technische Universität Hamburg-Harburg, Arbeitsbereich Umweltschutztechnik, Eißendorfer Str. 40, D-2100 Hamburg 90, FRG

1. ABSTRACT

For the solidification of oily and contaminated wastes an-organic as well as organic fillers and binders were tested. The selection of suitable materials included the use of descriptive criteria (consistence, thixotropy, properties when immersed in water) as well as oil extruding tests, compressive strength tests, vane shear tests, leaching tests and stripping tests for volatiles. In addition sorption and desorption studies using hexachlorobenzene as a hydrophobic organic model micropollutant were performed.

The anorganic binders and fillers showed little success; submersed in water, e.g., the solidification products decomposed to the phases they consisted of. Good success, on the other side, was found using organic solids such as natural asphalt or lignite powder. The quantity of solids necessary for successful solidification, however, was relatively high (75 %). The sorptivity was considerably higher than that of inorganic materials. Consecutive desorption tests yielded indications, that above high sorptivity chemical bonding of the pollutants to the solids were established.

2. INTRODUCTION

In the former Georgswerder waste dump site, waste oils contained in the landfill as well as seeping out of it, and which are contaminated with highly toxic organic pollutants, cause a serious problem for remedial actions. By solidification procedures, such as admixture of different organic and inorganic binders and fillers, these waste liquids are to be brought to stiff or concrete consistency in order to improve transport and disposal facilities. Above all, solidification is expected to decrease water permeability and to reduce the mobility of the pollutants.

Solidification and stabilization procedures on wastes, which are rich in inorganic contaminants such as heavy metals mostly entail a significant change of chemical bonding [1]. Solidification of contaminated materials containing organic pollutants, however, mostly consists only in dilution measures. A significant change of the pollutants property does not occur when inorganic binding agents or fillers are used. If any a change in the equilibria conditions occur, a remobilization of the pollutants can make them available again to

the biological system. The use of organic solidification agents on the other hand aims to cause, if possible, irreversible reactions entailing either relatively harmless products (even with hardly any improved immobility) or bonding strengthes which make leachable concentrations of the contaminant tolerable. From the point of view of environmental policy as well as technology it seems to be aspirable to take an ultimate elimination of the pollutant as an option into account: this seems to be possible when using organic fillers and binders. After a time of intermediate disposal of such a way immobilized organic wastes and after environmental tolerable incineration techniques are available, the hazardous waste could ultimately be eliminated.

3. MATERIALS AND TESTING SUBSTANCES

Because of the contamination of the waste oils with highly toxic substances (dioxins), experiments with these materials can only be carried out under extensive safety precautions. For solidification tests therefor a special model waste was mixed containing 65 w/w of a basic oil (based on poly-"-ole fine) with a dynamic viscosity of 42 cP, 15 w/w trichlorobenzene (TCB), 5 w/w dichloromethane (DCM), 5 w/w toluene, and 10 w/w water. The composition of this synthetic oil - water-mixture corresponds to that found in some waste lagoons in the Georgswerder landfill.

For solidification experiments the following binding agents and fillers were applied:

- inorganic fillers: quartz, ground slate, bentonite, several other clays, chalk
- inorganic binders: gypsum, lime, cement, waste kiln dust, coal fly ash
- organic fillers : brown coal powder, raw brown coal, fine coke, dry-burning brown coal
- organic binders : Trinidad asphalt (50/50; 60/40), cationic and anionic bitumen emulsions

4. RESULTS

4.1. Descriptive findings

In a first series of descriptive studies the minimum limits for additives were determined and subsequently compared. A defined quantity of oil was mixed with additives until it reached stiff consistency.

The necessary amount of solids varied considerably. Whereas only 40 w/w percent of calcium hydroxide (related to the resulting solidification product) were necessary, for Trinidad asphalt (50/50) 82 w/w percent were required. Some inorganic solids seemed at first sight to be suitable because of the small amount necessary, but after some days, however, considerable amounts of oil seeped out, and the samples lost their shape and stability.

Using organic binders and fillers, a minimum amount of about 65 w/w percent of solids is necessary to reach stiff consistency. These samples remain stable during longer

periods of experimentation. Lignite powder and Trinidad asphalt 60/40 (i.e. 60 % natural asphalt and 40 % diatomaceous earth) seem to fit best for solidification of oil - with the exception of Trinidad 50/50, which, because of its content of lime stone dust (50 %), absorbs less oil.

A second series of experiments were performed with regard to combinations of several solid materials. Brown coal dust (fine grained)/fine coke (coarse grained) and Trinidad asphalt (fine grained)/fine coke (coarse grained) and Trinidad Asphalt/brown coal dust turned out to be the most effective combinations concerning the following criteria: small quantity of additive necessary, minimum oil seepage, certain stability. The grain size of the additive was found to be an important factor. Fine grained material must be involved; combinations of fine coke and dry-burning brown coal (both coarse grained) for instance proved to be not suitable because of considerable oil seeping. Admixture of only small amounts of organic material to inorganic additives does not improve the results.

As a third descriptive experiment solidified samples were submitted to a shaking test in order to study their behavior with water. It became apparent, that solidification products containing inorganic material decomposed in water into the phases water, solids, oil and/or oil emulsion. Organic additives, however, retained oil to a much better extent than inorganic ones. In water the solidified material formed compact lumps, any a visible oil phase did not seep out. In particular suitable were those mixtures containing more than 50 w/w percent brown coal dust or Trinidad asphalt. As the only exception, raw brown coal behaved like an inorganic additive, that means, it decomposed in water to the consisting phases .

4.2 Laboratory experiments with selected solid materials used at varied proportions

As a result of the above described findings, the following additives have been picked out for further examination, mixing amounts of 60, 65, 70, 75 and 80 w/w percent of the solids with the respective amount of 40 to 20 % of oil:

lime; calcium hydroxide; coal fly ash; waste kiln dust + coal fly ash; brown coal dust; fine coke; dry-burning brown coal; Trinidad asphalt.

Besides that, the following combinations (in percent, in relation to total solids content) were used in the same way:

- | | | |
|------------------------------|---|----------------------------|
| - 75% meliotonite | + | 25% calcium hydroxide |
| - 90% brown coal powder | + | 10% calcium hydroxide |
| - 90% brown coal powder | + | 10% coal fly ash |
| - 50% brown coal powder | + | 50% fine coke |
| - 50% brown coal powder | + | 50% raw brown coal |
| - 80% fine coke | + | 20% brown coal powder |
| - 80% Trinidad asphalt | + | 20% brown coal powder |
| - 80% dry-burning brown coal | + | 20% brown coal powder |
| - 80% Trinidad asphalt | + | 20% fine coke |
| - 80% dry-burning brown coal | + | 20% Trinidad asphalt |
| - 50% fine coke | + | 50% dry-burning brown coal |

The solidified products have been submitted to the following tests:

4.2.1. Oil squeeze test: The bottom of a proctor-apparatus was covered with 10 previously weighed round filter papers (diameter: 110 mm) and then filled with a known quantity of solidified material. The sample was compacted by ten strikes with a 2,5 kg proctor-hammer. After a pause of 30 minutes the filter papers were weighed again and the percentage of oily seepage was calculated in relation to the initial oil content of the probe. Representative results of this tests, as well as descriptions of the consistency of the probes and thixotropy when shaken are to be found in table 1.

From about 100 test mixtures submitted to this procedure, a mixture was selected which showed the best oil retention at minimum content of additives. It consisted of 25 w/w percent oil and 75 w/w percent additives (i.e. 80 w/w percent Trinidad (60/40)-powder and 20 w/w brown coal dust). The oil was extrudeable to an amount of less than 0,1%.

4.2.2. Soil mechanical tests:

For the above mentioned mixture a compressive strength of 0,34 N/mm² was determined by means of a compression piston (sewage sludge stabilisation procedure [2]). A minimum standard of 0,04-0,05 N/mm² is demanded for deposition of e.g. sludges stabilized with lime. The furthermore measured vane shear strength amounted to 0,04 N/mm². Stability of domestic waste and sewage sludge disposal needs a minimum standard of 0,01 N/mm². Thus the mixture fulfills the soil mechanical standards for disposal of solidified sludges.

4.2.3. Optimized standard-leaching test (based on the West German standard method DEV S4 /5/):

The solidified sample, contaminated with oil, toluene, dichlormethane, and trichlorbenzene was mixed with deionized water and then gently shaken. After 24 hours the eluate was separated and dichlormethane and trichlorbenzene were analysed by gas chromatography analysis (Tabell 2)

Table 2: Results from the standard leaching test

Pollutant	Solidified Substance before leaching mg	Concentr. in the water phase mg/l	Water Solubility mg/l	K _p -Value
Dichloromethan	625	34,7	20 000	359
Trichlorobenzene	1875	4,0	30	3125

Table 1: Oil extrusion (in percent, regarding the original oil content), thixotropy when shaken, and consistence of the probes at solidification experiments with different fillers and binders and increasing solids content [8].

Solids used in percent	% Oil ex- truded	Thixotropy	Consistence
<u>Brown coal dust</u>			
60 %	5,7	severe	tough, pasty, oil seeping out
65 %	1,0	no	crumbly, dry, weakly shiny
70 %	0,6	no	crumbly dry
75 %	0,5	no	crumbly, dry
<u>Trinidad asphalt 60/40</u>			
65 %	2,1	weak	tough, pasty, oil seeping out
70 %	0,8	weak	lumpy, weakly shiny
75 %	< 0,1	no	crumbly, dry
<u>Trinidad asphalt 60/40, 80% + brown coal dust, 20%</u>			
65 %	2,8	severe	soft, pasty, oil seeping out
70 %	1,3	weak	compact, massy shiny
75 %	< 0,1	no	crumbly, dry
<u>Trinidad Asphalt 60/40, 80 % + fine coke, 20 %</u>			
65 %	1,4	weak	soft, pasty, oil seeping out
70 %	1,0	weak	lumpy, shiny
75 %	< 0,1	no	crumbly, dry
<u>Coal fly ash, Rea Braunschweig</u>			
60 %	2,9	weak	soft, shiny, weak oil seeping
65 %	1,7	no	soft, massy, weakly shiny
70 %	0,3	no	powder-crumbly, dry
75 %	0,1	no	like powder, dry
<u>Meliotonite, 75 % + Weißkalkhydrat (lime), 25 %</u>			
65 %	1,3	weak	soft, massy, shiny
70 %	1,1	no	compact, massy, no oil seeping
75 %	0,4	no	crumbly, dry

The results show, that only a small amount of the total dichlormethane was leached out of the solidified matrix. If one considers, that no additional fixation to the solid phase would occur, the whole dichlormethane should have been dissolved regarding to its high water solubility (20 000 mg/l). The relatively high K_p -values suggest, however, that the predominant part of pollutants remained in the solid matter. Head space analysis showed that during the leaching procedure only small amounts of dichlormethane (0,2 mg/l of air in the head space) and toluene (2,5 mg/l of air) had escaped.

4.2.4. Stripping test for determining the volatilization:

At 60° C and a gas stream of 2 l of nitrogen per hour, the solidified sample was examined in a stripping apparatus (content of solidified material: 450 g) for highly volatile pollutants, especially dichlormethane and toluene. The test lasted 10 days. After the first day no dichlormethane could be detected in the stripping gas any more, whereas toluene was found until the 8th day. From the contaminants introduced to the experiment only an overall amount of 4% dichlormethane and 34% toluene was found in the stripping gas. Actual experiments using C-14 labelled substances will examine the type of bonding or the ways of loss of the contaminants not refound in the gas phase.

4.3. Experiments on the immobilization of organic micropollutants

When the solidified materials are leached with water, the behavior of organic micropollutants is of special concern especially if they exhibit physico-chemical properties similar to those of the dioxins or similar extremely hydrophobic and waterinsoluble chemicals. Several bonding types can be taken into account, which govern water/solids equilibria in the leaching tests. Type 1: Solubility partition between the oily phases bound to the solids and the water phase. Type 2: Sorption partition between the solids and the water. Type 3: Bonding to the solid phase or solid bound oily phase by several types of chemical reactions resulting in e.g. hydrogen bonding, covalent bonding or bondings through δ -electrons exchange. In any case, however, the equilibria are to be brought as far as possible to the side of the solids or to the oilphases bound to the solids, so that no or extremely low and tolerable concentrations of toxic micropollutants can occur in the water phase.

Sorption studies usually are conducted equilibrating known amounts of solids with aqueous solutions of the contaminants to be examined. The amount of sorbate being sorbed is determined in relation to the concentration of the chemical of interest in solution at equilibrium. Such a relationship is called a sorption isotherm. The empirical Freundlich isotherm $S = K_f C^{1/n}$ in most cases describes adequately the sorption of organic compounds. In many cases the term $1/n$ equal or is near to 1, and the isotherm gets the form $S = K_p C$, where K_p is termed the linear partition coefficient (S: amount sorbed by

Table 3: Partition coefficients solids/water (K_p) for the sorption of hexachlorobenzene by different solids used for solidification experiments with hazardous organic oily wastes (Means from at least 3 measurements) [9].

Solid phases	$K_p \pm s$ Partition coefficients		
<u>Anorganic fillers</u>			
Quartz		2,8	\pm 0,6
Infusorial	0,015 - 0,040 mm	113	\pm 6
silica	0,040 - 0,063 mm	25	\pm 3
	0,063 - 0,200 mm	23	\pm 5
Ground slate		5 200	to 12 500 *
Marl		31	\pm 7
Chalk		33	\pm 6
<u>Clays</u>			
Kaolinitic clay		88	\pm 18
Illitic clay		1 320	\pm 150
Illitic and smectitic clay		990	\pm 80
Meliotonite		35	\pm 6
Na-Bentonite		132	\pm 70
Ca-Bentonite		68	\pm 5
<u>Binders, anorganic</u>			
Kiln cement (HOZ 35)		29	\pm 4
Aquafirm (cement)		36	\pm 10
Waste kiln dust		75	\pm 6
Waste kiln dust + Coal fly ash (50/50)		14 000	\pm 3 100
Coal fly ash		6 100	to 15 890 *
<u>Organic sorbents</u>			
Fine coke	< 0,2 mm	87 000	\pm 22 000
	0,20 - 0,63 mm	9 100	\pm 1 300
	0,63 - 1,0 mm	6 000	\pm 460
	1,0 - 1,5 mm	5 100	\pm 390
Raw brown coal		26 000	\pm 7 100
Dry burning brown coal		37 400	\pm 4 800
Brown coal dust		80 000	\pm 15 000
<u>Natural asphalts</u>			
Trinidad 60/40		65 000	\pm 9 500
Trinidad 50/50		22 000	\pm 3 000
<u>Organic solidification formulation</u>			
Trinidad 50/50	80 %		
Brown coal dust	20 %	75 %	
Machine oil	65 %		73 000 \pm 22 000
Trichlorobenzene	15 %		
Dichloromethan	5 %	25 %	
Toluene	5 %		
Water	10 %		

* : Sorption isotherm not linear

the solids; C: concentration of the compound in solution; K_f , K_p and $1/n$ are empiric constants).

The remobilization of organic micropollutants from the solid phase depends on the type and strength of bonding. Those molecules being bound by weak physicosorptive forces are generally thought to be reversibly sorbed. Sorption as well as desorption experiments must gain the same solids/water equilibria, sorption and desorption isotherms are identical in this case. If there are remarkable differences, however, a hysteresis effect is identified. Such hysteresis indicate strong differences in sorption and desorption kinetics. They are generally characteristic for bondings of the above mentioned type 3.

As a model compound simulating hydrophobic and extremely poor water soluble organic micropollutant, C-14 labelled hexachlorobenzene was introduced to the experiments. In some cases after the sorption step up to three consecutive desorption tests were performed. The methods used are described in detail by [6].

The results of the determinations of solid/water equilibria can be found in Table 3. The partition coefficients are extremely different and range from about 3 for the weak sorbent ground quarts up to as high as 87000 for the fine grained fraction of fine coke. In general the anorganic solids were only weak sorbents; this is even true for the fully extendable clays despite of their huge surface. Exceptions are ground slate and coal fly ash; both exhibit k_p -values of about 10^4 . As in both cases the sorption isotherms were not linear, table 3 contains only the range of k_p -values for them. The fly ash used comprised about 3 % of organic carbon, which should preferentially be highly sorptive soot. Contrasting the anorganic solids, the organic fillers and binders exhibited very high partition coefficients; with the exception of coarse grained coke, they were exceeding 10^4 . Also the solidified mixture including the test oil showed this extremely high sorptivity.

While hexachlorobenzene is reversibly sorbed by aquatic sediments [7] or by remedial construction materials such as cut off wall formulations [8], the experiments using Trinidad asphalt (Fig. 1) or raw lignite (Fig. 2), however, exhibited a marked hysteresis: the partition coefficients increased from the sorption to the third consecutive desorption step more than fivefold. The same was true with the oil containing solidified mixture: The k_p -value increased from 73 000 (sorption step) over 140 000 (1st desorption), 190 000 (2nd desorption) up to 210 000 (3rd desorption).

As can be concluded from the experiments on the immobilization of organic micropollutants, organic binders and fillers are particularly suitable for the solidification of contaminated organic materials because of their very high sorptivity. Above that there are indications that chemical bonds (Type 3) of the contaminants to the solid phase have established.

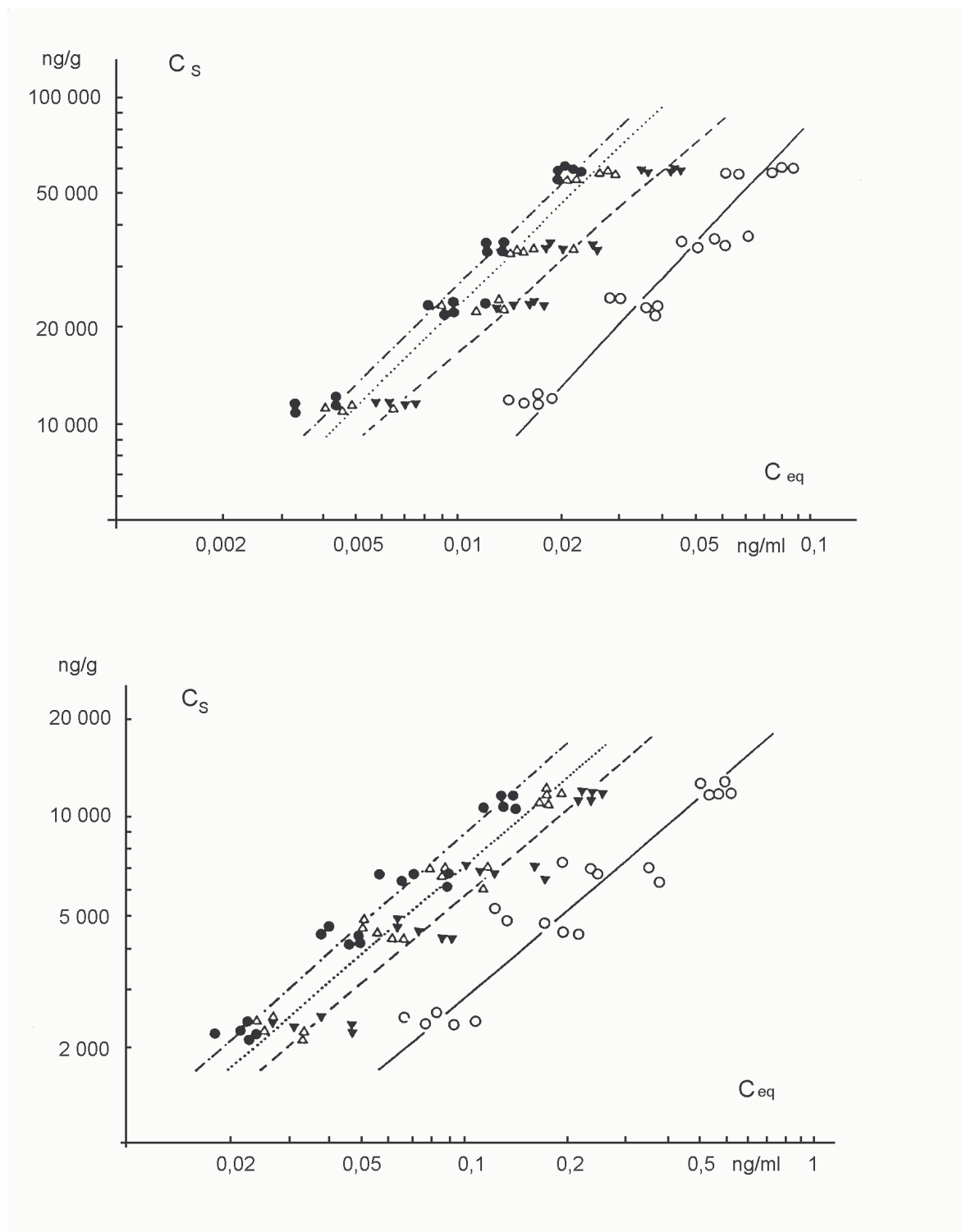


Figure 1 (above) and 2 (down): Sorption and desorption isotherms for hexachlorobenzene sorbed at Trinidad asphalt (above) and raw lignite (down). " : Sorption; - : 1st desorption;) : 2nd desorption; ! : 3rd desorption /9/

REFERENCES

- 1 Förstner U: Immobilisierung von Schwermetallen in Schlämmen und festen Abfallstoffen.- In: Straub H, Hösel G, Schenkel W, (Eds): Müll und Abfallbeseitigung, Erich Schmidt Verl Berlin 1987
- 2 Gehrke R: Anwendung von Kalk in kommunalen Kläranlagen. Korrespondenz Abwasser **25** (11), 375-389 (1978)
- 3 Möller U, Kassner W, Köhlhoff D, Loll U, Otte-Witte R: Neudefinition der Deponiefähigkeit von Klärschlämmen. Korrespondenz Abwasser **31** (11), 928-933 (1984)
- 4 Gay ChGW, Henke KF, Rettenberger G, Tabasaran O: Stand-sicherheit von Deponien für Hausmüll und Klärschlamm. Stuttgarter Ber. Abfallwirtsch. **14**, Erich Schmidt Verl Bielefeld 1981
- 5 Deutsche Einheitsverfahren zur Wasser- Abwasser- und Schlammuntersuchung, Bestimmung der Eluierbarkeit mit Wasser, DIN 38 414 Teil 4
- 6 Wienberg R, Heinze E: Spread of organic contaminants in remedial construction materials as effected by dissolving agents and surfactants.- In: Lester JN, Perry R, Sterrit RM (Eds): Chemicals in the environment, pp 733-744 Selper Ltd London 1986
- 7 Wienberg R, Förstner U, Haug T, Kienz W: Sediment- Wasser- Gleichgewichte. Verhalten flüchtiger Chlorkohlenwasser stoffe und der Dichlorbenzole an Gewässersedimenten. Berichte des Arbeitsbereichs Umweltschutztechnik der Technischen Universität Hamburg-Harburg **1**, 117 pp, Hamburg, 1988
- 8 Schwer C: Unpubl Data, Technische Univ Hamburg-Harburg, 1987
- 9 Wils S: Unpubl Data, Technische Univ Hamburg-Harburg, 1987

Source:

Khorasani, R., Wienberg, R., Förstner, U.: Solidification, stabilization and encapsulation of organic compounds from remedial actions using inorganic and organic fillers and binding agents.- In: Wolf, K., van den Brink, W.J., Colon, F.J. (Hrsg.): Contaminated Soil '88. Kluwer Academic Publ., Dordrecht, 967-976 (1988)