SPREAD OF ORGANIC CONTAMINANTS IN REMEDIAL CONSTRUCTION MATERIALS AS EFFECTED BY DISSOLVING AGENTS AND SURFACTANTS

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ABSTRACT

Construction materials for remedial measures for cleaning up hazardous spills or improper hazardous waste disposal sites should exhibit high retardation of dissolved contaminants by sorption or irreversible chemical fixation. Sorption and desorption of hydrophobic organic compounds such as toluene, parathion and hexachlorobenzene was examined conducting batch equilibrium sorption experiments.

Sorption and desorption should be effected by the presence of dissolving agents or surfactants. Ethanole, however, did not alter the sorption properties of HCB when used at concentrations up to 20 g/l. Surfactants showed marked sorption reducing effects when added at concentrations exceeding the critical micelle concentrations.

INTRODUCTION

Cleaning up hazardous spills or improper hazardous waste disposal sites requires engineered measures such as excavation, on site treatment, or encapsulation. The latter includes (i) surface sealing or capping, by which surface areas are covered to minimize surface water infiltration, control erosion, and contain contaminated wastes and volatiles; a variety of low permeability cover materials and sealing techniques are available for such purposes; (ii) Subsurface horizontal sealing by a low permeability formation such as clay or silty clay or the underlaying bedrock or by a supplementary lining or grouting, and (iii) subsurface vertical sealing by cut off walls or slurry trenches, keying in the confining layer below it, to contain contaminants that mix with or sink to the bottom of the aquifer. A comprehensive description of slurry wall application, configuration and construction was made by US EPA (1). By the technique of slurry trenching, a trench of the desired configuration is excavated using a bentonite and water slurry to support the sides; thus trenches can be constructed having a width of up to 1 m and a depth of more than 50 m without using any additional support (2,3). Several methods of slurry trenching are in use. The single phase method uses a slurry containing cement, and the solidified mixture operates as the ultimate cut off wall. The two phase method requires the substitution of the primary supporting slurry by a second denser and more impervious material.

Slurry trench materials usually consist of bentonite, cement, sand, and in some cases of additional inert fillers, thinners and dispersing agents, flocculants, polyelectrolytes, and chemical additives. According to US EPA (1), the mixtures should have the following properties: low water permeability, resistance to hydraulic pressure and chemical attack. Our paper deals with an additional demand: they should exhibit high specific retardation of the movement of dissolved contaminants by sorption or irreversible chemical fixation.

Leachates of improper hazardous waste disposal sites usually comprise a great variety of contaminants. Sorption and desorption of organic substances should be effected by co-contaminants such as dissolving agents or surface active substances. Results of experiments on this aspect are reported too.

MATERIALS

Sorbates: Results of experiments with the following compounds will be reported here: (i) Toluene, introduced as an example for nonionic, volatile substances, mainly used as dissolving agents. They interact by hydrophobic bonding. However, only weak sorption by soils and sediments has been observed. (ii) Parathion, a nonionic, slight water soluble (21 mg/l) pesticide. Because of its polar $N0_2$- and thiogroup, it may interact with the sorbents via hydrogen bonding. (iii) Hexachlorobenzene, which is an extreme water insoluble (5 µg/l) inpolar, and highly sorptive compound. In soils and sediments, organic matter is the main sorbent.

Dissolving agent: As an additional dissolving agent ethanol was chosen.

Surfactants: A representative of each of the major groups of detegents was selected: (i) Tetrapropylene benzene sulfonate, an anionic compound, (ii) N,N,N-trimethyl N-cethyl ammoniumbromide as a cationic surfactant and (iii) the nonionic detergent TWEEN 20, polyoxyethylene sorbitane monolaurat

Sorbents: The sorbents used are given in Table l,including their organic carbon content and pH (measured in a 0.01 m $CaCl_2$ solution at a solution/solids ratio of 1 : 2.5).

TABLE 1: pH and organic matter content of the slurry components and slurry formulations used

	pH	o.c. %
Ground quartz	6.2	0.00
Cement, HOZ 35	12.7	0.00
Fly ash	11.5	2.80
Ground slate	7.8	0.31
Na-Bentonite	9.6	
Ca-Bentonite	7.1	0.00
"White" clay	6.1	0.09
"Blue" clay	6.2	0.86
"Green" clay	8.0	0.08
Slurry mixture DW 2	9.8	0.07
Slurry mixture DW 4	11.9	0.01
Slurry mixture DW 11	10.0	0.07
Slurry mixture DW 13	10.6	0.48

The slurry formulations used were developed by the Institut für Grundbau und Bodenmechanik, Hannover, Prof. Dr. Müller- Kirchenbauer. They were optimized with respect to impermeability and construction requirements. The Formulations are compiled in Tab. 2. The additive Dynagrout$^{\circledR}$ T is a Na-aluminate, Dynagrout$^{\circledR}$ SP an organo silane (4) both produced by Dynamit Nobel, Troisdorf.

Table 2: Composition of the slurry wall formulations (developed by Institut für Grundbau und Bodenmechanik, Hannover)

	DW 02	DW 04	DW 11	DW 13	DW 22	DW 23	DW 05A
Water	40.6	40.8	32.6	37.7	21.4	38.8	19.4
Ca-Bentonite	10.2	10.4	5.2	9.4	4.5	3.9	
Cement, HOZ 35	4.6	4.7		8.6		3.9	
"White" Clay	4.6	11.1	5.2	4.3	4.5		36.5
Fly Ash				17.1			
Ground Slate	20.0		22.1		19.3		
Ground Quartz	20.0	32.0	26.0	22.9	34.1	51.8	43.3
Dynagrout$^{\copyright}$ T							0.25
Dynagrout$^{\copyright}$ SP					2.4	1.6	1.0
Na-Aluminate			1.0				
Na-Water Glass			7.9		13.8		

METHODS

Sorption studies were conducted by equilibrating known amounts of solids with solutions of the contaminants. The amount of sorbate being sorbed is determined in relation to the concentration of the chemical in solution at equilibrium. These batch equilibrium experiments were performed using C-14 labelled toluene, parathion and hexachlorobenzene. They were dissolved in distilled water to about half of their solubility and diluted in the order of 1:2:4:8:20 or in some cases 1:5:25. 25 ml of these solutions were transferred to centrifuge vials containing 0.1 (strong sorbing media) to 10 g (weak sorbing media) of solids (triplicates). The vials were glass stoppered and shaken over head for 20 hours. Then the vials were centrifuged, 5 ml of the supernatant was taken off and the activity was determined by liquid scintillation counting. Further 15 ml of solution was taken off and discharged, and the vials were refilled with distilled water to 25 ml and shaken again for 25 hours for consecutive desorption determination. After the last desorption step (or, if no desorption was conducted, after the adsorption), instead of water, the vials were refilled with 20 ml of a non gelating scintillation fluid, which was added to extract the sorbate from the solids. The probe was treated with ultrasonic, centrifuged and the activity in the supernatant measured. Pretests showed a good extraction efficiency (more than 90 %).

The experiments on the additional effects of ethanol and surfactants were conducted using ground slate, fly ash, and the formulations DW 2 and DW 23 as sorbents. Ethanol was added to distilled water to yield concentrations from 2×10^{-3} to 20 g/l, the surfactants at concentrations ranging from 10^{-3} to 10 g/l (steps of a power to ten). The sorbate concentration was 20 % of the solubility of the compounds.

In sorbate-surfactant-sorbent interactions, the surface charge of the sorbent particles should be an important factor. To characterize surface charge, the zeta potentials were measured using RIDDICK's zeta-meter (5). A very dilute suspension of the construction materials was prepared by a modified pipett method yielding a fraction <20 µm,suspended in bi-distilled water or surfactant solutions ranging from 10^{-2} to 10 g/l (steps of a power to ten). For theoretical background and calculation of zeta potentials see (6).

RESULTS

Sorption and desorption experiments

The results of the sorption experiments can adequately be described by the empirical Freundlich isotherm

$$q_e = K_F \, C_e^{\frac{1}{n}}$$

(q_e: amount sorbed; C_e: concentration of compound in solution; K_F and n: empiric constants). In many cases the term 1/n was near or equal to 1, and the isotherm gets the form:

$$q_e = K_p C_e$$

where K_p is termed the partition coefficient. This is the case of constant partitioning or linear sorption. The resulting K_p values are provided in Table 3.

Hexachlorobenzene, (HCB), in accordance to its low water solubility, exhibited the highest sorption throughout. With the exception of ground slate, fly ash, and the slurries DW4, DW11 and DW13, linear sorption isotherms are well approximating their sorptive behaviour. Sorption of HCB by the slurry components was generally reversible, that means, sorption and consecutive desorption experiments yielded the same isotherms. Quartz, however, showed a marked irreversibility. Quartz had the lowest K_p -value (2.8). An other weak sorbent was cement (HOZ 35) ($K_p = 29$). Two groups of clays can be stated: the low sorbing bentonites and the "white" clay (K_p about 100) and the "green"and "blue" clay with tenfold higher partition coefficients. The highest partition exhibited ground slate and fly ash, both in the range of 5000 to 15000. Aluminate treated quartz showed no better sorption than quartz alone. The silane Dynagrout® SP, however, increased the sorption by quartz more than 20 fold. Two groups of slurry mixtures can be established; DW4 and DNO5A, both containing neither fly ash nor ground slate, are weak sorbents (K_p in the order of 50), while the other had values in the order of 1000.

Parathion has a relatively high solubility, and the sorption is therefore much less than that of HCB. While quartz and the clays exhibited linear sorption, cement, ground slate and fly ash did not: decreasing the sorbate concentration increases the partition coefficients. The sorption isothems of the slurry mixtures DW4 and DNO5A were linear, the other were not. While the desorption of ground slate, fly ash and cement seemed to exhibit a slight irreversible component, desorption of the other sorbents was reversible.

The best sorbent, as in the test with HCB, was ground slate, with a K_p span from 34 to 124. It was followed by "green" clay (K_p max = 65), "blue" clay (35), Na- and Ca-bentonite(18 and 17, resp.). Fly ash (a very good sorbent for HCB) exhibited only a medium sorption of parathion. Quartz, aluminate treated quartz and cement as well as "white" clay are very weak sorbents. Dynagrout® SP enhanced sorption of quartz about threefold. The slurry formulations DW4 and DW 05A, as in HCB, are also very weak sorbing media. On the other hand,K_p values of parathion sorbed by the other mixtures are in the magnitude of 100.

TABLE 3. Partition coefficients (µg sorbate/g of soil per µg of sorbate/g of solution at equilibrium) for HCB, parathion and toluene on different slurry components and formulations. (Batch equilibrium experiments. Water solutions of 0.1 to 5 µg/l HCB, 0.5 to 15 mg/l parathion and 1 to 50, in some cases up to 200 (ground slate) mg toluene. n.l. means no linear sorption, n.s. no measurable sorption.

Sorbens	Sor-bens conc. [g/l]	HCB				Sor-bens conc. [g/l]	Parathion				Sor-bens conc. [g/l]	Toluene			
		$K_p$min	$K_p$max	$K_p$mean	± s		$K_p$min	$K_p$max	$K_p$mean	± s		$K_p$min	$K_p$max	$K_p$mean	± s
Qartz	1000	1.2	4.3	2.8	0.6	40	0.23	1.5	0.74	0.44	250	n.s.	n.s.		
Quartz + 1% Na-Aluminate	40	2.7	8.5	4.4	1.8	40	< 0	0.9	0.35	0.37	40	n.s.	n.s.		
Quartz + 1% Dynagrout T	40	2.8	6.2	4.2	1.1	40	n.s.	n.s.			40	n.s.	n.s.		
Quartz + 1% Dynagrout SP	40	63	96	73	10	40	0.4	5.3	2.7	1.7	40	n.s.	n.s.		
Ground Slate	2.5	5200	12500	n.l.		4	34	124	n.l.		125	0.5	96	n.l.	
Fly Ash	4	6150	15890	n.l.		40	3.7	17	n.l.		50	1.4	11	n.l.	
Cement (HOZ 35)	40	24	35	29	4.1	40	0.07	0.50	n.l.		80	n.s.	n.s.		
Na-Bentonite	25	47	350	132	70	40	4	18	12	3.6					
Ca Bentonite	25	61	79	68	5.3	40	13	17	14	1.4	80	0.1	2.6	n.l.	
Clay "white"	25	50	114	88	18	40	2.0	3.4	2.6	0.50	50	0.4	1.4	0.8	0.4
Clay "Green"	40	1060	1640	1320	150	40	42	65	48	8.0	50	n.s.	n.s.		
Clay "Blue"	40	860	1130	990	80	40	35	24	27	5.0	50	2.6	3.8	3.0	0.5
Formulation DW 2	40	1040	2410	1750	530	40	10	76	n.l.		200	0.5	2.4		
Formulation DW 4	40	26	64	n.l.		40					200	0.2	0.4	0.27	0.06
Formulation DW 11	4	830	2480	n.l.		40	14	224	n.l.		40	0.6	4.0	n.l	
Formulation DW 13	40	412	736	n.l.		40	2	21	n.l.		200	0.2	0.8	0.5	0.23
Formulation DW 22	4	760	1040	940	100	40	13	59	n.l.		200	1.4	3.6	2.2	0.8
Formulation DW 23	4	904	1574	1248	241										
Formulation DW 05A	4	47	70	55	7	40	1.4	3.9	2.8	0.9	200	0.2	0.5	0.3	0.1

Toluene was chosen as an extreme, because of its expected low sorption on mineralic surfaces. Ground slate,however, had still remarkable sorption coefficients. Sorption followed the Freundlich isotherm and ranged from K_p = 0.5 (sorbate concentration: 227 mg/l) to 96 (sorbate concentration 4.1 mg/l). Fly ash exhibited similar properties with K_p values from 1.4 to 10.8. "Blue" clay had a maximum K_p of 3.8, Ca bentonite of 2.6 and "white" clay of 1.4. The other components showed no sorption.

The slurry mixtures are generally weak sorbing media according to toluene. The partition coefficients are below 5, in the case of DW4 and DW 05A even below 1, what means, that on unit weight basis, there is more toluene in solution than sorbed.

Influence of ethanol and surfactants

Ethanol As shown by Figure 1, ethanol, at concentrations up to 20 g/l did not exhibit any influence on the sorption of the highly sorptive hexachlorobenzene.

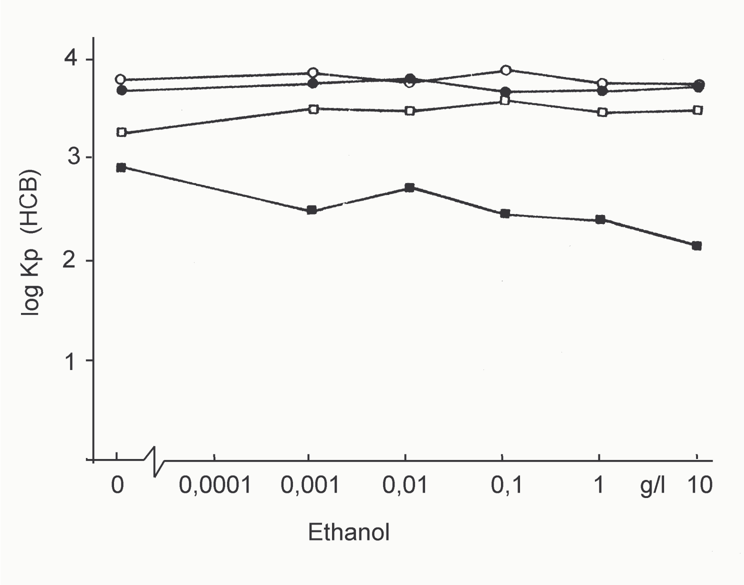

Figure 1: Influence of ethanol on the sorption coefficient (log K_p) of hexachlorobenzene (batch equilibrium experiment using a 1 µg/l solution of radiolabelled HCB and 8 g/l of sorbents). !:Ground slate; ": Fly ash; G: DW 2; #: DW 23

Non ionic detergent: (Figure 2) Sorption of HCB was reduced by Tween 20 by about a power to ten at a concentration of 1 g/l of tensid, and another power to ten at 10 g/l. In the case of DW 23, the K_p was lowered to a value near 1. Parathion, though showing a greater variation of the K_p's exhibited the same significant reduction of the sorption at 1 g/l of tensid. Toluene showed the same tendency, but the values are scattering very much because of the low sorption of this compound.

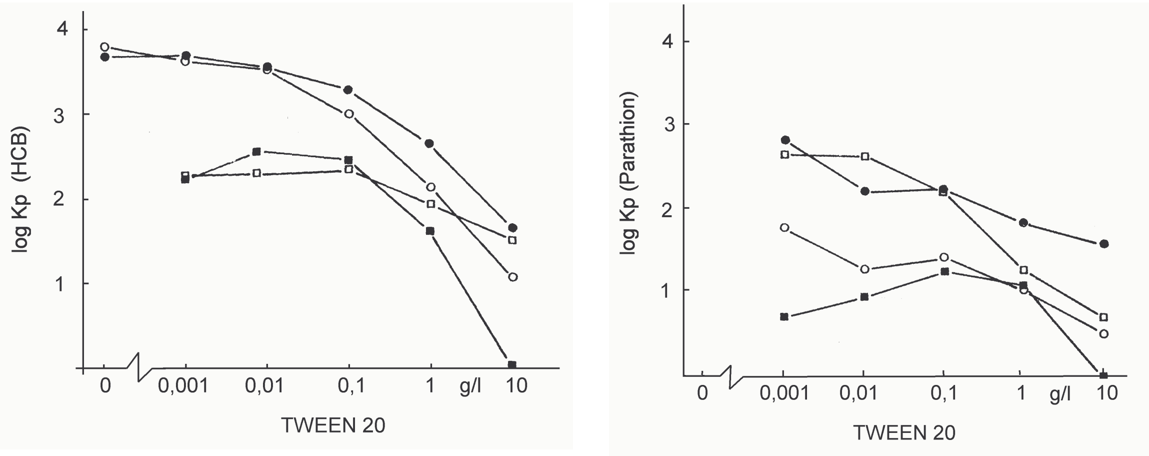

Figure 2: Influence of a nonionic detergent (polyoxy ethylene sorbitane mono-laurate, TWEEN 20) on the sorption coefficient of hexachlorobenzene (left) and parathion (right). The sorbents are !:Ground slate; ": Fly ash; G: DW 2; #: DW 23

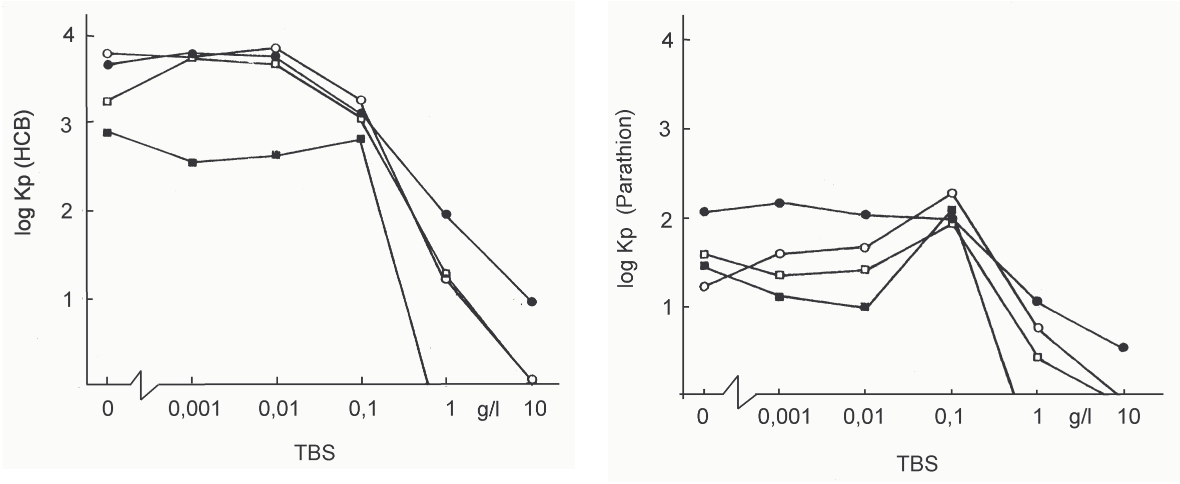

Figure 3: Influence of an anionic detergent (tetrapropylene benzene sulfonate, TBS) on the sorptin coefficients of hexachlorobenzene (left) and parathion (right). Sorbents: !: Ground slate; ": Fly ash; G: DW 2; #: DW 23

Anionic detergent: The sorption of HCB was effected by the anionic TBS in the same way as by Tween 20. A slight reduction of the K_p is found with fly ash, ground slate, and DW 2 at 0,1 gIl, followed by a -100 fold decrease at 1 g/l: the sorption coefficient of e.g. DW 23 is even beneath 1. At 10 g/l of TBS, the K_p's of fly ash and DW 2 also attain about 1, that of ground slate is near to 10. Parathion, however, exhibits a different behaviour. In opposite to HCB, sorption is increased at a tensid concentration of 0.1 g/l of TBS (with the exception of ground slate). At higher TBS concentrations, sorption decreases as in HCB. The experiments with toluene did not give conclusive results.

Cationic detergents: As shown by Figure 2, the cationic detergent exerted the same influence influence on the sorption of HCB and parathion as the anionic TBS. Ground slate, however, did not make any exception. Sorption of parathion by DW 2 was increased by the cationic compound even up to 1 g/l of tensid. Sorption by the other substrates decreased as expected. Toluene gave inconclusive results.

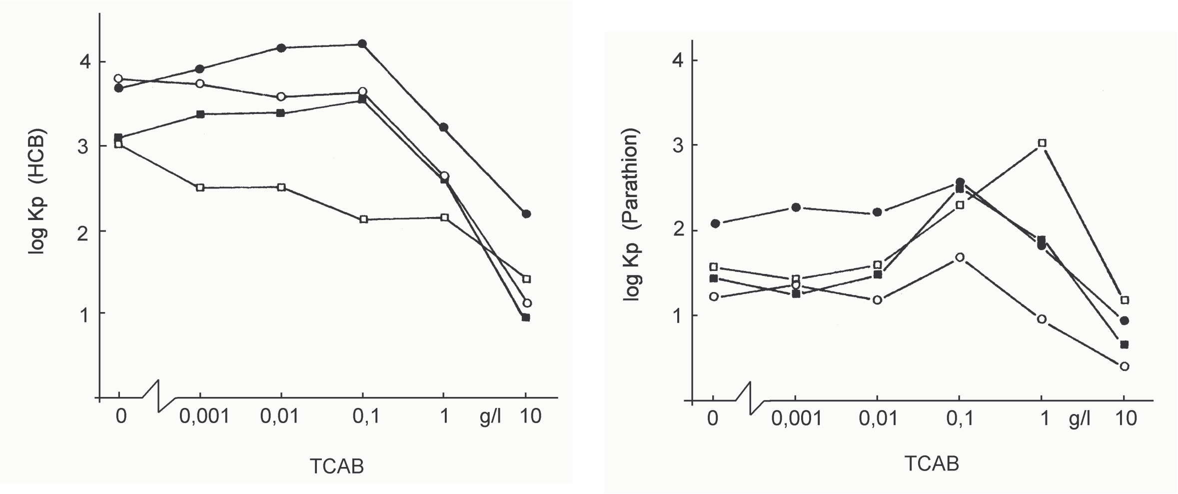

Figure 4: Influence of a cationic tensid (N,N,N-trimethyl N-cetyl ammonium bromide, TCAB) on the sorption coefficients of hexachlorobenzene (left) and parathion (right). Sorbents:
!: Ground slate; ": Fly ash; G: DW 2; #: DW23

DISCUSSION

As shown by several workers, for soils and sediments organic matter content is the "master factor" influencing sorption behaviour of non ionic organic substances (7). This seems not to be true for all of our experiments. Fly ash has the highest amount of organic carbon (2.8 %), and is, as expected, the best sorbing medium for HCB. Parathion, however, was sorbed by the carbon free Ca-bentonite to the same amount as by fly ash. Ground slate, having only about a tenth of organic corbon than fly ash, sorbes HCB the same quantity as fly ash. Parathion is even sorbed 5 to 10-fold more. "Blue" and "green" clay exhibit no difference in the sorption of HCB as well as of parathion. These clays, however, have quite different OC-contents (0.86 resp. 0.08 %).

The hypothesis, that dissolving agents could cause a drastic accelleration of the spread of highly sorptive organic contaminants could not be confirmed by the sorption experiment using relatively high concentrations of ethanol.

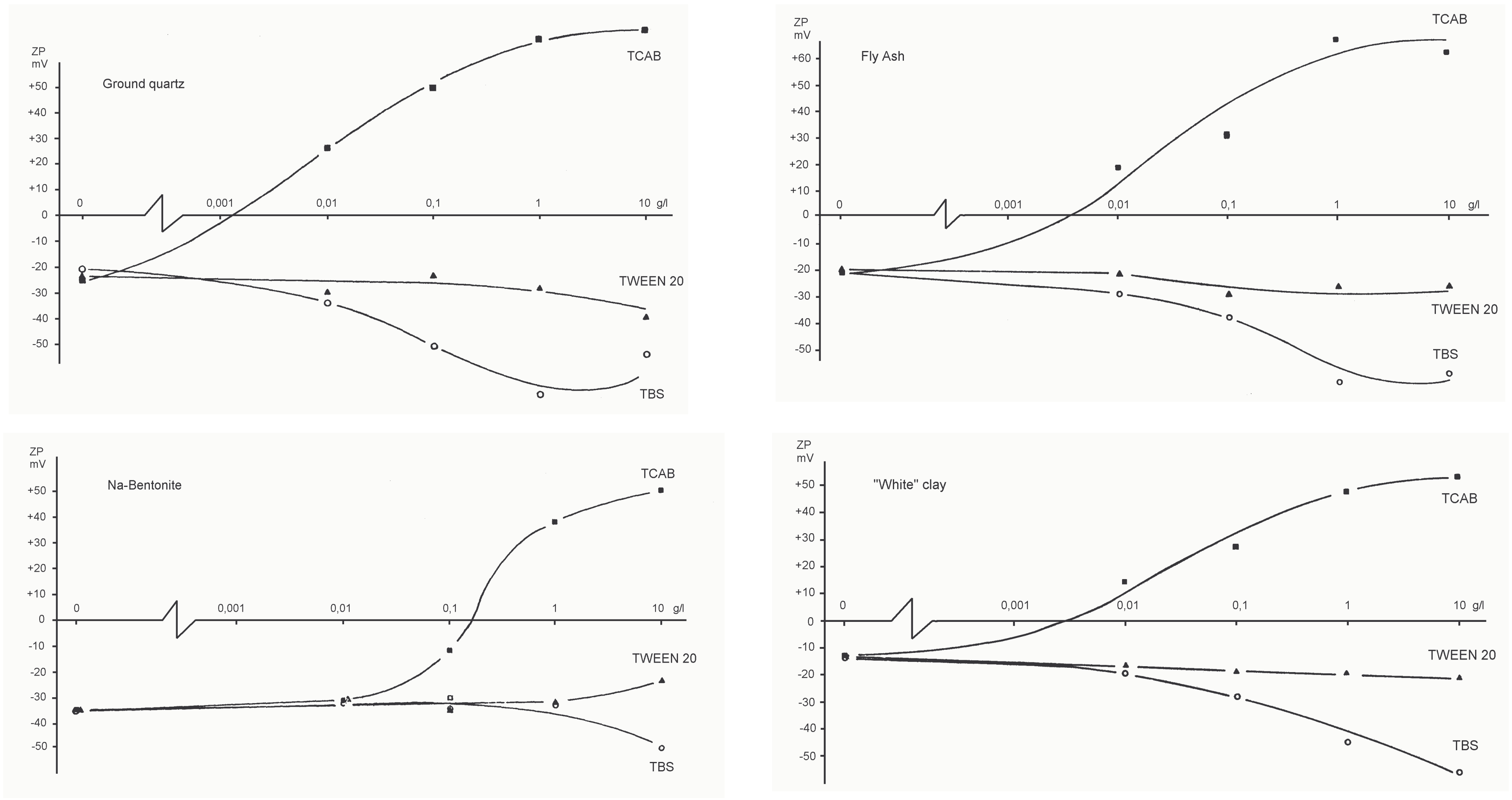

Figure 5: Zeta potentials of some slurry construction components as effected by the cationic detergent TCAB (#), the anionic detergent TBS (") and the nonionic detergent TWEEN 20 (•).

Tensids, however, showed marked effects at concentrations exceeding 0.1 to 1 g/l. These concentrations correspond with the cmc, the critical micelle concentration (8). These are: Tween 20: 0.14 g/l; TBS: 0.105 g/l; TCAB: 0.34 g/l at 25°C. As shown using other sorbents, this concentrations must be exceeded to produce desorption (9,10).

Parathion showed an increase in sorption with increasing concentrations of ionic compounds not exceeding the cmc. The same was found using the same cationic detergent and sediments (10). As the colloidal fraction of the sediments is usually negatively charged, the cations should be bound by coulombic forces. The hydrophobic "tails" of the tensid molecules produce new, additional hydrophobic sorption places and thus enhance hydrophobic sorption until the cmc is attained and desorption occurs. With increasing tensid concentration, the hydrophobic "tails" sorb a second layer with its cationic "heads" toward the bulk water, the negative charge of the particles should convert to positive values. Measurements of the influence of the cationic detergent on the zeta potentials of the slurry materials, in fact, revealed that change in the charge (Figure 3). However, only parathion and not HCB too, as should be expected, showed the resulting increase of sorption. In addition, parathion showed the increase also with the anionic TBS with slurry trench materials, whereas no such effect could be found with sediments (10).

The construction materials showed marked differences in their sorption properties. The inert filler ground slate is a much better sorbent than quartz. While fly ash showed good properties, cement should be minimized. The organosilane Dynagrout® SP enhanced sorption of non polar substances. Slurry trench formulations should further be optimized not only concerning water permeability and construction requirements, but also for sorptivity. The materials tested did not show significant irreversible chemical fixation of the organic contaminants, further work should be assigned to this aspect.

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