Shale as a Sorbent Additive to Increase Containment Barrier Efficiency

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Abstract: A variety of sorbents have been suggested for use as additives to soil containment barriers to reduce transport of organic chemicals from hazardous waste sites to the outside environment. This study investigated sorption capacities and mechanisms for a natural shale rock and four synthetic organoclays, along with the effects of addition of these sorbents on soil-bentonite barrier diffusive transport and hydraulic conductivity. Transport model simulations combined these factors to generate estimates of contaminant breakthrough. Shale exhibited substantial sorption capacity for a variety of organic contaminants, and proved to be an exceptionally cost-effective sorbent. In addition, the shale and a short-chain organoclay had no adverse impacts on soil-bentonite barrier hydraulic conductivity. In contrast, addition of 5% (w/w) hydrophobic long-chain organoclay sorbents increased hydraulic conductivity by up to an order of magnitude. Sorbent addition had little effect on barrier tortuosity, and diffusion coefficients were not significantly affected. Overall, shale was shown to have tremendous promise as a sorbent additive as a result of its high sorption capacity, lack of adverse effects on soil-bentonite barrier hydraulic conductivity or diffusive transport, inherent long-term viability, ability to be pulverized to allow for good mixing with backfill soil, and availability in many areas at minimal cost. Shale would likely be ideal for flow-through reactive barrier applications as well.

This research program was designed to identify practical and effective sorbents for possible inclusion in soil-bentonite (S-B) slurry walls, to determine any potential deleterious or beneficial effects their addition might have in terms of advective and diffusive transport of inorganic and organic chemicals, and to utilize these findings to predict the impact of sorbent addition on long-term barrier performance. The sorbents examined included a natural shale material (Ohio Shale); two organoclays with a long (16 carbon) aliphatic hydrocarbon chain (hexadecyltrimethyl ammonium bentonite, HDTMA-bent; and cetyl pyridinium bentonite, CPC-bent); a short-chain organoclay (trimethylphenyl ammonium bentonite, TMPA-bent), and a commercial long-chain dialkyl organoclay (SM-399; CETCO, Arlington Heights, IL). The shale was obtained from a natural outcrop along the southern border of Lake Erie in northwestern Ohio (Gullick, 1998). It is part of the Ohio Shale Formation of the Upper Devonian time period and is ~370 million years old (Gutschick and Sandberg, 1991). The sorbents were sieved to a size of 38-53 μm (270-400 mesh; 'fine'); a larger particle size of 500 -710 μm (25/35 mesh; 'coarse') was also used for the shale.

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Bottle point equilibrium sorption isotherms were generated for 1,2,4-trichlorobenzene (TCB), trichloroethylene (TCE), and methyl isobutyl ketone (Gullick and Weber, 2001). Experiments were also performed to assess the effects of sorbent addition on barrier hydraulic conductivity (K_C), and on the diffusion of both bromide and TCE using a diffusion cell/falling-head permeameter that allowed for adjustment of barrier confining pressure (~0 or 10 psi were used). The sorbent-S-B slurry wall barriers were ~1 to 2 cm thick, and included either 0 or 4% Wyoming sodium bentonite (SWy-1 or SWy-2), variable amounts of sorbent, with the remainder a synthetic background soil (77% silica sand, 10.5% silica flour, and 12.5% kaolinite) (Gullick, 1998).

TMPA-bent showed the highest sorption capacity for all three solutes, followed by Ohio Shale for TCB and TCE (Gullick and Weber, 2001). Adsorption onto shale is likely to the condensed kerogen organic matter present in this material. Shale was by far the most cost-effective of the sorbents examined, costing roughly \$10-\$50/ton compared to \$0.50 to \$2.50/lb or more for organoclays. Cost-normalized isotherms for TCB are presented in Figure 1, using \$0.55/lb for TMPA-bent, HDTMA-bent and CPC-bent, \$1.17/lb for SM-399, and \$0.01/lb (or \$20/ton) for ground shale. Sorption on unmodified bentonite and on the background soil was negligible.

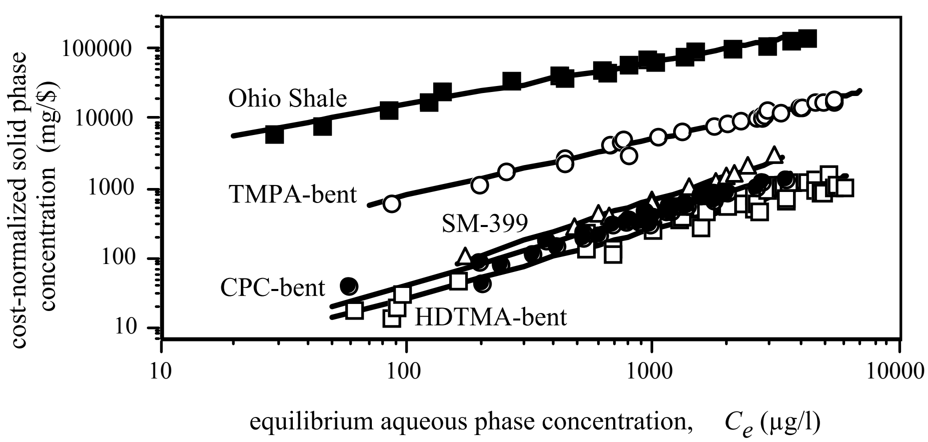

Figure 1. Sorption of TCB Normalized to Sorbent Cost

Addition of fine shale (≤ 20%) or organoclays (≤ 5%) to the soil with no bentonite slightly decreased K_C (by less than an order of magnitude), assumably as a result of physical particle size effects and resulting changes in soil gradation. The presence of 4% bentonite decreased background soil K_C by 2 to 3 orders of magnitude. Addition of shale or TMPA-bent to soil with 4% bentonite had little effect on K_C (Figure 2), as the effect of the bentonite in controlling K_C dominated over any particle size effects. In contrast, addition of 5% HDTMA-bent or 10% CPC-bent to soil with 4% bentonite at 10 psi increased K_C by about an order of magnitude (Figure 2). This phenomenon is attributed to these relatively hydrophobic organoclays disrupting the dispersion of the bentonite particles. No effects of sorbent addition on S-B barrier porosity or bulk density were observed, other than an increase in porosity with HDTMA-bent and CPC-bent.

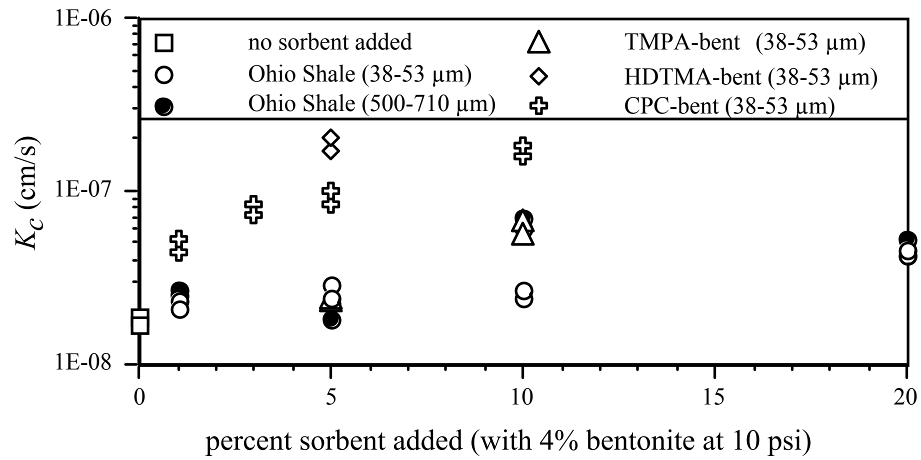

Figure 2. Effects of Sorbent Addition on K_C (with 4% Bentonite at 10 psi)

Although bentonite addition lowered K_C by several orders of magnitude, it only decreased the effective diffusion coefficients for TCE and bromide by roughly a factor of two, a result of increased soil tortuosity. As expected, addition of organoclay (5%) or Ohio Shale (≤ 20%) to the S-B barriers had no effect on the diffusion coefficients, and retardation of TCE diffusive transport correlated with sorbent capacity (TMPA-bent > Ohio Shale > HDTMA-bent ≈ CPC-bent).

Using the sorption, diffusion, and permeability parameters generated in the laboratory, one-dimensional contaminant transport model simulations were performed to predict barrier performance. Addition of TMPA-bent or shale can significantly retard organic chemical transport. However, though initially sorption by HDTMA-bent and CPC-bent also results in retardation, after a time the increase in K_C resulting from these sorbents can lead to greater breakthrough. The effects of sorbent addition on organic chemical transport in S-B cutoff walls depend on the sorption capacity of the materials, changes in hydraulic conductivity, the applied hydraulic gradient, and the amount of contaminant present.

Sorbent cost implications are extremely important since addition to a landfill barrier would require very large quantities of material. For example, a 1,350,000 ft^3 (~9,000 ft long, ~3 ft wide, ~50 ft deep) soil-bentonite slurry cutoff wall was recently built for a total project cost of over $4,500,000. Addition of 5% sorbent (dry weight) to a barrier that size would require over 3,300 tons of sorbent, with material costs alone (excluding transportation and mixing costs) of over $3,300,000 for organoclays (at $0.50/lb), but roughly only $33,000 to $170,000 for ground shale (at $10 to $50/ton). Large amounts of shale can be economically used, thus allowing for better and more consistent mixing of the sorbent with the barrier soil materials.

Maintaining low permeability is the most important factor for containment barrier design, and prospective sorbents should be examined for potential effects on barrier K_C, as well as their sorption capacity for the contaminants of interest (including competitive sorption and solids concentration effects). It is recognized that shale is a class of geologic materials with variability in content, and no blanket endorsement of all shale is intended. It would be prudent to test any sorbent for metals content and potential toxicity; no problems were found with Ohio Shale for metals content or via the Toxicity Characteristic Leaching Procedure (Gullick, 1998). Other inexpensive natural materials that have a fairly substantial composition of geologically-aged organic matter (e.g., various types of shale and coal) may also prove to be good sorbent additives.

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