

Organically Modified Clays

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Organically modified clays are prepared by replacing the exchangeable inorganic cations present in the natural clays. Organic cations used in this replacement process are then able to adsorb other organic compounds. Thus, an organically modified clay can adsorb organic constituents that are otherwise unaffected or possibly adversely affected by unmodified clays. Organically modified clays may be mixed with additional stabilization agents (such as cement, cement kiln dust, or fly ash) to solidify contaminated soils or organic wastes into a stable mass. The stabilized mass has improved bearing properties and a reduced potential for leaching hazardous constituents into the environment. Because organically modified clays swell in the presence of organic fluids, such as gasoline or fuel oil, they may also be used as sorbents in spill control or in liners for fuel oil tank containment areas. The sorption capabilities of a number of both unmodified and organically modified clays are compared. Data are also presented on the use of organically modified clays for organic sludge stabilization. The findings indicate the feasibility of stabilization technology for remediation of organically contaminated sites as compared with the excavate-and-remove option. The adsorption of organics by organically modified clays is critical to this process.

The need to stabilize or solidify organically contaminated soils and wastes has become increasingly important. The stabilized material must attain a minimum shear strength (typically as evaluated quantitatively in an unconfined compression test). More important, the rate of leaching of hazardous constituents from the stabilized matrix must be minimized. The success of conventional stabilization agents, such as cement or fly ash, is usually limited to metal-bearing wastes. Organically modified clays (organophilic clays) may be used to adsorb organic waste constituents, thus enhancing the stabilization of the organic hazardous waste.

Testing and evaluation criteria are available to judge the effects of a stabilization process. The solidification aspect is evaluated quantitatively by the unconfined compression test. A measure of the effectiveness of stabilization is the rate of leaching of hazardous constituents from the stabilized matrix into the environment. This stabilization characteristic is most often evaluated by the Toxicity Characteristic Leaching Procedure, or TCLP (1).

When used in conjunction with conventional cement-based or pozzolanic additives, organically modified clays can effectively reduce the movement of organic constituents into the environment. Several methods of reducing the mobility of organic contaminants using organically modified clays in a solidified matrix have been patented (2,3). The organically modified clays are mixed with the waste to adsorb the organic materials and provide the necessary chemical bonding. In this

manner, the organics do not significantly interfere with the normal cement reactions and lattice formation when the cement or pozzolan is added. Because less cement or pozzolan is needed when the organics are bound to the clay, volume increases can be minimized. In addition to the bonding between the organically modified clay and the organic contaminants, the clay is physically trapped within the cementitious matrix formed by the cement or pozzolan. With both chemical bonding and physical entrapment, the leaching potential of organic constituents is minimized, even when the solidified matrix is broken down by environmental stresses (as modeled in the TCLP).

ORGANICALLY MODIFIED CLAYS

Unmodified Structure

The clay minerals used to produce organically modified clays are primarily smectites and attapulgite. The smectites most frequently used are montmorillonite and hectorite. The structure of each clay type differs; thus, the performance of the resulting organically modified clay likewise varies.

Smectitic clays are classified by their two-to-one sheet structure, which forms the clay's crystal lattice (see Figure 1). A tetrahedral sheet is composed of linked silica tetrahedra. In montmorillonite, the octahedral sheet is composed of aluminum octahedra. Hectorite is characterized by a magnesium atom as the central atom in the octahedral layer. The unit cell comprises a single octahedral sheet sandwiched between two silica tetrahedral sheets (the two-to-one structure). These structures are then stacked one upon the other to form the clay particle. Found between each of these unit cell layers are randomly located anions, cations, and water molecules. Montmorillonite is thus designated a hydrated aluminosilicate.

The crystalline structure of smectitic clays found in nature differs from the idealized lattice structure previously described. A net negative electrical charge exists within the lattice structure because of isomorphous substitutions within the lattice. Cations of a lower valence may replace the principal cation (aluminum for montmorillonite and magnesium for hectorite) within the octahedral layer and, occasionally, the silica ion in the tetrahedral layer. As a result, there is a charge deficiency within the lattice structure and a net negative charge on the clay particle. The charge deficiency is balanced by cations between unit layers and around their edges. These cations, not part of the crystalline lattice, are loosely bound and may be relatively easily exchanged. A quantitative measure of exchangeable cations is termed the *cation exchange capacity* and is usually expressed in milliequivalents (meq) per 100 g of dry clay. The cation exchange capacity for a smectite ranges

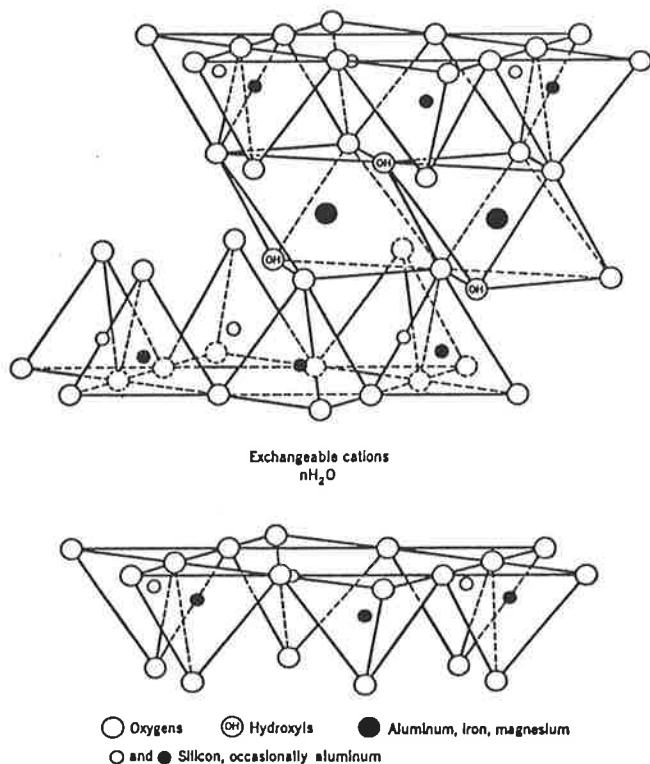


FIGURE 1 Structure of smectite [from Grim (4)].

from 50 to 120 meq/g; for attapulgite, it is typically 5 to 20 meq/g. The principal exchangeable ions are usually calcium, sodium, and magnesium. The sodium ion is the most easily replaceable, followed by calcium and magnesium.

Attapulgite (now known as palygorskite) has a significantly different structure from smectite. It is a fibrous mineral that lacks continuous octahedral sheets. Attapulgite is a hydrated magnesium aluminosilicate that can be considered to have three-dimensional ribbons (or chains). The individual ribbons are joined by inverted silica tetrahedra, resulting in an open structure containing channels running parallel to the ribbon edges and along the length of the fiber axis. This lends a needle- or rodlike structure to the mineral. Further details of the structure of smectite and attapulgite can be found elsewhere (4,5).

Organic Modification

The study of clay mineral-organic reactions was initiated in the early 1930s. In 1934, Smith reacted organic bases and their salts with montmorillonites and presented evidence that the reaction was one of ion exchange (4). Other early experiments with simple organic chemicals and pure bentonitic clay revealed that the exchangeable inorganic cations could be replaced by organic cations and that uncharged polar compounds could enter the interlayer space without releasing cations (6).

A wide variety of clay mineral-organic interactions have been investigated. Hauser discovered that when bentonite is reacted with certain organic compounds, it has the properties

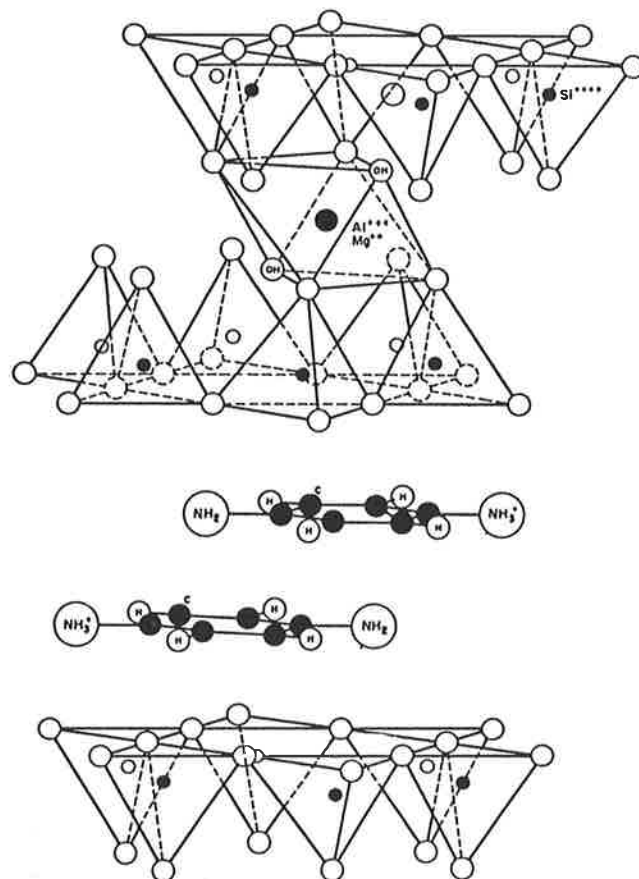


FIGURE 2 Structure of organically modified smectite layers [from Grim (4)].

of swelling and dispersing in organic liquids (7). This paper describes those clay-organic interactions that impart organophilic characteristics to the clay-organic compounds. These interactions have been proven effective and, in some cases, commercially usable in transforming the untreated clay into an organophilic clay.

In the modification of clays with organic cations, a number of interactions are possible between the clay and the organic compound. The most important reactions are adsorption, intercalation, and cation exchange. It is beyond the scope of this paper to discuss in detail all the factors that influence the organic modification of clays. However, these reactions include ion exchange, protonation of the organic molecules at clay surfaces, hemisalt formation, anion exchange, ion-dipole and coordination, hydrogen bonding, pi-bonding, entropy effects, and covalent bonding (8).

The organic modification of a clay is generally accomplished by ion exchange. In this process, a cationic surfactant, such as a quaternary amine, replaces the exchangeable inorganic sodium, calcium, or magnesium ions (or all three) on the surface of the clay. Figure 2 shows a typical organically modified clay structure. With the replacement of the inorganic exchangeable cations by organic cations, the clay is converted from the hydrophilic to the organophilic condition. Reaction of the clay with an appropriate organic cation, such as a quaternary amine, will cause the clay to swell and disperse in the

presence of a variety of organic fluids. When replacing the exchangeable cation, the surfactant forces the clay platelets apart (termed *pillaring* the clay), thus giving the organically modified clay additional porosity to aid in the adsorption of organics.

The organic compound used to modify the clay is usually a quaternary ammonium salt, which is a type of organic nitrogen compound in which the molecular structure includes a central nitrogen atom joined to four organic groups along with an acid radical. They are all cationic surface-active coordination compounds and tend to be adsorbed on surfaces (surfactants). The types of quaternary ammonium compounds used to modify the clays are primarily dimethyl ammonium, methyl benzyl ammonium, dibenzyl methyl ammonium, and benzyl dimethyl ammonium.

Data first reported by Jordan indicate that the organophilic properties of a clay do not become significant until an amine with a carbon chain length of at least 10 is reached (7). Jordan used nitrobenzene, benzene, and isoamyl alcohol to illustrate this phenomenon, and maximum swelling capacity for these organic fluids was reached with 12 carbon atoms. It was also determined that the liquid with a high dielectric constant, nitrobenzene, had a much greater swell volume than benzene or isoamyl alcohol.

The swelling characteristics of the clay are altered by varying the chain length of the quaternary ammonium salt compounds. The compounds substituted onto the clay may have organic groups attached to the clay that range from aliphatic hydrocarbons with a chain length of 1 to 24 carbons to aromatic organic molecules, such as benzyl groups that could have a variety of groups substituted on the benzyl ring (2). The number of benzyl versus straight-chain hydrocarbons substituted on the ammonium ion can vary from three to zero. These quaternary ammonium salts are usually reacted with the clay in stoichiometric amounts, and the amount substituted on the clay can vary between 0.5 and 50 percent (2).

According to Jordan, a carbon chain length of 12 or more carbon atoms and a surface coating of more than 50 percent are necessary for optimum swelling (9). Additional space on the clay surface not coated with the organic is generally covered by water. Jordan also indicated that the liquids most effectively sorbed were those that combined highly polar with highly organic characteristics, such as nitrobenzene. As a highly polar organic liquid is adsorbed onto the portion of the clay surface not covered by the amine chain, the clay becomes more organophilic and thus able to sorb more organics. Polar organics occupy similar sites to the polar water molecule at the silicate surface to satisfy the net negative charge of the interlayer cations. Nonpolar organic compounds are adsorbed onto the clay surface by relatively weak, nonspecific London-van der Waals (dispersion) forces (10).

The fundamental bonds between the organic cations and the charged clay surface are electrostatic; however, physical, noncoulombic forces also contribute to adsorption (6). The adsorption process in the organic modification of clays is controlled by van der Waals forces when large cations are involved because the principal interactions occur among the adsorbed organics and not between the organics and the clay surface. Hydrogen bonding may be prevalent if the organic cations contain radicals, such as $-NH_2^+$ groups, which interact with the surface oxygens of the silicates.

The fibrous attapulgite clay minerals interact with organic compounds in a manner different from that of the smectite

structures. The organics interact mainly with the edges of the silicate ribbons in intracrystalline channels or at external ribbon surfaces (6). The exposed magnesium cations perform a similar function to that of the interlayer exchangeable cations in smectites, but the attapulgites are nonexpansible, and steric hindrance restricts intracrystalline adsorption. Only a limited number of molecules with a high polarity and a small size can enter the structural channels. The adsorption of larger organic molecules occurs, in general, on the open channels at external clay surfaces.

Manufacture

Organically modified clays can be manufactured by either a wet or a dry process. In the wet process, the unmodified clay is placed in a slurry and centrifuged to remove the inert, nonclay materials. The supernatant, which contains ultrapure clay, is then reacted with a specific organic compound, usually a quaternary ammonium compound. After the organic has been added to the clay, the mixture is filtered, dried, and ground. Several drying methods are used, including spray drying, fluidized bed drying, and belt drying. Spray drying generally produces the best results, because the clay particles are randomly oriented for increased sorption capacity. In the dry process, limited amounts of moisture are first added to the clay. The clay is then reacted with the organic compound in a mixer, pug mill, or extrusion device. Finally, the reacted material is dried and ground. Centrifugation is not performed in the dry process, and therefore some impurities still exist in the finished clay product. A finishing, or polishing, step may also be performed with either process after the reaction of the clay with the organic compound. This step consists of washing the clay with a mild (sulfuric) acid solution to remove any acid-soluble impurities.

Adsorption

It is theorized by Cowan and White (11) that the adsorption of soluble organic compounds from dilute aqueous solutions by an organophilic clay occurs through electrostatic-hydrogen bond forces at the hydrophilic sites and by van der Waals forces at the organophilic sites. The adsorption of organic compounds in dilute aqueous solutions is affected by several factors: (a) the nature of the adsorption sites; (b) the nature of the organic molecules to be adsorbed (adsorbate); (c) spatial considerations; (d) thermodynamic quantities; and (e) solubility of the adsorbate in the solvent (11). On the organically modified clay surfaces, areas may exist that were not modified by organic molecules during the manufacturing process and are thus still hydrophilic. As a result, adsorption by electrostatic-hydrogen bonding with the hydrophilic portion of the adsorbate molecule occurs at the hydrophilic clay sites, and van der Waals bonding occurs with the organophilic portion of the adsorbate molecule at the organophilic clay sites. Because adsorption occurs at both types of sites on the clay surface, a balance between the organophilic and hydrophilic surfaces is necessary. Maximum adsorption occurs when there is a balance between the hydrophilic and organophilic surfaces (11).

Adsorption of a particular molecule results from the product of two controlling factors: adsorbent-adsorbate interac-

tions and adsorbate-solvent interactions (12). The adsorption capacity of an organically modified clay is thus dependent on the amine used to convert the clay coupled with the properties of the medium (such as pH, type of solvent, and temperature).

When the organophilic clay is mixed with solidification agents, such as cement, for waste solidification, it is possible that pillaring of the clay occurs because of the presence of inorganic polymer macromolecules. This pillaring would then be helpful in the sorption of toxic organics (13). Because the clay is not completely covered by the surfactant, it is furthermore likely that some organic molecules are adsorbed by the hydrophilic clay surface through other bonding mechanisms. Possible mechanisms of organic molecule fixation include adsorption on the surfactant, exchange or adsorption (or both) onto the hydrophilic clay surface, and adsorption due to pillaring of the clay by the surfactant (intercalation). Studies using differential scanning calorimetry (DSC), gas chromatography/mass spectroscopy (GC/MS), Fourier transform infrared (FTIR), and thermogravimetric analysis (TGA) techniques indicate that a variety of both weak and strong bonds exists between the organic compound and the clay mineral (14).

LABORATORY TESTING PROGRAM

In an effort to quantify the sorption capacity of a number of organically modified clays, free-swell tests (also termed *modified sedimentation* tests) were performed. In each test, 50 ml of the test fluid was poured into a 100-ml graduated cylinder and 2.5 g of the clay was rained into the fluid. The clay then typically settled to the bottom. If necessary, the mixture was periodically swirled to enhance contact of the clay with the test fluid. The volume of the clay in the graduated cylinder (the free-swell volume) was recorded immediately after the clay settled to the cylinder bottom and again after approximately 24 hr (considered equilibrium). In general, no change or only a slight change was observed between the initial and 24-hr free-swell volumes. The value recorded at 24 hr was determined to be the equilibrium sediment, or free-swell, volume. This procedure was modified from laboratory procedures described elsewhere (15). The major modification from the originally published procedure was a reduction in the quantity of clay and test fluid used in the test. This investigation parallels a study published by Jordan (7) in which a single, organically modified clay type was evaluated.

A list of the clays tested in this study, along with the supplier, is shown below.

Clay	Manufacturer
Attapulgit	Engelhard Specialty Chemicals Division
Attatone J	Bentec
Attatone T	Bentec
BC 90	Bentec
Bentonite	NL Baroid
Bondtone	NL Baroid
Claytone APA	Southern Clay Products
Claytone 40	Southern Clay Products
2HT	NL Baroid
2HT Aberdeen	Bentec
P-1	Bentec
P-11	Bentec
P-40	Silicate Technology Corporation
PC-1	Bentec
PT-1	Bentec
Suspentone	NL Baroid
TS-55	NL Baroid

Table 1 shows the type of process used to modify the clay, the specific base clay, and the organic compound reacted with the base clay. The organic compounds are quaternary ammonium salts, typically dimethyl di(hydrogenated tallow) ammonium chlorides. Tallow is an animal fat in which each organic molecule contains 16 to 18 carbon atoms. For some of the organic compounds, one of the methyl groups was replaced by a benzyl group in an attempt to provide better dispersion.

The test fluids used in these studies were acetic acid, acetone, aniline, carbon tetrachloride, deionized water, hexane, kerosene, and xylene. The classification, or grouping, of each organic test fluid is given below.

Test Fluid	Grouping
Acetic acid	Organic acid
Aniline	Organic base
Acetone	Neutral polar organic
Carbon tetrachloride, hexane, kerosene, xylene	Neutral nonpolar organic

All of these fluids were tested in concentrated form with each of the clays studied. The results of these free-swell tests are summarized in Table 2 and in Figures 3 through 5. Shown in Figure 6 is the average free-swell volume of each clay for the seven organic fluids used in these studies.

DISCUSSION OF RESULTS

The test fluids used in this study can be classified into four groups on the basis of the physical and chemical properties that govern their interactions with clay minerals (16). The first grouping consists of organic acids, which are organic fluids with acidic functional groups such as phenols and carboxylic acids. These fluids are capable of donating protons to react with, and dissolve, clays. Acetic acid was used in this investigation as a representative organic acid. In the free-swell tests, the largest swell volume (19 ml) occurred with Claytone APA, and the other organophilic clays had slightly lower free-swell volumes. Bentonite had the smallest volume (4.5 ml), indicating little interaction with this unmodified clay.

Organic bases, the second group, are those organic fluids that can accept a proton and become an ionized cation. These fluids are positively charged and therefore have a strong affinity for the negatively charged clay surface. Organic bases may also be strong enough proton acceptors to dissolve components of the clay, causing a collapse of the unmodified clay structures. The organic base used here was aniline, which is an aromatic amine. Claytone APA had a swell volume of 23 ml, the largest for this test fluid. The next greatest swell volumes (Attatone J, Claytone 40, and P-1) were considerably lower (14.5 ml, 12 ml, and 11 ml, respectively). Most of the other organophilic clays had values of approximately 8 ml. Bentonite, with a swell volume of 4.5 ml, was the lowest of all the clays tested with aniline.

The third group, neutral polar organic compounds, comprises compounds that have a net charge of zero but possess an asymmetrical distribution of electron density, which creates a significant dipole moment. As a result of the dipole moment, the fluid competes for adsorption sites on the negatively charged clay particles. Acetone, a ketone, was used as a representative of this organic fluid grouping. PC-1 had the highest swell volume (26 ml) followed by PT-1 (22 ml), Attatone T (20 ml), and Attatone J (19 ml). The majority of

TABLE 1 ORGANICALLY MODIFIED CLAYS

CLAY	PROCESS	BASE CLAY	ORGANIC MODIFIER
Claytone APA	Wet	Bentonite	Proprietary amine
Claytone 40	Wet	Bentonite	Dimethyl di(hydrogenated tallow) ammonium quat
P-40	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium quat
2HT	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat
TS-55	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat with a polymer (elastomer) added
Bondtone	Dry	Bentonite	Methyl benzyl di(hydrogenated tallow) ammonium quat
Suspentone	Dry	Attapulgate	Dimethyl di(hydrogenated tallow) ammonium quat
Attatone J	Dry	Attapulgate	Dimethyl di(hydrogenated tallow) ammonium chloride
Attatone T	Dry	Attapulgate	Dimethyl di(hydrogenated tallow) ammonium chloride
2HT Aberdeen	Dry	Calcium Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
BC 90	Dry	Hectorite	Dimethyl di(hydrogenated tallow) ammonium chloride
P-1	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
P-11	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
PC-1	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride
PT-1	Dry	Bentonite	Dimethyl di(hydrogenated tallow) ammonium chloride

TABLE 2 FREE-SWELL TEST RESULTS

CLAY	DENSITY (g/cm ³)	DEFONIZED		ACETIC		CARBON					AVERAGE (ml)
		WATER (ml)	ACID (ml)	ACETONE (ml)	ANILINE (ml)	TETRACHLORIDE (ml)	HEXANE (ml)	KEROSENE (ml)	XYLENE (ml)		
Attapulgate	0.52	15.5	7.0	6.5	8.0	6.0	7.0	7.0	7.0	7.0	6.9
Attatone J (Bentec)	0.25	16.0	8.0	19.0	14.5	23.0	15.0	17.5	26.0	17.6	
Attatone T (Bentec)	0.58	8.5	13.0	20.0	7.0	11.0	8.0	8.5	12.0	11.4	
BC 90 (Bentec)	0.40	8.5	11.0	11.5	7.5	7.0	18.0	18.0	20.0	13.3	
Bentonite	0.78	34.0	4.5	6.0	4.5	5.0	5.0	5.0	5.0	5.0	
Bondtone (NL Baroid)	0.53	7.0	8.0	13.0	7.5	0.0	40.0	20.0	36.0	17.8	
Claytone APA (Southern Clay Products)	0.24	14.0	19.0	17.5	23.0	0.0	9.0	21.0	50.0	19.9	
Claytone 40 (Southern Clay Products)	0.47	0.0	13.0	14.0	12.0	0.0	12.0	22.0	48.0	17.3	
2HT (NL Baroid)	0.52	6.0	8.0	11.0	8.0	15.0	47.0	27.0	43.0	22.7	
2HT Aberdeen (Bentec)	0.51	10.0	10.0	16.0	8.5	3.0	12.0	18.0	18.0	12.2	
P-1 (Bentec)	0.36	9.0	12.0	13.5	11.0	0.0	13.0	18.0	27.0	13.5	
P-11 (Bentec)	0.34	8.0	9.0	10.0	9.0	25.0	25.0	22.0	25.0	17.9	
P-40 (Silicate Technology)	0.51	7.0	9.0	13.0	8.0	33.0	13.0	26.0	20.0	17.4	
PC-1 (Bentec)	0.39	8.0	8.0	26.0	8.0	20.0	45.0	33.0	24.0	23.4	
PT-1 (Bentec)	0.44	7.0	9.0	22.0	8.0	10.0	15.0	32.0	22.0	16.9	
Suspentone (NL Baroid)	0.50	10.0	11.0	15.0	9.0	6.0	28.0	35.0	33.0	19.6	
TS-55 (NL Baroid)	0.41	6.0	7.0	8.0	7.0	40.0	34.0	24.0	28.0	21.1	

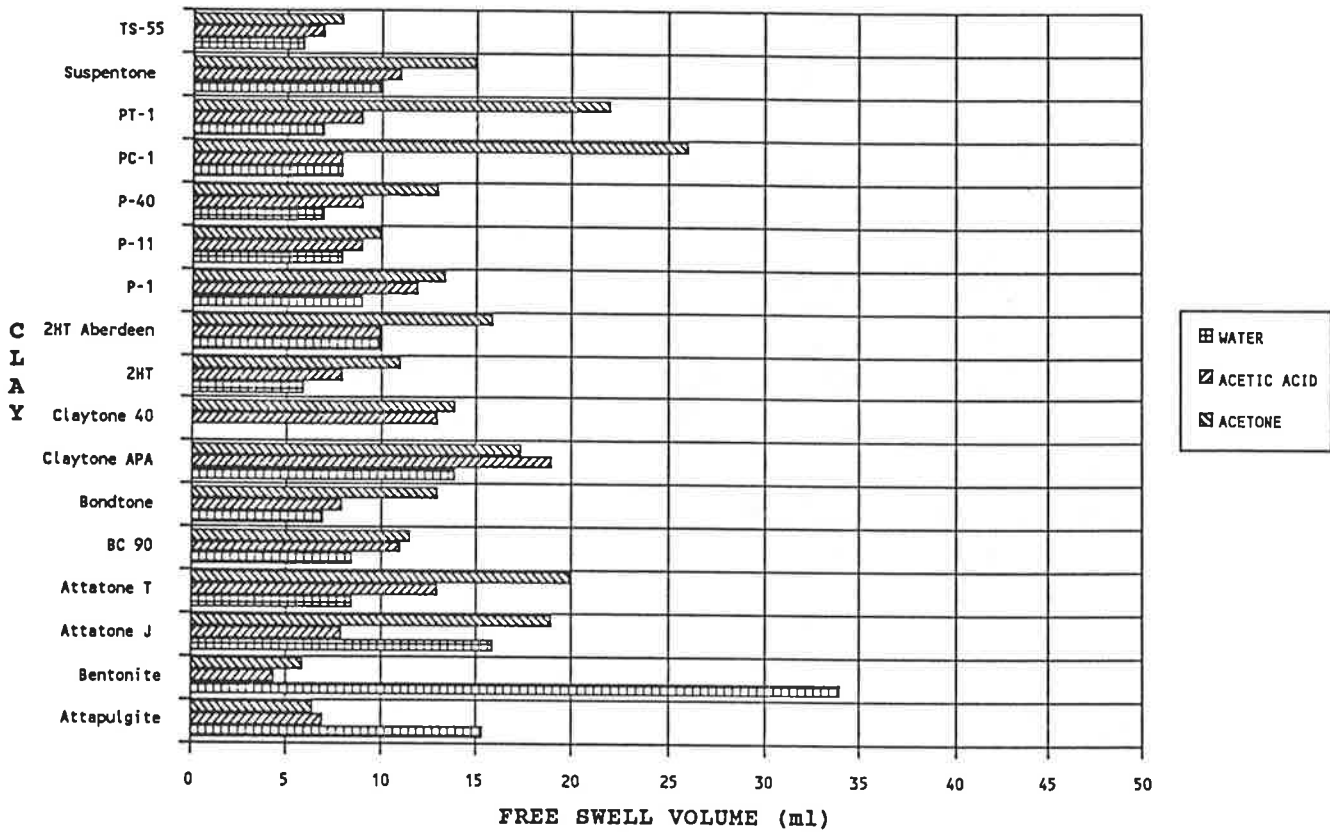


FIGURE 3 Free-swell tests (water, acetic acid, and acetone).

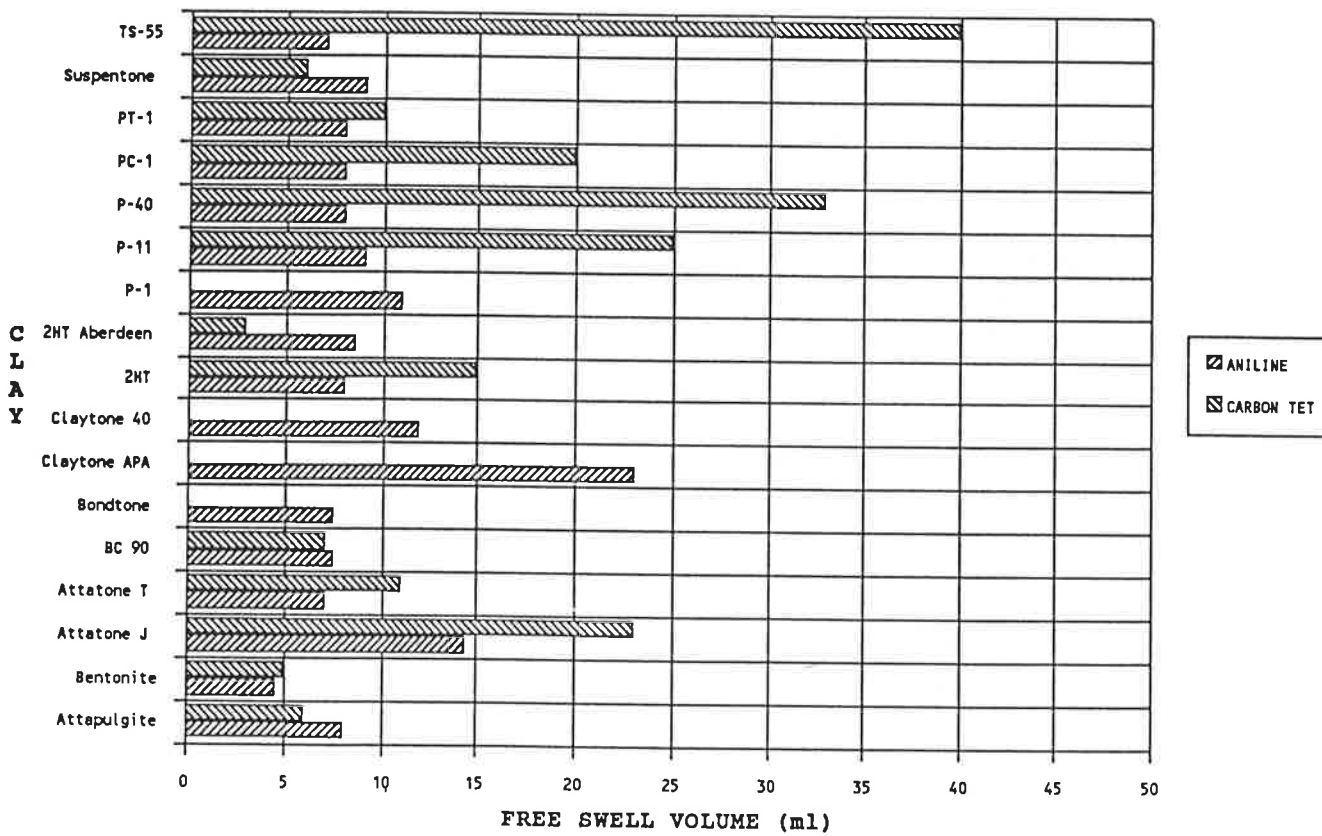


FIGURE 4 Free-swell tests (aniline and carbon tetrachloride).

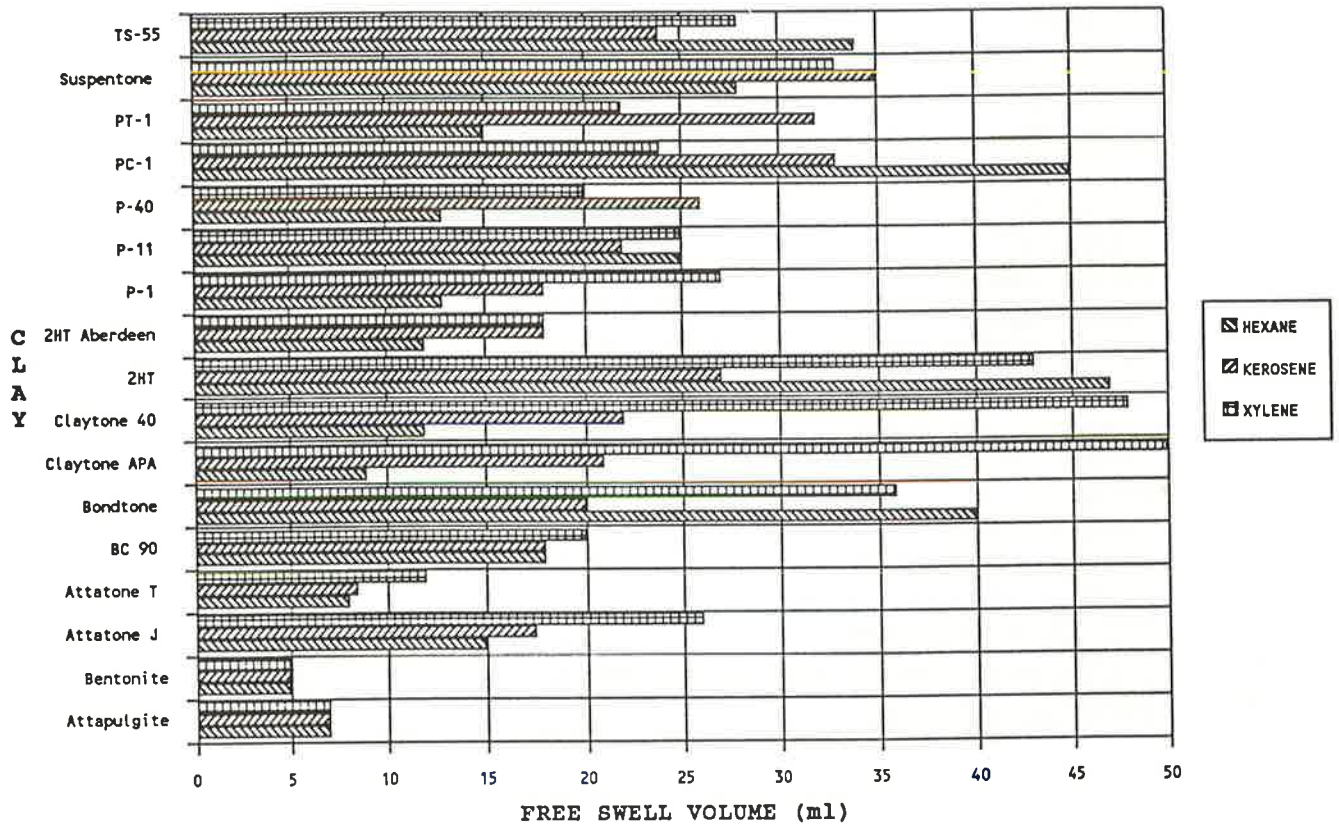


FIGURE 5 Free-swell tests (hexane, kerosene, and xylene).

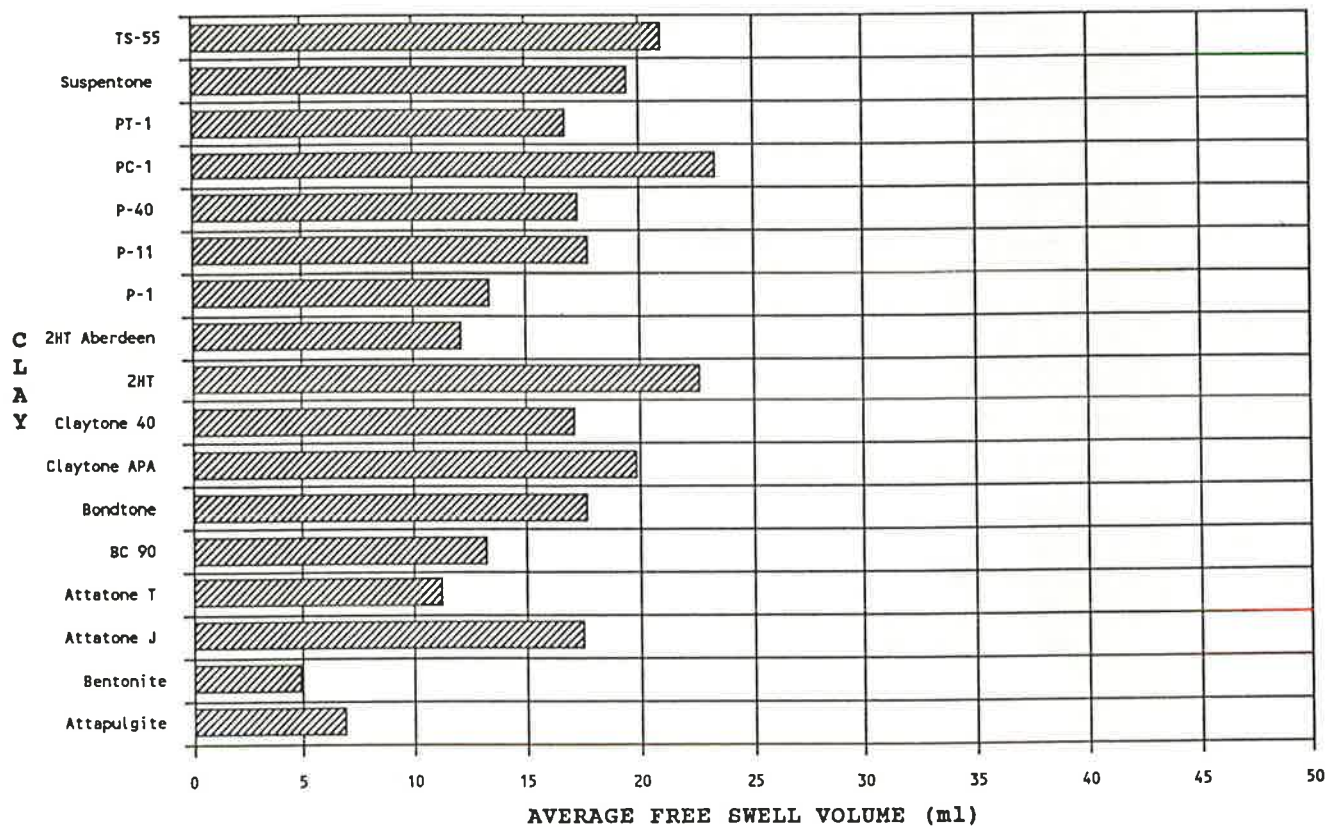


FIGURE 6 Average free-swell volumes.

the other clays had somewhat lower values. The lowest swell volumes were reported for the unmodified clays, bentonite and attapulgite.

The fourth and final grouping of organic fluids is the neutral nonpolar organic compounds. These compounds have a zero net charge and do not exhibit a significant dipole moment. They have little affinity for unmodified clays and therefore do not interact readily with them. Carbon tetrachloride, hexane, kerosene, and xylene were the neutral nonpolar organic fluids used in this investigation. Carbon tetrachloride produced some cloudy solutions that were recorded as having swell volumes of zero. In other cases, some portions of the clay were on the bottom of the graduated cylinder, and other portions were floating on the top. For these situations, the two volumes were added together, with the sum representing the free-swell volume. TS-55 had the largest swell volume, 40 ml, and P-40 was next with 33 ml. P-11, Attatone J, and PC-1 also had significant free-swell volumes, with values of 25 ml, 23 ml, and 20 ml, respectively. All of the other clays had comparatively smaller swell volumes, or were completely cloudy and reported a swell volume of 0 ml.

Hexane, kerosene, and xylene produced significantly higher swell volumes in the organophilic clays than the other test fluids. The unmodified clays, bentonite and attapulgite, had the lowest values for all three test fluids. For bentonite, the swell volume was consistently 5 ml in the three tests, and the swell volume for attapulgite was either 6 or 7 ml. For hexane, 2HT had a swell volume of 47 ml, which was the largest value, and PC-1 was next, with a volume of 45 ml. Some of the other organophilic clays also had high free-swell volumes, such as Bondtone with a swell volume of 40. However, Claytone APA, which swelled the most in some of the other fluids, had the second lowest swell volume of the organically modified clays, with a volume of only 9 ml. Kerosene produced a maximum swell volume of 35 ml with Suspentone, and slightly lower values of 33 ml and 32 ml were reported for PC-1 and PT-1, respectively. Other clays with high swell volumes in kerosene include 2HT (27 ml) and P-40 (26 ml). With xylene, Claytone APA sorbed the entire 50 ml of test fluid and Claytone 40 sorbed 48 ml. The next highest swell volume belonged to 2HT, 43 ml, and most of the organophilic clays had swell volumes of 20 ml or greater.

The other test fluid incorporated into this investigation was deionized water. This fluid is polar in nature and is attracted to the negative surface of unmodified clays. Bentonite swelled to 34 ml, whereas attapulgite had a swell volume of 15.5 ml. The organically modified clays are generally hydrophobic, and this characteristic was reflected in their low swell volumes in deionized water. Attatone J (16 ml) and Claytone APA (14 ml) had somewhat higher free-swell volumes because they have lower densities and therefore higher initial volumes than the other clays. One product, Claytone 40, was so hydrophobic that it would not be wetted by the water and floated on the top. This clay was recorded as having a free-swell volume of 0 ml in deionized water.

To view the free-swell tests in another way, the average free-swell volume of each clay, excluding the volume swelled in deionized water, is shown in Figure 6, a comparison of the various organophilic clays based on the average amount of organic fluid that they were able to sorb. The free-swell volumes with deionized water were excluded in order to measure the ability of each clay to take up a range of organic com-

pounds. Viewing the test results in this way, all of the organically modified clays except one have average free-swell volumes between 11 and 24 ml. The clays with the highest average free-swell volumes were PC-1 (23.4 ml) and 2HT (22.7 ml). TS-55, Claytone APA, and Suspentone have the next highest average free-swell volumes. The two unmodified clays, bentonite and attapulgite, have average free-swell volumes below 7 ml, indicating that they did not swell appreciably when in the presence of the concentrated organic test fluids.

The clays that contain benzyl quats (Bondtone, 2HT, and TS-55) had low swell volumes in acetic acid, acetone, and aniline and high swell volumes in hexane, kerosene, and xylene. The benzyl compound appeared to inhibit sorption of the organic acid, organic base, and neutral polar organic compound, while enhancing sorption of three of the four neutral nonpolar organic compounds. The three organophilic clays with the base clay attapulgite produced results similar to the other organophilic clays. BC 90, the clay with hectorite as its base clay, and 2HT Aberdeen, the clay with calcium bentonite as its base clay, both had low to average free-swell volumes in comparison with the other organically modified clays, which had bentonite or attapulgite as their base clay. The two wet-process clays, Claytone APA and Claytone 40, had free-swell volumes that were, in general, above average as compared with the other clays. This may be due, in part, to the removal of the inert, nonclay materials by the wet process.

SOURCES OF VARIABILITY

Variability may have been introduced into the free-swell tests described above from several sources. The amount of each clay was constant from test to test on a gravimetric basis but not on a volumetric basis. Because of different product densities (see Table 2), the initial volumes varied significantly with the clay type. The lighter clays had a larger initial volume; therefore, their final swell volume may be larger when compared with the heavier clays, which had a smaller initial volume.

The density of the clays is largely determined by the way in which they are processed when organically modified. As previously described, there are two processes, wet and dry, which are applied to modify a clay organically. The wet process (the more expensive of the two) generally produces a lighter product as inert materials are removed. Organically modified clays manufactured by a dry process usually contain about 20 to 30 percent inert minerals, which result in a more dense and less reactive product (G. W. Beall, personal communication, 1988). Therefore, the type of manufacturing process may have a significant impact on the cost and performance of the organically modified clay. In these investigations, Claytone APA and Attatone J were much lighter than the other clays and therefore started out with larger volumes of material. In evaluating the sorption capacity through the free-swell test, the density of the material was not factored in. In a similar vein, the cost of the clay was not considered in these studies.

Another source of variability among organically modified clays is the type and quality of the base clay, coupled with the kind of organic compound that is reacted with the clay. The base clays can vary with regard to their reactivity and the amount of impurities that are present. The type of qua-

ternary ammonium salt used (as previously discussed) will affect the extent of coverage of the clay interlayer surface and the affinity for sorbing other organics.

CONCLUSIONS AND SUMMARY

From these investigations, it was concluded that clays that have been organically modified, through different processes and with different organics, will have different sorption capacities for organic fluids. The free-swell tests conducted in the laboratory provided one measure of the sorption capacity of organically modified clays. Differences among clays were observed, in that the same clay did not yield the highest swell volume for all the test fluids. As shown on Figures 3 through 5, the interaction between organic fluids and individual organically modified clays varied significantly. However, when clays are taken as a group (Figure 6), their responses are similar. It is therefore concluded that the organic modification of clays can be customized for optimum interaction with specific organic fluids or organic waste streams.

Unmodified clays can be tailored, through organic modifications, to sorb specific organic constituents of a hazardous waste. The degree of swelling is related to the amount of clay surface covered by the organic compound, the extent of cation exchange of the clay by the organic compound, and the chemical characteristics of the organic constituents that are to be sorbed. With the addition of other stabilization/solidification ingredients, such as cement or fly ash, a physical matrix is formed around the clay particles that have adsorbed the organic hazardous wastes. In this way, the organic contaminants are held by the clay and are also contained in the physical matrix formed by the cement or pozzolanic material. Some preliminary success in stabilizing organic hazardous wastes with organically modified clays has been achieved in the laboratory, but further analysis is necessary (17). In a similar manner, organophilic clays may be used as sorbents for petroleum spills. They could also be used as liners for fuel oil storage tank containment areas.

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REFERENCES

1. Environmental Protection Agency. Appendix I to Part 268—Toxicity Characteristic Leaching Procedure (TCLP). *Federal Register*, 40 CFR Part 268, Vol. 51, No. 216, Nov. 7, 1986, pp. 40643–40653.
2. G. W. Beall. *Method of Immobilizing Organic Contaminants to Form Non-Flowable Matrix Therefrom*. U.S. Patent No. 4,650,590, March 17, 1987.
3. G. W. Beall. *Method of Removing Organic Contaminants from Aqueous Compositions*. U.S. Patent No. 4,549,966, Oct. 29, 1985.
4. R. E. Grim. *Clay Mineralogy*. 2nd ed., McGraw-Hill, New York, 1968.
5. A. C. D. Newman and G. Brown. The Chemical Constitution of Clays. In *Chemistry of Clays and Clay Minerals* (A. C. D. Newman, ed.), John Wiley & Sons, New York, 1987, pp. 1–128.
6. J. A. Raussell-Colom and J. M. Serratos. Reactions of Clays with Organic Substances. In *Chemistry of Clays and Clay Minerals* (A. C. D. Newman, ed.), John Wiley & Sons, New York, 1987, pp. 371–422.
7. J. W. Jordan. Organophilic Bentonites. I, Swelling in Organic Liquids. *Journal of Physical and Colloidal Chemistry*, Vol. 53, No. 2, Feb. 1949, pp. 294–306.
8. M. M. Mortland. Clay-Organic Complexes and Interactions. *Advances in Agronomy*, Vol. 22, 1970, pp. 75–117.
9. J. W. Jordan. Alteration of the Properties of Bentonite by Reaction with Amines. *Mineralogical Magazine and Journal of the Mineralogical Society*, Vol. 28, No. 205, June 1949, pp. 598–605.
10. B. K. G. Theng. *The Chemistry of Clay-Organic Reactions*. Halsted Press, John Wiley & Sons, Inc., New York, 1974.
11. C. T. Cowan and D. White. Adsorption of Organo-Clay Complexes. In *Proc., 9th National Conference on Clays and Clay Minerals*, Oct. 5–8, 1960, National Academy of Sciences-National Research Council, Washington, D.C., 1962, pp. 459–467.
12. M. M. Mortland, S. Shaobai, and S. A. Boyd. Clay-Organic Complexes as Adsorbents for Phenol and Chlorophenols. *Clay and Clay Minerals*, Vol. 34, No. 5, 1986, pp. 581–585.
13. J. Newton. *Advanced Chemical Fixation of Organic and Inorganic Waste*. International Waste Technologies, Wichita, Kansas, 1985.
14. J. J. Gibbons and R. Soundararajan. The Nature of Chemical Bonding Between Modified Clay Minerals and Organic Waste Materials. *American Laboratory*, Vol. 20, No. 7, July 1988, pp. 38–46.
15. J. P. A. Hettiaratchi and S. E. Hruday. Influence of Contaminant Organic-Water Mixtures on Shrinkage of Impermeable Clay Soils with Regard to Hazardous Waste Landfill Liners. *Hazardous Waste and Hazardous Materials*, Vol. 4, No. 4, 1987, pp. 377–388.
16. K. W. Brown and D. C. Anderson. *Effects of Organic Solvents on the Permeability of Clay Soils*. Report No. EPA-600/2-83-016. Environmental Protection Agency, Municipal Environmental Research Laboratory, March 1983.
17. J. C. Evans, M. D. LaGrega, S. E. Pancoski, and A. Raymond. Methodology for the Laboratory Investigation of the Stabilization/Solidification of Petroleum Sludges. In *Proc., Superfund '88*, Nov. 1988.