By J.J. Gibbons and R. Soundararajan

The nature of chemical bonding between modified clay minerals and organic waste materials

CLAY MINERAL/organics reactions have been studied extensively by way of infrared (IR) spectra,[1-3] x-ray diffraction,[4] and other physicochemical methods. Many of these studies explain the role of silicates, including their dehydration, which subsequently catalyzes the polymerization of compounds such as styrene. Furthermore, there has been a considerable amount of work done in the areas of adsorption of organics, Lewis acid-base reactions, and adduct formation between the clay and the organic compounds. A review of all of these papers reveals the following:

1) In general, clays have alternating layers of alumina (hydrated) and silica, with both tetrahedral and octahedral sites available to retain organics. 2) For charge balance, Group IA elements, such as Li^+, Na^+, and K^+, as well as Group IIA elements, such as Cr^{3+}, Mg^{2+}, and Fe^{3+}, are usually present between the silica and alumina [illegible]. 3) [illegible] cations (such as Li^+, Mg^{2+}, [illegible] Fe^{3+}) can [illegible] replaced by [illegible] ammonium cations (R_4N^+) or other organic cationic species. This substitution causes the clay to [illegible] organophilic in nature. 4) After quaternization, the clay can be used along with cement and other compounds, such as fly ash or slag powder, in hazardous waste treatment (the so-called "solidification" or "encapsulation" technology).

Recently, it was shown that there is more than one type of bonding between the clay mineral and the organic waste[5] by infrared TCLP (Toxicity Characteristic Leachate Procedure), total extraction, and thermogravimetric analysis. These studies clearly indicate that there are all kinds of weak to strong bonding between the organics and the clay minerals.

In order to determine the practicality of the containment technology, we have continued our investigations using more powerful tools, such as differential scanning calorimetry (DSC) and gas chromatography-mass spectroscopy (GC-MS), in addition to Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) techniques. In this paper, we present our conclusions drawn on the basis of FTIR, TGA, DSC, and GC-MS results, concerning the reliability of this newly emerging technology. In order to minimize [illegible] variables, pure, known organic compounds representing the [illegible] in the hazardous [illegible] were used in this study. However, even for a more complex organic sludge, we believe that the conclusions are still valid.

Experimental

The material [illegible] was HWT-22 pr[illegible] tional Waste [illegible] (Wichita, Kansas). Known amounts of the organics (trichloroethylene, chloroaniline, phenol, nitrobenzene, and triethanolamine) were treated with fixed amounts of HWT-22 and were allowed to cure at room temperature. The addition of cement, slag powder, and water was avoided, since we did not want: 1) water to mask the IR spectra, or 2) the silicate hydration reaction to interfere with the clay mineral-organic reactions.

After 48 hr, the samples were subjected to FTIR analyses with a Perkin-Elmer model 1710 FTIR instrument scanning KBr pellets. The FTIR spectra of the pure organics were also run using this technique.

The DSCs were run using a Perkin-Elmer DSC-2 instrument in nitrogen atmosphere. The heating rate was 10°C/min.

To determine the effluents evolved during DSC scanning, the gases were absorbed on activated charcoal cartridges, preserved in dry ice, and then desorbed [illegible] Finnigan [illegible] and [illegible] was [illegible] range was 30-[illegible] as the [illegible] and other FTIR [illegible] elsewhere.[5]

[illegible]

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with HWT-22, are also shown in the same table. The types of possible bonds are predicted in *Figures 1-5*, with the actual DSC curves shown in *Figures 6-10*. The reconstructed ion chromatograms of the effluent gases from DSC are shown in *Figures 11* and *12*. The DSC endothermic peak temperatures, along with ΔH of vaporization, are given in *Table 2*.

Infrared spectra

A careful examination of Table 1 reveals IR shifts in both directions. These IR shifts are explained on the basis of each individual compound:

Nitrobenzene. There is a shift from 1175 cm^{-1} to 1150 cm^{-1} which is one characteristic of mono-substituted aromatic compounds. This lowering is due to the restrictions imposed by intercalation (i.e., the organic compound is sandwiched between layers of alumina and silica). There is another reduction in the frequency at the C—N stretching region, from 1349 cm^{-1} to 1345 cm^{-1}, indicating that the motion of the nitro group is restricted. A cause of this restriction

Table 1

Infrared frequencies before and after treatment (cm^{-1})

Nitrobenzene	Nitrobenzene + treatment material	Shift	Peak assignment
1175	1150	−25	Aromatic mono-substitution
1349	1345	−4	N—O stretch
3106	3102	−6	
2934	2929	−5	C—H stretch
2861	2857	−4	
2831	2812	−19	
Phenol	**Phenol + treatment material**		
962	934	−28	C—O stretch
3640	3632	−8	H—bonded OH
Triethanolamine	**Triethanolamine + treatment material**		
2104	2297	193	Amine salt formation
1075	1070	−5	H bonding
Chloroaniline	**Chloroaniline + treatment material**		
540	562	22	C—Cl stretch
3500	3542	−48	N—H stretch
Trichloroethylene	**Trichloroethylene + treatment material**		
641	630	19	C—Cl stretch
2286	2281	−5	
2848	2811	−37	C—H stretch
3057	3047	−10	Ethylenic (characteristic)

could be the interaction between outer orbital electrons in the oxygen and the matrix, which has the electron deficient aluminum. Due to this bonding, the C—N bond order is decreased and hence the reduction in wavenumber. There are four other frequencies due to C—H stretch which are also restricted. This, of course, can be explained in terms of feeble hydrogen bonding between the five corner hydrogens and the silica and alumina oxygens.

Phenol. The IR spectrum of phenol is rather simple. The C—O stretching is reduced by 28 cm^{-1} from 962 cm^{-1} to 934 cm^{-1}. This is again due to hydrogen bonding between the —OH hydrogen and oxygen in the silica and alumina. This causes a flow of electron density from carbon to oxygen, thereby reducing the C—O bond order. Also, there is evidence for a hydrogen bonded —OH group at 3640 cm^{-1} and 3632 cm^{-1}.

Chloroaniline. There is a positive shift seen at the C—Cl bond. This is due to the decreased electron density on the benzene, which is caused by the coordination of the amino group nitrogen with the aluminum (a Lewis acid). This effect in turn draws the ring electrons toward the amino group. The electron-rich chlorine shifts its electron density closer to the ring carbon, which is indicated by the positive shift.

There is also a strong reduction in the N—H stretching frequency which may be attributed to N—H—O bonding of the matrix oxygens.

Trichloroethylene. There is again a positive shift in the C—Cl absorption frequencies, as was seen in the case of chloroaniline. The characteristic ethylene frequency and the C—H stretching frequencies are both lowered. It appears that intercalation causes the former, and residual hydrogen bonding causes the latter.

Triethanolamine. We have seen several weak to moderate interac-

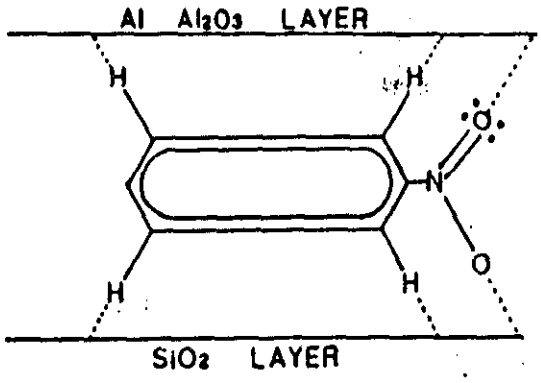

Figure 1 *Possible interactions between nitrobenzene and clay matrix.*

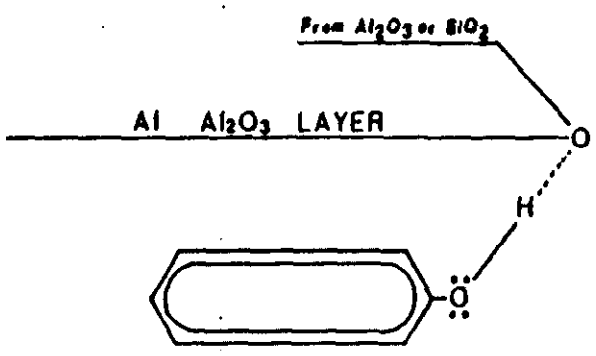

Figure 2 *Possible interactions between phenol and clay matrix.*

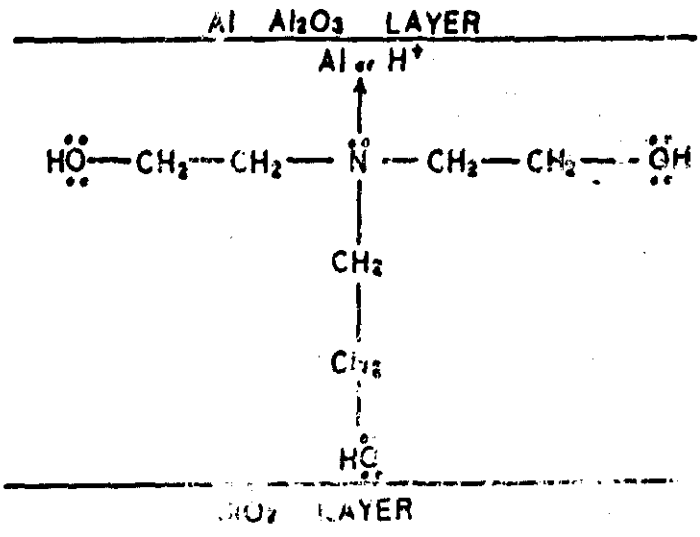

Figure 3 *Possible interactions between triethanolamine and clay matrix.*

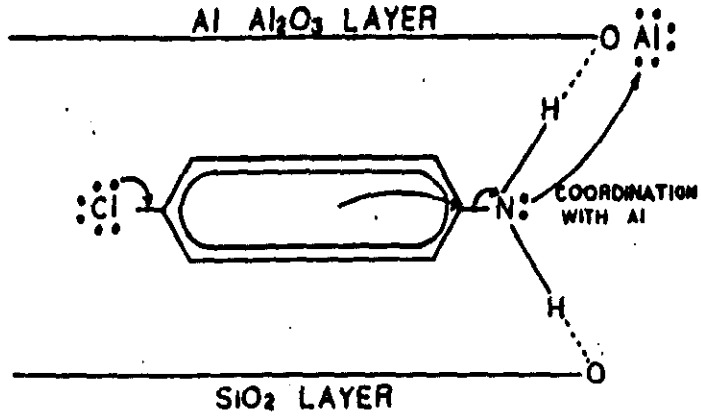

Figure 4 Possible interactions between chlorvanilline and clay matrix.

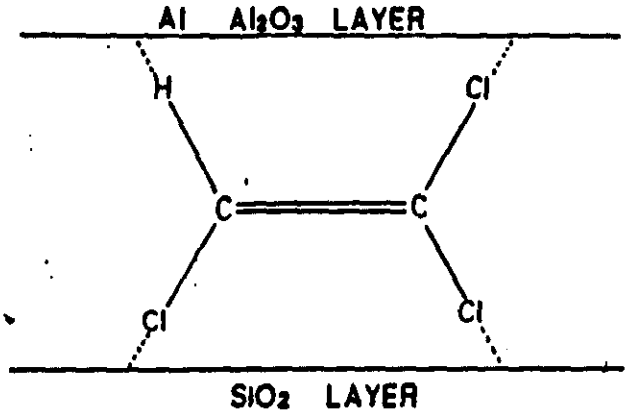

Figure 5 Possible interactions between trichloroethylene and clay matrix.

tions (or bonds) in the previous cases. However, in the case of triethanolamine, we are able to establish the presence of a coordinate covalent bond between the lone pair of electrons on the nitrogen and the matrix (aluminum). The C—N stretching frequency has dramatically shifted by 193 cm^{-1} toward the positive direction, which is very characteristic of amine salt formation. Protonation of organic compounds by clay minerals is a well-known reaction. It appears that there is a combined effect of this coordination bond with aluminum as well as with a proton which produces such a large shift. We also see a shift in the negative direction in the alcohol –OH stretching frequency. This phenomenon is due to the hydrogen bonding of the hydroxyl hydrogen with the substrate oxygens.

In general, it appears that there are numerous types of complex interactions involved in the case of clay mineral-organics reactions. The operating forces range from dipole-dipole attractions to pure coordinate covalent bonds. Hydrogen bonding and intercalation also appear to play important roles. Chelation is another possibility, provided transition metals (Fe, Co, Ni, etc.) are present in the clay mineral. The presence of organic cations also seems to play a part in retaining certain anionic species, such as carboxylates. We have also seen evidence for the above-mentioned facts in the past through FTIR and other sources. Another possibility could arise from the interaction between the partially filled d-π orbitals of transition metals and filled pπ orbitals of the ring system.

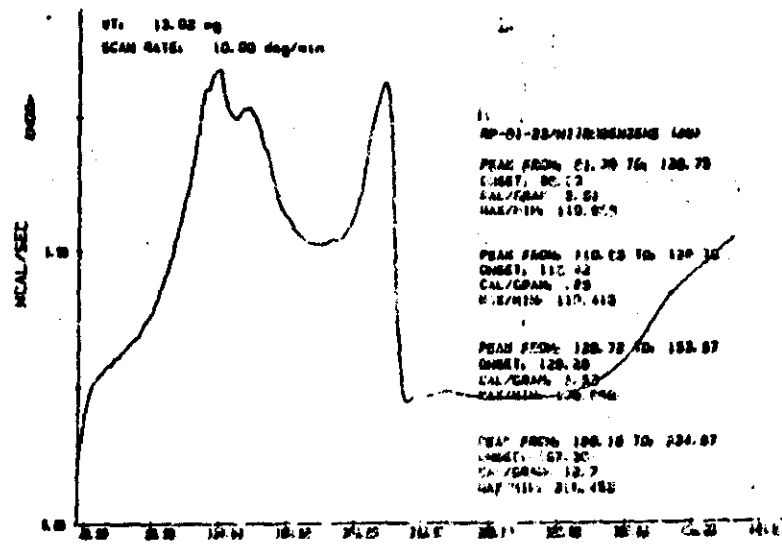

Figure 6 DSC scan of nitrobenzene + treatment material.

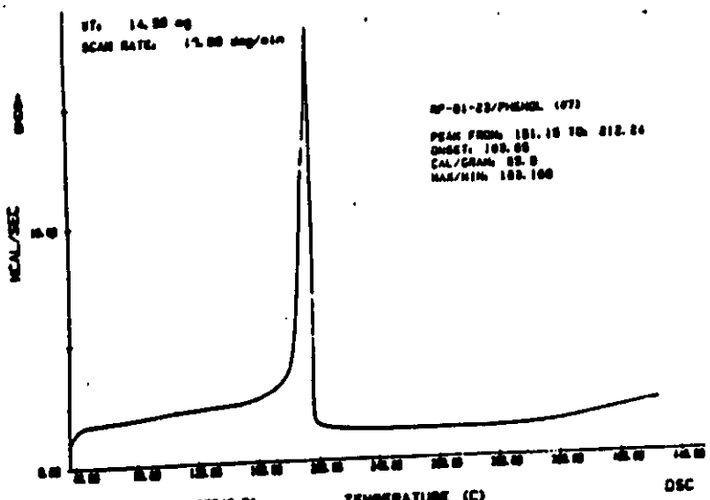

Figure 7 *DSC scan of phenol + treatment material.*

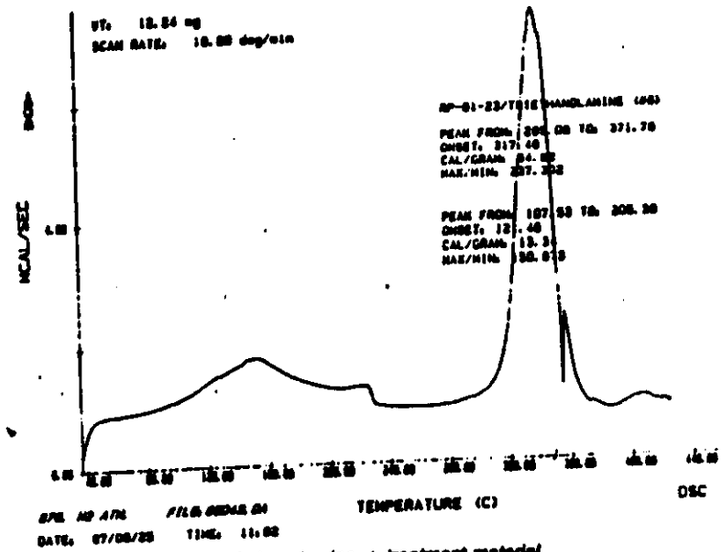

Figure 8 *DSC scan of triethanolamine + treatment material.*

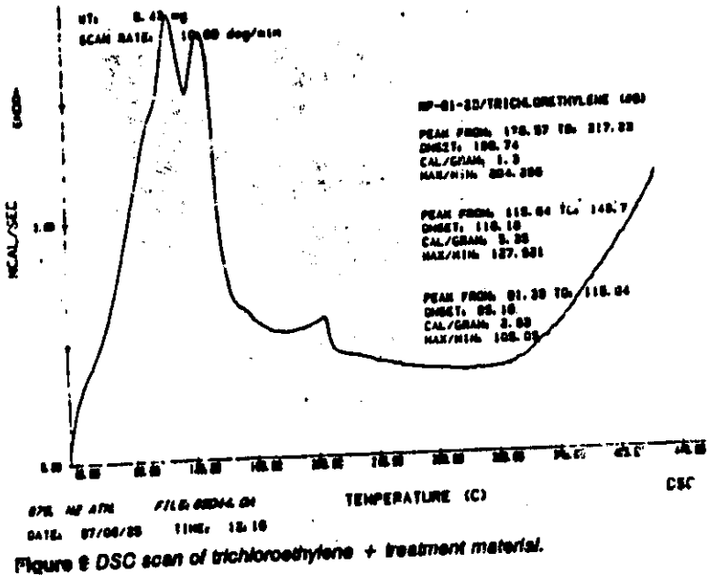

Figure 9 *DSC scan of trichloroethylene + treatment material.*

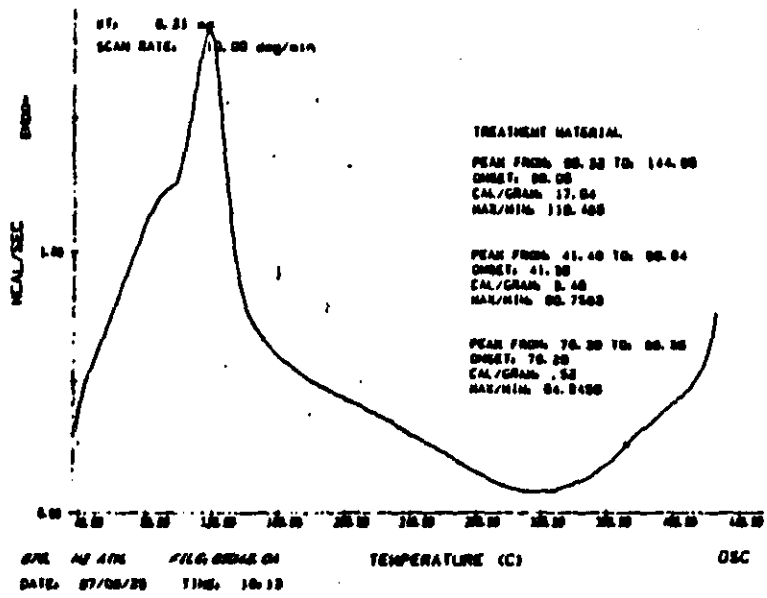

Figure 10 *DSC scan of pure treatment material.*

Differential scanning calorimetry

DSC scans were done in order to determine the kind of bonding involved, and the amount of energy that would be necessary to release the compounds from the matrix. The experimental DSCs are shown in Figures 6-10. The actual ΔH of vaporization of some of the chosen compounds are compared with ΔHs from the treated compounds along with their normal boiling points in Table 2. The molar ΔH of vaporization for the compounds were computed from the weight loss at their boiling point as determined by dynamic TGA. Three important observations can be made from DSC data: 1) All the compounds are leaving the matrix (except phenol) at more than one temperature, and in the case of phenol, the boiling point in the matrix is higher than its normal boiling point by 10°C. 2) The multiple endotherms do not in any way correspond with that of the treatment material itself and the total energy involved in the treated matrix is much higher than the heat of vaporization of the original organic compounds themselves. 3) When the effluent gases from DSC were identified with the aid of GC-MS, neither the original compounds, nor any of their fragments, were seen. These facts unequivocally indicate that: a) The compounds are bonded with the matrix in more than one way at more than one site. b) When heated, the weakest bond is broken first, at the first (lowest temperature) endotherm, followed by the stronger bonds, which are seen as the succes-

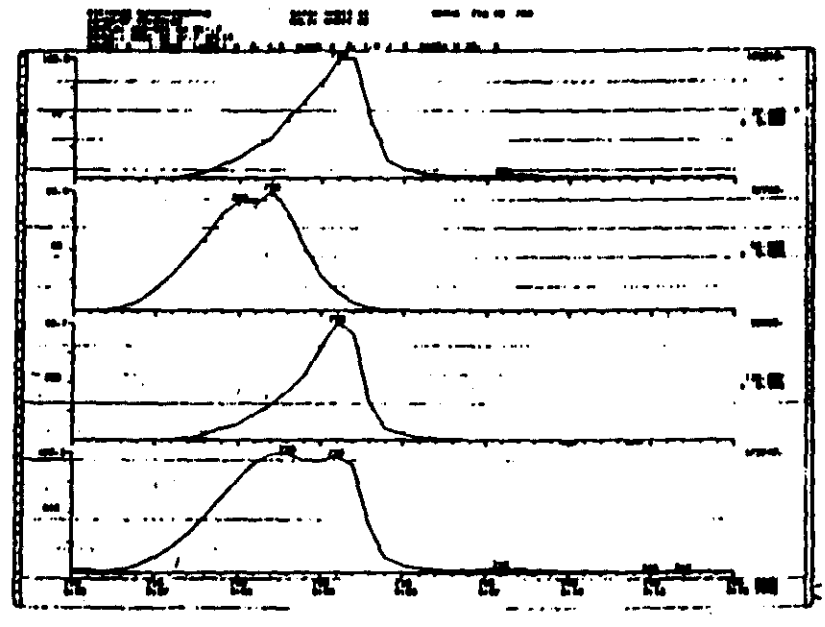

Figure 11 *GC-MS scan for nitrobenzene before treatment.*

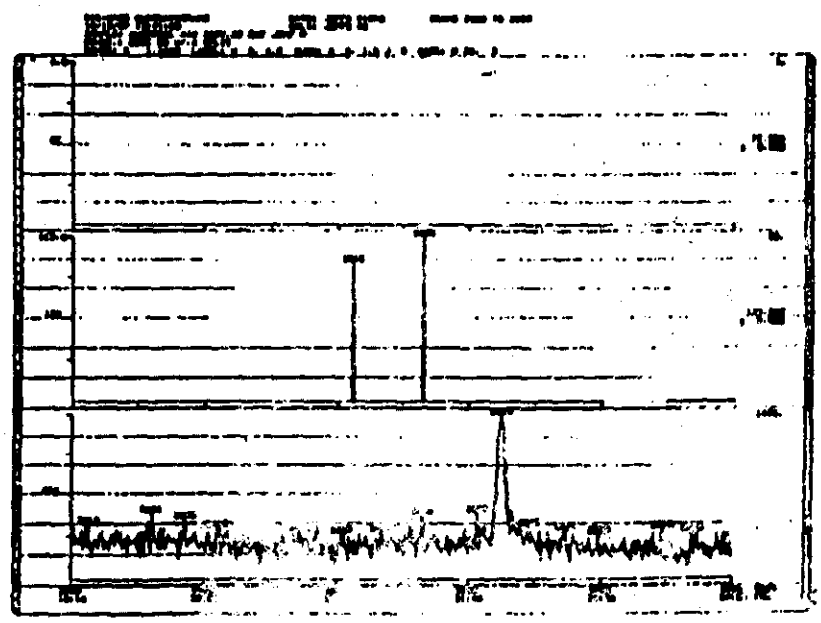

Figure 12 *GC-MS scan for nitrobenzene after treatment*

Table 2

DSC Data

Compound	Endotherms (°C)	ΔH of vaporization (literature) Kcal/mol	Observed ΔH of vaporization Kcal/mol	Percentage increase in energy	Boiling point (°C)	Highest endothermic temperature (°C)
Phenol	193.17	11.89	38.13	220.7	182.0	193.17
Trichloroethylene	106.06 127.92 204.26	9.16	34.43	275.9	113.8	204.26
Triethanolamine	150.97 337.30	12.78	24.16	89.0	335.4	337.30
Nitrobenzene	110.99 119.42 136.87 218.45	12.17	18.60	52.8	210.2	218.45

sive endotherms at higher temperatures. c) The sum of all these endotherms is much higher than the ΔH of vaporization of the individual compounds. This clearly shows that one has to expend much more energy to break the matrix-compounds bonds. d) The GC-MS evidence is surprising. In the case of nitrobenzene, which is depicted here as an example, neither the molecular ions (m/z = 123) nor the benzene ring (m/z = 77) were seen. This suggests that once the hazardous waste is bonded, it does not reappear in its own original form; instead, smaller fragments result when forced out. e) At higher temperatures, some rather unusual long chain nitrated compounds were detected. These compounds, of course, were never detected in the DSC-GC-MS run of the pure treatment materials before treating them with nitrobenzene.

This evidence clearly predicts that there are some kinds of reverse Friedel-Crafts type reactions, along with other polymerization reactions, taking place due to the presence of aluminum in the matrix. From a purely environmental viewpoint, these observations confirm that organophilic clays can indeed bond with organics, and can easily be used as a true containment material. Addition of cement and slag powder helps to improve mechanical and leaching characteristics. It also appears certain that the longer the aging time, the more effective will be the containment. Other compounds discussed in the infrared section also gave similar results in the GC-MS studies. These observations are in agreement with conclusions drawn by other authors.

The entire containment mechanism may be visualized in the following manner:

- The $(R_4N)^+$ groups make the clay organophilic and widen the interplanar distances by acting as pillars.
- The waste materials are sandwiched between the alternating layers of silica and alumina.
- Apart from intercalation, there seems to be dipole-dipole interaction, hydrogen bonding, coordinate covalent bonding, Lewis acid-base reactions, Friedel-Craft reactions, and Diels-Alder type reactions involved during containment.
- When cement and slag powder are added and hydrated, these materials seal the clay mineral-organic layers and crystallize. In the long run, there could be intertwining crystals of clay minerals and cement. The slag powder (due to its fineness) could plug any flaws (or holes) in the structure. The fact that such a mix gives a low leachate value on the EPA TCLP* supports this hypothesis.

*In 1984, Congress modified the Resource Conservation and Recovery Act (RCRA), passed in 1976, with the Hazardous and Solid Waste Amendments (HSWA). These amendments provide an analytical method that would serve to monitor the success of detoxification techniques. This method involves multiple extractions with solvents and is called the Toxicity Characteristic Leaching Procedure (TCLP). EPA requires the TCLP to be performed on each type of solid waste to determine whether treatment is required. The rule establishes maximum allowable concentrations for 36 chemicals that may be contained in the extracts.

If test results meet TCLP standards, the waste involved will not be regulated or regulated and may be disposed of in an RCRA-permitted facility. If TCLP results exceed standards, the waste must first be treated by the technology specified in the rule (or by an equivalent method) and the results must again be subjected to TCLP.

Conclusions

In light of the FTIR, DSC, and GC-MS evidence, it has been shown that:

1. There is true multiple bonding between the treatment material and the hazardous waste.
2. When forced out by natural forces such as heat, they fragment into simpler molecules.
3. The total energy to drive them out of the matrix is much higher than their normal heats of vaporization.
4. The GC-MS evidence indicates that there are other reactions catalyzed by aluminum in the clay.
5. There cannot be any true containment without organophilic clays, and it is a viable alternative to the incineration of hazardous wastes.

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6. Appendix A: List of Extremely Hazardous Substances and Their Threshold Planning Quantities, *Fed. Reg.* 52, 77 (1987).

By J.J. Gibbons and R. Soundararajan

The nature of chemical bonding between organic wastes and organophilic binders, PART 2

THE TYPES of possible chemical bonding between hazardous organic compounds and organophilic binders have been reported recently.[1] However, during that investigation, the organic waste was selected from the hazardous substances list (HSL) and was used to react with the binder to simulate a solidification/stabilization (S/S) situation.

The authors wished to verify the conclusions drawn from their previous study (see *Am. Lab. 20* [7], 38-46 [1988]) by subjecting a sample from a confirmed waste site to solidification, followed by Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential scanning calorimetry coupled with GC-MS (DSC-GC-MS), and leaching tests, since these data will be of great practical value.

In light of results from the previous studies and the data from recent Best Demonstrated Available Technology (BDAT) studies,[2] the authors synthesized their own organophilic binder that would be compatible with the characterized waste in terms of polarity and the "d" spacings in between the two layers of organophilic clays.

Further, drastic solvent extraction was used in this investigation to assess the reliability of this technology under the worst possible leaching conditions, since it is believed by the authors that the existing leachate tests are inadequate to distinguish between a real bonding situation and an adsorption/dilution phenomenon.

In this paper, conclusions are presented on the nature and strength of bonds existing between the organic waste and the binders, along with drastic extraction data which could be used as an indicator of efficiency of various binders.

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Experimental

The waste samples were from an uncontrolled hazardous waste site. The waste sample (as soil) was extracted with methylene chloride for six hours. After proper clean-up procedures, the methylene chloride extract was passed through anhydrous sodium sulfate to dry it. The solvent was allowed to evaporate completely inside a fumehood and the end product was transferred to brown wide-mouth sample bottles and kept at 4°C for various tests.

A known amount of this sample was dissolved in methylene chloride and was subjected to characterization using a model 5100 GC-MS (Finnigan MAT, Cincinnati, Ohio). The pollutants were identified on a peak-by-peak basis and quantitated manually. After proper identification of the waste material, the organophilic clay was synthesized by mixing stoichiometric quantities of sodium bentonite and a quaternary ammonium chloride of the type $[R_3ArN]^+Cl^-$ in a water/isopropyl alcohol solution using a high speed blender for 30 min, followed by filtration and drying at 105°C. The quaternary ammonium chloride has been chosen so that: 1) the interplanar distance between the alumina and the silica was around 25 Å, and 2) the alkyl groups have comparable polarity indices to that of the characterized waste.

The synthesized clay (about 6% by weight) was mixed thoroughly with other binders such as Portland cement, fly ash, and slag powder. This new product was designated as the treatment binder for this study. The extract from the waste (preserved at 4°C) was thoroughly mixed with the binder at a binder:waste ratio of 60:40 by weight, and was allowed to cure for 48 hr (Sample 1). Data from Sample 1 are found in *Tables 1* and *2*.

Addition of water was avoided since it would interfere with collection of FTIR data and other physicochemical studies, and introduce exothermic reactions such as the cement hydration reaction. However, several samples were prepared starting with 50:50 mixtures of original contaminated soil and binder, a paste being made by adding sufficient water and allowing the slurry to cure at room temperature for 48 hr (Sample 2). Sample 2 was used to perform the leaching/extraction studies,

Table 1

Infrared data

Hazardous waste site: Waste extract	Hazardous waste site: Waste extract + binder Sample 1	Infrared frequency shift	Infrared functional group assignments
3394	3385	−9	OH stretch O—H···O
3362	3372	−10	NH stretch N—H···O
3373	3355	−18	
1597	1580	−17	Keto group C=O···H
1035	1005	−30	Hydrogen bonding Si–O···H

Table 3

GC-MS analysis data on identified priority pollutants*

No.	Compound	Concentration (mg/kg)	Method detection limit (mg/kg)
1	Bis (2-chloro iso propyl) ether	8528	5.7
2	Naphthalene	18,080	1.8
3	Phenanthrene	20,184	5.4
4	Benzo (A) anthracene	30,480	7.8

* Average surrogate recovery = 97%.

The other major components in the waste were found to be long chain aliphatic hydrocarbons, alcohols, amines, acids, and other oxidation products.

and results are described in that section.

The FTIR studies of 1) extracted waste, 2) pure binder, and 3) Sample 1 (binder + waste) were done by mixing milligram quantities of the respective samples with dry KBr and pelletizing them. These pelletized samples were scanned in the range of 4000 to 40 cm^{-1} in a model 1710 FTIR unit with a SEARCH-2 computerized database (The Perkin-Elmer Corp., Norwalk, Connecticut). The TGA and DSC studies were performed using 3-10 mg quantities in a DSC/TGA-2 unit (Perkin-Elmer) interfaced with a thermal analysis data system (TADS).

All the runs were carried out in air and the heating rate was 10°C/min. Once the endothermic peak temperatures were identified for Sample 1 (binder + waste), the effluent gases at those temperatures were collected using an activated charcoal cartridge. The adsorbed gases were then extracted with CS_2 and analyzed in the

Table 2

DSC data

	DSC endothermic peak values Temperature (°C)	ΔH (vaporization) (cal/g)
Hazardous waste site: Waste extract	136.60	18.63
Hazardous waste site: Waste extract + binder (Sample 1)	121.207	8.15
	414.39C	2.32
	414.49C	0.06
		10.53
	Hazardous waste site: Waste extract	Hazardous waste site: Waste extract + binder (Sample 1)
	Cal/g	Cal/g
Total Δ H (vaporization)	18.63	10.53
Total Δ H (vaporization) corrected to 100%		28.65
		Hazardous waste site: waste extract + binder (Sample 1)
TGA: % weight loss at given temperature range		36.46
% increase in Δ H (vaporization) for hazardous waste site waste extract + binder		54.03

GC-MS to identify the fragments of the solidified waste compounds.

Results and discussion

The results of the FTIR, DSC + TGA, and GC-MS analyses are shown in *Tables 1-3*. The actual DSC and DSC-GC-MS runs are shown in *Figures 1-9*. Before the physico-chemical data are discussed, it is relevant to discuss the general theory of the solidification/stabilization process.

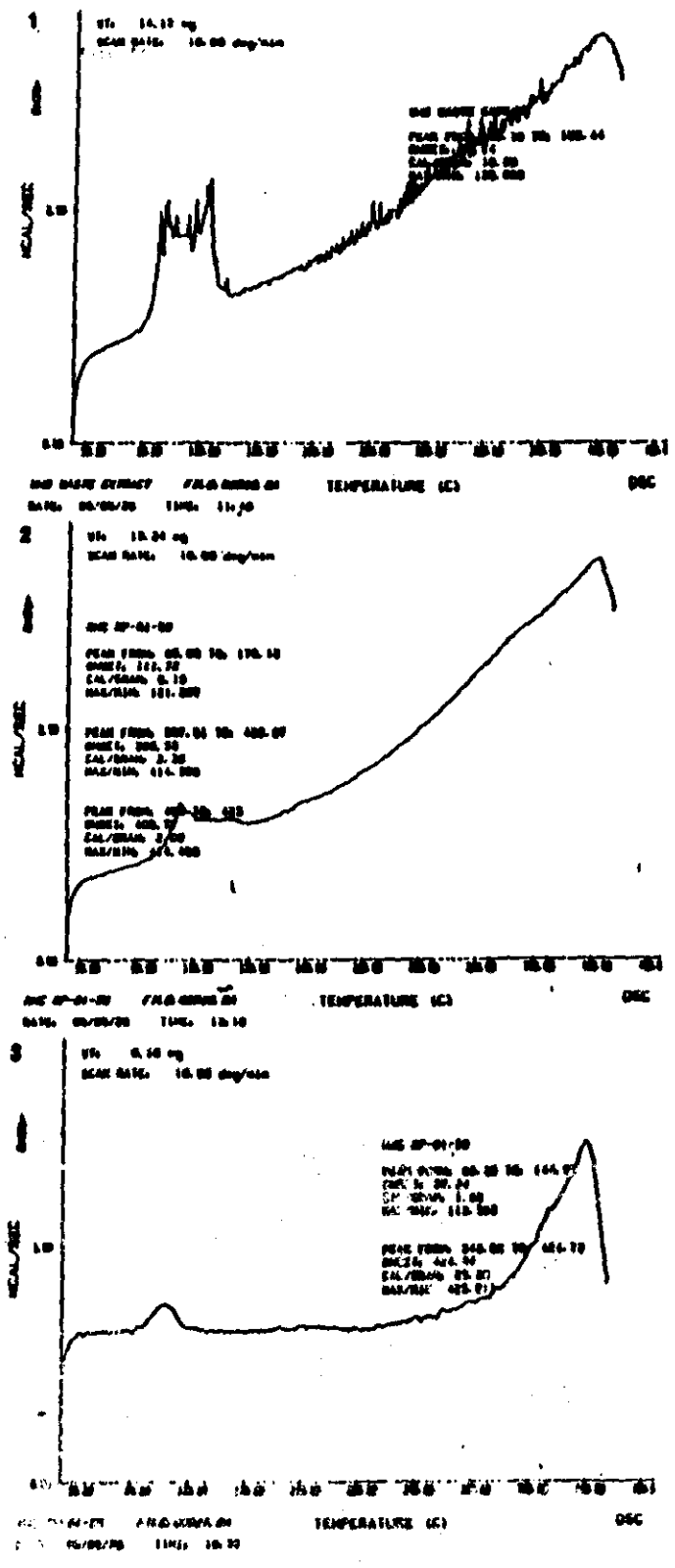
It is a well-known fact[3] that the Group IA and IIA metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Ba^{2+}), which are present between the layers of alumina and silica in clay minerals for electrical charge balance, can be substituted by quaternary ammonium ions such as $[R_4N]^+$ to yield clays that have both organic and inorganic properties. Introduction of these ions brings about two favorable effects on the clay matrix: 1) the interplanar distance increases approximately from 6 Å to 25 Å, and 2) the R groups in the quaternary ammonium compounds create a stationary phase whose polarity is compatible with the polarity of the waste to be stabilized.

When the organic wastes are intimately mixed with such binders, the stationary phase (due to its semi-organic nature) preferably attracts the organics to a region in between the expanded interplanar spacings in the modified clay matrix. After the organics are drawn between the layers of clay, there are possibilities for a multitude of chemical bonding to occur, ranging from weak Van der Waals forces to strong coordinate covalent bonds.

For instance, the alumina and silica oxygens can form hydrogen bonds with the hydrogens in the waste, or the transition metals in the clay may form coordination compounds with organic compounds, such as phenols, amines, amides, carboxylic acids, and hydroxy acids. Furthermore, the aluminum in the alumina can bring about Lewis Acid-Base reactions due to its electron deficiency.

In the past, we have seen evidence for the various types of bonds discussed above. Apart from the chemical reactions, when water is added to treat the waste, cement hydration seals off the organic molecules drawn into the clay layers. Addition of inert materials (such as slag powder) plugs the holes in the solidified matrix, thereby minimizing the leaching of the wastes.

The choice of the R groups in the $[R_4N]^+$ is the key to the success of the solidification process. In this study, the $[R_4N]^+$ groups were synthesized with adequate aliphatic chain lengths (decided from the nature of the waste) with polyfunctional groups that would favor Lewis Acid-Base reactions, hydrogen bonding, coordi-



Figures 1-9 *Actual DSC and DSC-GC-MS runs.*

Certain types of clays that contain traces of various metals when converted into organophilic clays bind ligands like phenols very strongly. With this background, the results from physico-chemical techniques used in these investigations will be discussed.

FTIR

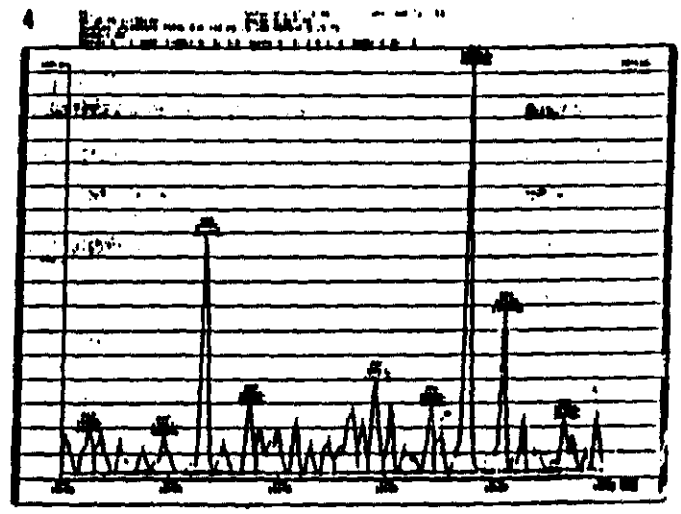
The FTIR absorption frequencies, their assignments, and the shifts in the assigned frequencies in Sample 1 are shown in Table 1. From the GC-MS data, it was confirmed that the waste consists of large quantities of long-chain hydrocarbons, alcohols, aldehydes, ketones, and amines, with trace quantities of four priority pollutants. Due to low concentrations of these compounds, their characteristic frequencies could not be observed in the FTIR studies.

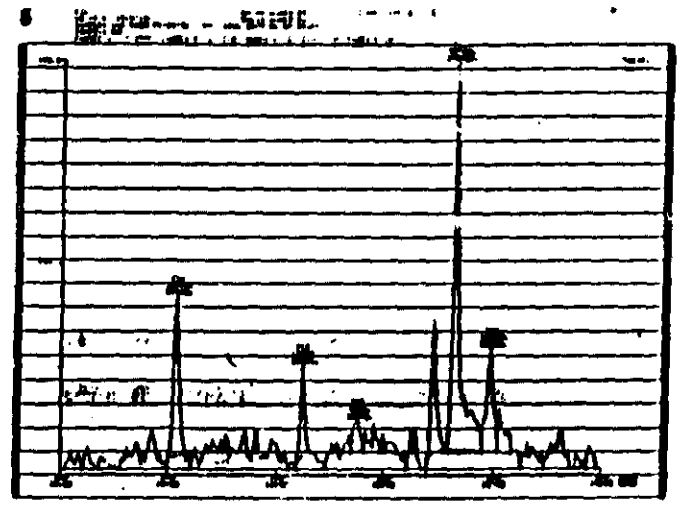
Because of this problem, it was decided to study the bonding between the major components and the binder. There are three shifts in the regions assigned to N-H and O-H vibrational frequencies: from 3394 to 3385, from 3382 to 3372, and from 3373 to 3355, indicating weak to moderate perturbations. All these shifts toward lower frequencies could be attributed to hydrogen bonding between N-H and O-H hydrogens and the clay oxygens. There are also weak interactions in the C-H region, which can be attributed to the C-H---O bonding. The shift from 1597 cm^{-1} to 1580 cm^{-1} is explained by an amine salt formation, which is the result of a Lewis Acid-Base reaction. The most significant shift is seen in the region assigned to Si-O-Si, from 1035 cm^{-1} to 1005 cm^{-1}. This can be explained by the fact that the oxygens of the silica strongly interact with the hydrogens from alkyl groups, hydroxyl groups, and amino groups, which result in reduction of the O-Si-O bond order.

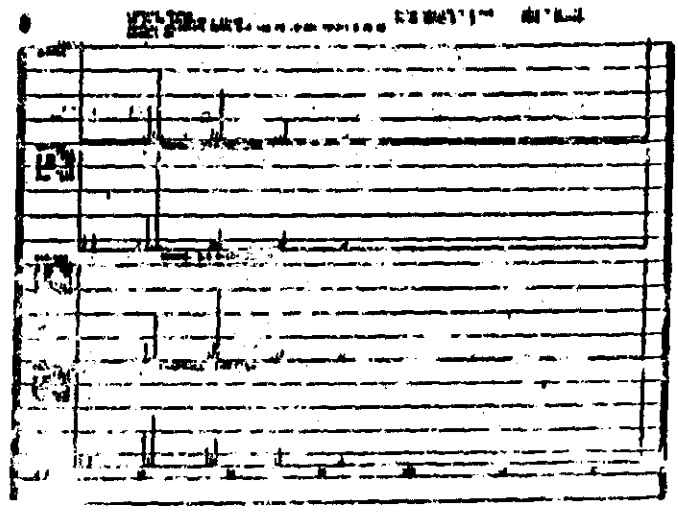
DSC

The DSC data are shown in Table 2. The extracted waste shows an endothermic peak maximum (Figure 1) at 136.9°C. The energy required to volatilize the waste at that temperature has been found to be 18.65 cal/g. However, the DSC of Sample 1 (waste + binder) shows three endotherms at 121.2°C, 414.4°C, and 414.5°C, respectively. When the energies for these endothermic peaks were added together and corrected for 100% (the weight loss in the sample from the hazardous waste site due to the waste was found to be 36.48% by TGA), the heat required to drive the waste out of the system turns out to be 28.86 cal/g. This is considerably higher (by 54.94%) than the energy required to evaporate the waste without the binder.

It is also interesting to note in the DSC scans of our synthetic binder that there are endotherms in the regions







the fact that the presence of similar compounds in the clay structure favor better binding characteristics. The fact that the waste requires an additional 54.94% energy to leave the system indicates that it is bound rather strongly to the matrix.

GC-MS studies on the effluents from the solidified waste

The reconstructed ion chromatograms (RIC) of the extracted waste at its first endothermic temperature range, as well as the solidified waste (Sample 1), are shown in Figures 4 and 5. These RICs reveal that there are at least two distinct peaks at scan numbers 665 and 787 in the untreated waste. However, the solidified waste at the same temperature shows two major peaks at 654 and 782.

The first inference would be that these peaks elute earlier than their untreated counterparts and hence could be different compounds. Secondly, early elution could indicate a compound with a low boiling point/molecular weight. This observation is confirmed by the library search procedures (Figures 6-9).

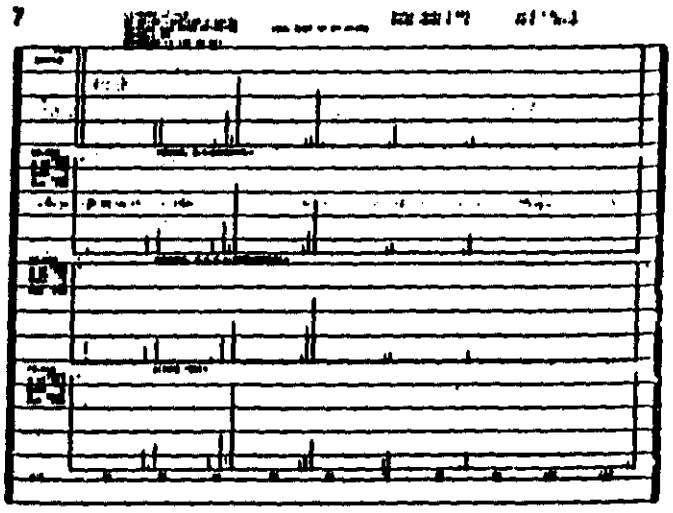
The peak at scan number 665 in the untreated waste was identified as 2,3,4-trimethyl hexane, but the untreated waste yielded a peak at scan number 654, which was found to be 3,4-dimethyl hexane. This same trend is observed for scan numbers 787 (in the untreated waste) and 782 (in Sample 1). In this case, the compounds were identified as 2,5,6-trimethyl decane and 2,4,6-trimethyl octane, respectively.

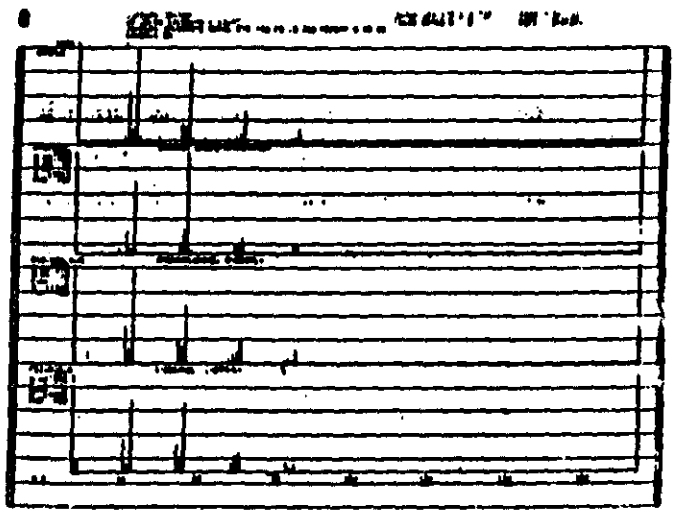
It is evident from these data that when any element of nature (such as heat) is applied to force out the bound waste from the matrix, it breaks down the waste into smaller fragments. This trend was also observed in our previous investigations. It appears in the case of long chain aliphatics, that both main chains (as well as side chains) cleave when the molecules are forced to evaporate.

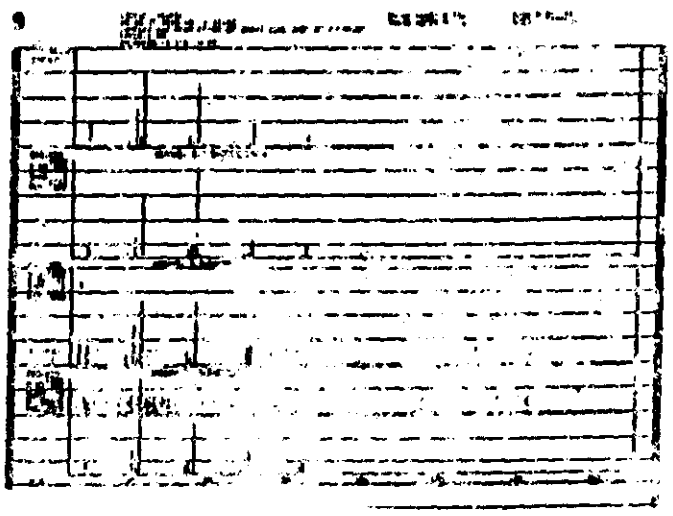
Leaching/extraction studies

When compared with the amounts of the priority pollutants present in the extracted waste, the leaching test results using Sample 2 were impressive. However, this conclusion can be misleading at times.

In our earlier investigations, we attempted to evaluate the reliability of the existing test methods that are normally used for radioactive wastes to distinguish a good solidification technology from the less satisfactory ones. Several binders which contained organophilic clays with synthesized organic waste were spiked along with another binder that did not have any organophilic clays at all. The tests that are currently available did not show any distinction between the leachate data in spite of the organophilic clays did form chemical bonds







Although such drastic leaching conditions do not exist in nature, there should be a means of distinguishing a workable technology from the others in order to protect the interests of potential users of the technology and the regulatory agencies.

Barring a few variables (which could be kept relatively constant) such as surface area and temperature, the main thermodynamic forces involved in the leaching process are: 1) heat of solution (ΔHsoln) of the waste in the extracting solvent, and 2) the bond energy of the bonds between the waste and the binder. When the bond energy exceeds the ΔHsoln, the waste material will be retained in the matrix. On the other hand, when the ΔHsoln is greater than the bond energy, the wastes will be leached out.

It has been our experience that successful encapsulation occurs when the solidification matrix is designed in such a way that: 1) it has an interplanar "d" spacings that would "snugly fit" the waste molecules; 2) it has polyfunctional groups that would interact with the waste in many different ways to permit chemical bonding; 3) it has a polarity index comparable to that of the compounds in the waste; and 4) it has other binders that would seal the bonded compounds and "plug up the holes" to prevent physical contact between the waste and the solvent.

Conclusions

1. Under suitable conditions, the organic wastes form a myriad of bonds with the stabilization binders. The types of bonds include hydrogen bonding, Lewis Acid-Base reactions, coordinate covalent bonds, and metal-ligand bonds.

2. The bond strength depends upon the nature of the waste material and the functional groups present in the compounds.

3. Also, to enhance the bonding, it is essential to have an organophilic clay with favorable polarity.

4. It is technically possible to synthesize "tailor-made" binders for specific waste products.

5. The DSC-TGA data indicate that more energy is required to remove a bound waste from the matrix than is needed for an unbound waste.

6. DSC-GC-MS studies confirm that when forced out, the organic waste molecules break down into simpler substances.

7. The conclusions from the authors' previous studies have been found to be valid in an actual waste site solidification/stabilization situation.

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