

AN OVERVIEW OF PRESENT DAY IMMOBILIZATION TECHNOLOGIES*

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Summary

Several immobilization technologies are emerging at the present time. Due to their versatility, simplicity, and cost effectiveness solidification/stabilization technologies are widely used. While there are numerous claims of a “magic binder” many of them turn out to be simple adsorbents and diluants of the waste.

In this paper, we present the physico-chemical evidence that distinguishes a binder that chemically bonds with the waste from one that simply adsorbs on the surface. Those evidences come from well accepted techniques, such as Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), DSC coupled with Gas Chromatography and Mass Spectroscopy (DSC/GC/MS), and Toxicity Characteristic Leaching Procedure (TCLP). The practicality of vitrification and our findings on the “quick lime” solidification will also be discussed.

Introduction

Two new immobilization technologies, at least on the basis of pilot-scale studies, seem to stand up and they are: (i) *in situ* vitrification [1] and (ii) stabilization/solidification. Unfortunately, the former, in spite of its proven efficiency, is extremely costly [1] and hence it has not been used on a commercial scale as yet.

Because of their simplicity, cost effectiveness, and other desirable characteristics, stabilization/solidification (S/S) is widely used today. While there are numerous claims of “magic binders” for both organic and inorganic wastes, basic research reveals that many of these binders are simple adsorbents and diluants. There are, of course, a number of organophilic clay-based binders which bring about true chemical bonding [2–6].

In this paper the physico-chemical evidence that distinguishes a binder that chemically bonds with the waste from one that simply adsorbs the waste on the surface is presented. Also, the hazards associated with the so-called “quick lime stabilization”, which is not a true stabilization but is very commonly used in Europe, are presented with experimental evidence.

In order to determine the practicality of the containment technology, we

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conducted our investigations using more powerful tools, such as Differential Scanning Calorimetry (DSC) and GC/MS in addition to FTIR and TGA techniques. In this paper we present our conclusions, drawn on the basis of above techniques, about reliability of this newly emerging S/S technology. In order to minimize the variables, pure known organic compounds representing various classes on the hazardous substances list were used at first. A second waste sample from a confirmed waste site was also used to evaluate bonding. In both cases, the experimental evidence showed unequivocally the existence of a myriad of chemical bonds between the binder and the waste. In the case of "quick lime stabilized" waste, the stabilized waste upon acidification (simulated acid rain) released carbon monoxide and acetylene.

Experimental

The treatment materials were provided by International Waste Technologies, Inc., Wichita, Kansas. The material used in our study was the HWT-22. Known amounts of the organics (chloronaphthalene, chloroaniline, phenol, nitrobenzene, and triethanolamine) were treated with fixed amounts of HWT-22 and allowed to cure at room temperature. The addition of cement, slag powder, and water was avoided since we did not want (a) water to mask our IR Spectra and (b) the silicate hydration reaction to interfere with the clay-mineral-organic reactions.

After 48 hours, the samples were subjected to FTIR analyses using a Perkin Elmer 1710 FTIR instrument using KBr pellets. The FTIR spectra of the pure organics were also run using KBr pellets.

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 during DSC scanning, the gases were absorbed in activated charcoal cartridges, preserved in dry ice, desorbed into a Finnigan MAT GC/MS system, and then analyzed. The scan rate was 2 scans/second. The mass range was 30–500. The heating rate at the GC was 6.5°C/min. The TGA and other FTIR parts are discussed elsewhere [5]. The TCLP data was obtained from another study under the "Superfund Innovative Technology Evaluation" (SITE) program. The binder for that study was synthesized in our own lab after the total characterization of the waste. The "quick lime stabilized waste" was sent to us for characterization from a state-owned oil refinery in Europe.

Results and discussion

The absorption frequencies for three different classes of compounds are shown in Table 1. The peak assignments and the shift in the frequencies after bonding with HWT-22 are also shown in the same table. The types of possible

bonds are predicted in Figs. 1 and 2. The reconstructed ion chromatograms of the effluent gases from DSC are shown in Figs. 3 and 4. The DSC endothermic peak temperatures along with ΔH of vaporization are shown in Table 2. The DSCs of "quick lime stabilized waste" are shown in Figs. 7 and 8; the CG/MS run of the effluent gases upon acidification is shown in Fig. 9, the compounds identification in Fig. 10.

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 [7].

Nitrobenzene: There is a shift from $1,175\text{ cm}^{-1}$ to $1,150\text{ cm}^{-1}$ which is assigned to mono substituted aromatic compounds. This lowering is due to the restrictions imposed by intercalation (i.e., the compound sandwiched between layers of alumina and silica). There is another reduction frequency at the C–N stretching region, $1,349\text{ cm}^{-1}$ to $1,345\text{ cm}^{-1}$, indicating the motion of the nitro-group is restricted. This restriction could be due to the interaction between outer orbital electrons in the oxygen and the matrix which has the electron deficient aluminium. Due to this bonding the C–N bond order is decreased and hence the reduction in wavenumber. There are four other frequencies due

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	Ar–NO N–O stretch
3108	3102	–6	
2934	2929	–5	C–H stretch
2861	2857	–4	
2631	2612	–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

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 O-H hydrogen and oxygen in the silica and alumina. This causes the shift in electron density from carbon to oxygen thereby reducing the C-O bond order. Also, there is evidence for hydrogen bonded O-H group at $3,640\text{ cm}^{-1}$ and $3,632\text{ cm}^{-1}$.

Triethanolamine: We have seen several weak to moderate interactions (bonds) in the previous cases. However, in the case of triethanolamine we are able to establish the presence of coordinate covalent bonds between the lone pair of electrons of the nitrogen and the matrix (aluminum). The C-N stretching frequency has dramatically shifted by 193 cm^{-1} in the positive direction. This 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 coordination bond with aluminum, as well as with a proton (hence the large shift). We also see a shift in the negative direction in the

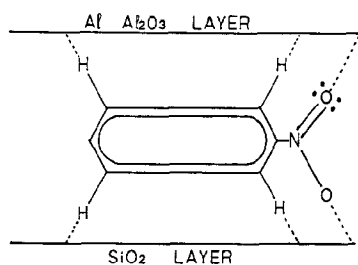


Fig. 1. Nitrobenzene molecule sandwiched between layers of alumina and silica.

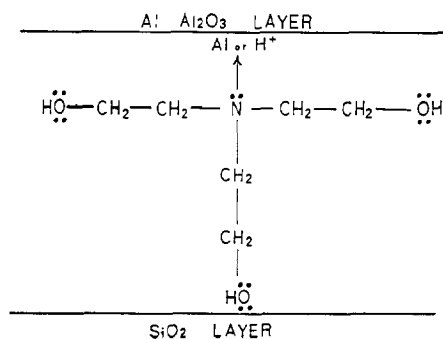


Fig. 2. Triethanolamine molecule sandwiched between layers of alumina and silica.

alcohol O-H stretching frequency. This chemical phenomenon is due to the hydrogen bonding of the hydroxyl hydrogen with the substrate oxygen.

In general it appears that there are numerous types of complex reactions involved in the case of claymineral/organics reaction. The operating forces

TABLE 2

DSC data

Compound	Endotherms	ΔH of vaporization (literature) kcal/mol	Observed ΔH of vaporization kcal/mol	Percentage increase in energy	Boiling point ($^{\circ}\text{C}$)	Highest endothermic temperature ($^{\circ}\text{C}$)
Phenol	193.17	11.89	38.13	220.7	182.0	193.17
Trichloroethylene	105.05 127.92 204.26	9.16	34.34	275.9	113.8	204.26
Triethanolamine	150.97 337.30	12.78	24.16	89.0	335.4	337.30
Nitrobenzene	110.99 119.42 138.87 218.45	12.17	24.16	52.8	210.2	218.45

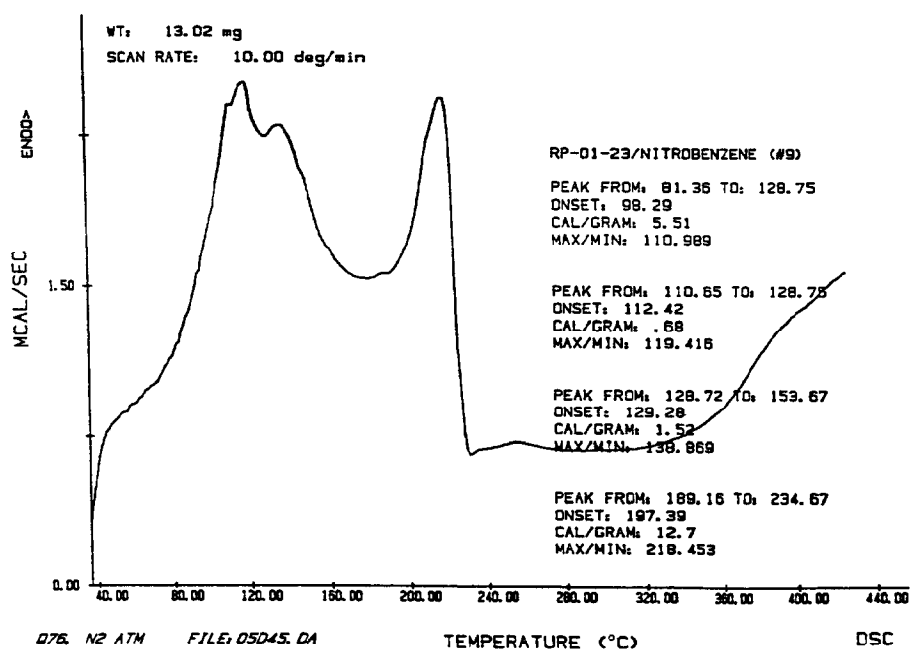


Fig. 5. DSC graph of nitrobenzene-laden clay matrix material.

range from dipole–dipole interaction to pure coordinate covalent bond formation. Hydrogen bonding and intercalation do seem to play important roles. Chelation is also a possibility provided transition metals (Fe, Co, Ni etc.) are present in the claymineral [8]. The presence of organic cations also seems to play a part in retaining certain anionic species, such as carboxylates. We have seen evidence for the above-mentioned facts in the past through FTIR and other sources. The other possibility could be the interaction between the partially filled orbitals of transition metals and filled *p* orbitals of the ring systems.

Differential scanning calorimetry

Scans were done in order to determine the kind of bonding involved, and the extent of energy that would be necessary to release the compounds from the matrix [9]. The actual DSCs are shown in Figs. 5 and 6. The actual ΔH of vaporization of some of the chosen compounds are compared with ΔH from the treated compound along with their normal boiling points in Table 2. The molar ΔH of vaporization for the compounds was computed from the weight loss at their boiling points by dynamic TGA. Three important observations were made from DSC data:

(1) All the compounds are leaving (except phenol) the matrix at more than one temperature and in the case of phenol the boiling point is higher than its normal boiling point by 10°C.

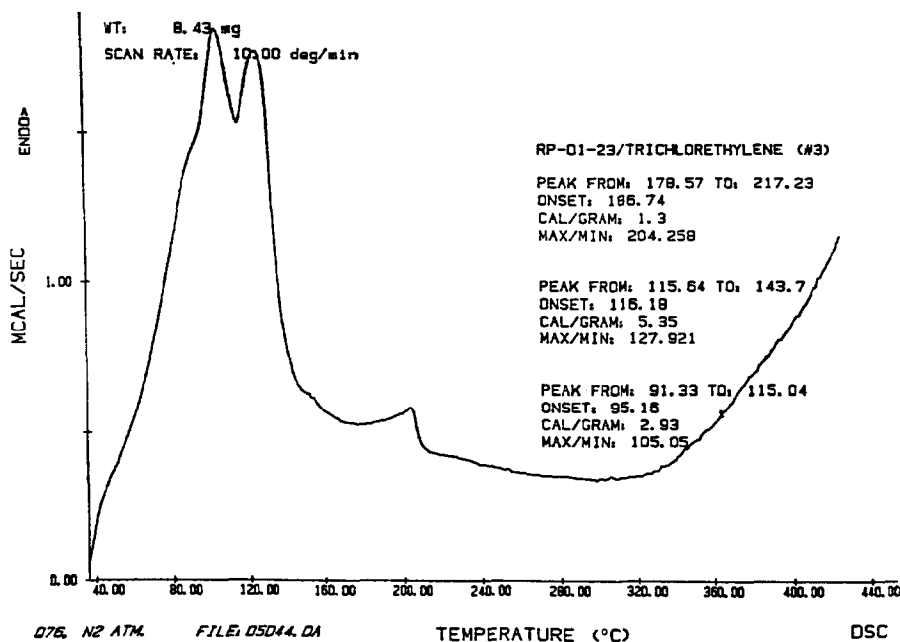


Fig. 6. DSC graph of trichloroethylene-laden clay matrix material.

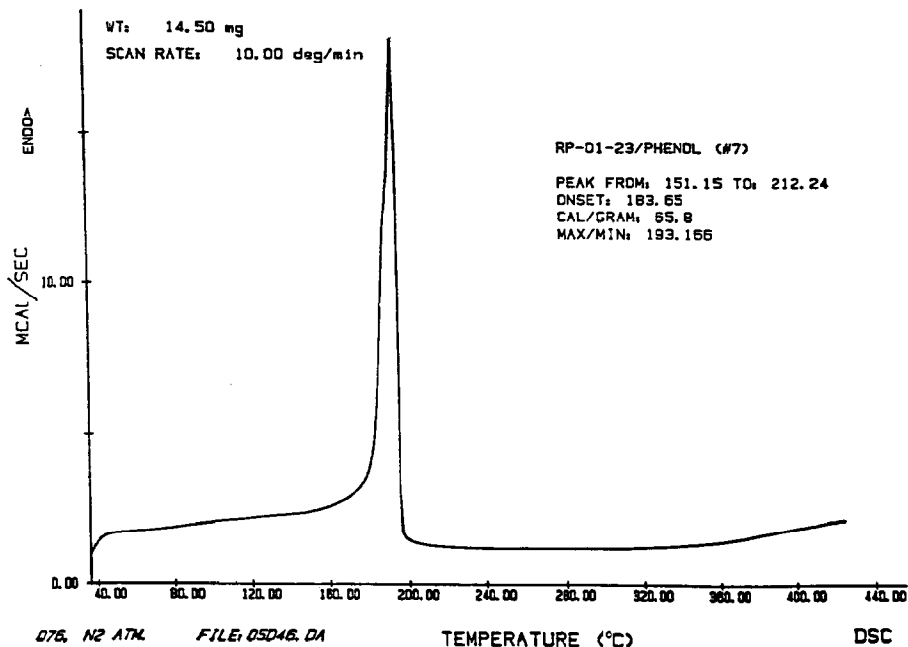


Fig. 7. DSC graph of phenol-laden clay matrix material.

(2) The multiple endotherms do not in any way match with the treatment material itself and the total energy involved in the treated matrix is much higher than the latent 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 compound, nor any of its fragments were seen. These facts unequivocally indicate that: (a) The compound is 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 (low temperature) endotherm, followed by stronger bonds, which are seen at the successive endotherms at higher temperatures; (c) The sum of ΔH of all these endotherms is much higher than the ΔH of vaporization of the individual compound. This clearly shows that one has to expend much more energy in order to break the matrix-compound bonds. (d) The GC/MS evidence is overwhelming. In the case of nitrobenzene, shown here for example, neither the molecular ions $m/z=123$ nor the benzene ring $m/z=77$ were seen. This would mean that once bonded the hazardous waste does not come out in its original form. Instead, smaller fragments are the result when forced out. (e) Further, at higher temperatures, rather unusual long-chain nitrated compounds were 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 reverse Friedel-Crafts

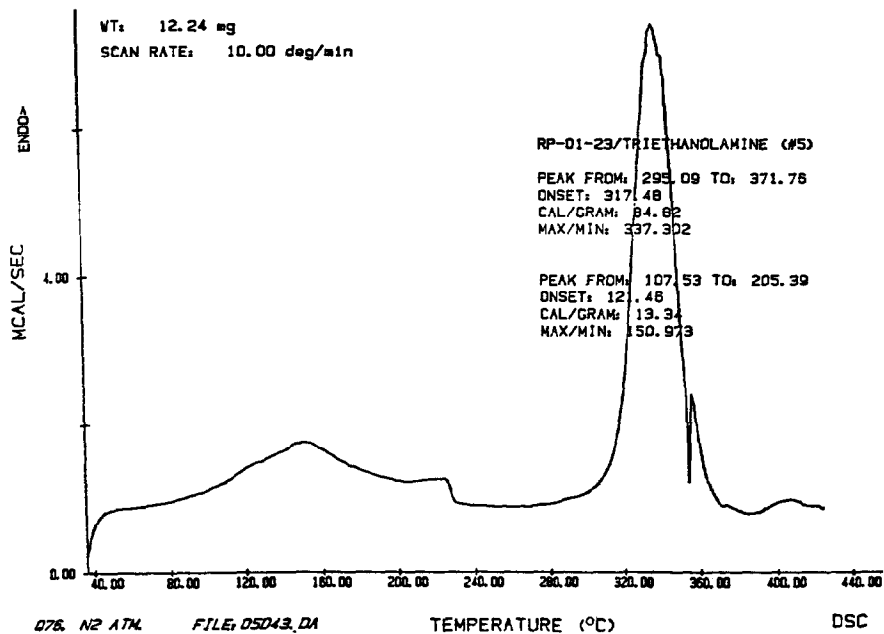


Fig. 8. DSC graph of triethanolamine clay matrix material.

type reactions along with polymerization reactions taking place, due to the presence of aluminum in the matrix. From an environmental standpoint these observations confirm that organophilic clays can indeed bond with organics, and can be used as a true containment material. Addition of cement and slag powder helps to improve mechanical and leaching characteristics. It also appears that the longer the aging time, the better will be the containment. Other compounds discussed in the infrared segment also gave similar results in the GC/MS studies. These observations are in agreement with conclusions drawn by other authors. The same type of results were obtained for bound PCBs also. The GC/MS analysis of decomposition products indicates a reverse Friedel-Crafts type reaction.

Quick lime stabilization

Quick lime and other pozzolanic materials are being used nowadays for stabilization/solidification work. However, this technology, when applied to the containment of organics, introduces more problems than it solves.

When treated with a sludge containing a heavy load of organics, water, and acid, the heat of mixing or solution (hydration/neutralization), which is rather high, causes a number of problems. In the first place, they volatilize many organics and when the temperature exceeds the flash points of the organics an

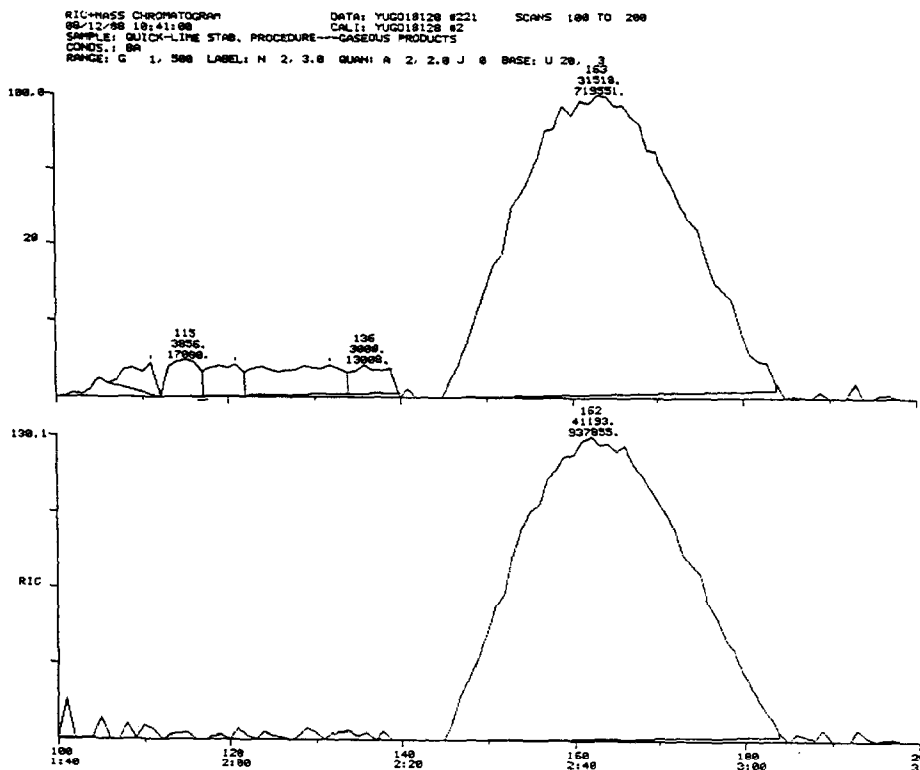


Fig. 9. GC/MS graphs of gases released during quick lime stabilized sample acidification (CO and C₂H₂).

Library Search Data: YUG018128 # 162 Base m/z: 28
 08/12/88 10:41:00 + 2:42 Call: YUG018128 # 2 RIC: 159231
 Sample: QUICK-LINE STAB. PROCEDURE--GASEOUS PRODUCTS
 Cond.: BA

42222 spectra in LIBRARYNB searched for maximum PURITY
 162 matched at least 3 of the 10 largest peaks in the unknown

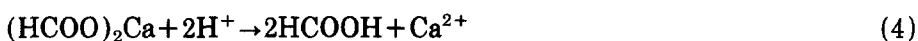
Rank	In.	Name
1	7	CARBON MONOXIDE (DOT)
2	1234	2,4-IMIDAZOLIDINEDIONE
3	4367	BUTYRALDEHYDE, 4-METHOXY-2,3-DIMETHYL-
4	322	1-PROPANOL, 2-AMINO-
5	7778	ETHANEDIAL, MONOHYDRATE, DIMER

Rank	Formula	M. Wt	B. Pk	Purity	Fit	RFit
1	C. O	28	28	573	993	573
2	C3. H4. O2. N2	100	28	535	730	696
3	C7. H14. O2	130	18	445	475	598
4	C3. H9. O. N	75	44	380	411	464
5	C2. H4. O13	152	29	286	306	420

Fig. 10. Identification of the products detected in Fig. 9.

explosion/fire accident can happen. Secondly, the heat causes the formation of carbides and formates as follows:





When a sample from a quick lime stabilization procedure was acidified for EP-Tox test, it started releasing gases. The gases then were identified by extensive GC/MS analysis to be the gases acetylene and carbon monoxide. These end products were due to the hydrolysis and dehydration products of calcium carbide and formic acid (reaction 3-5 above).

TCLP data

The TCLP data (Tables 3 and 4) reveal clearly that the aromatics used in the study are held rather strongly to the binder. It is interesting to note that

TABLE 3

Toxicity characteristic leaching procedure data^a

Compound	Concentration in waste (total waste) µg/kg	Concentration in TCLP µg/kg	% Retention in the matrix
Bis (2-chloro isopropyl) ether	8,528	ND ^b	100
Naphthalene	18,060	ND	100
Phenanthrene	20,184	ND	100
Benzo (A) anthracene	30,460	ND	100

^aAll values corrected for dilution.

^bND = not detected.

TABLE 4

Methylene chloride extraction data from solidified waste

Compound	Concentration in waste µg/kg	Concentration in methylene chloride extract µg/kg	% Retention in the matrix
Bis (2-chloro isopropyl) ether	8,528	ND ^a	100
Naphthalene	18,060	1445	92
Phenanthrene	20,184	ND	100
Benzo (A) anthracene	30,460	ND	100

^aND = not detected.

even when a drastic solvent like methylene chloride was used, except for naphthalene, all other PNAs had a 100 percent retention in the matrix. This phenomenon may be explained as follows:

The important forces that are involved during an extraction procedure are the heat of solution (ΔH) and the bond energy due to the bond between the matrix and the waste. If this bond energy is larger than the heat of solution, the bonded waste materials do not leach. On the other hand, if there is no bonding between the waste and the binder, but only adsorption is involved, the heat of solution will be larger than the adsorption energy, and hence the wastes will leach out into the solvent. The level of leaching is an indication of the strength of bonding between the binder and the waste.

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

- The $(R_4N)^+$ groups render 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, true co-ordinate covalent bonding, Lewis acid–base reactions, and Friedel–Crafts type reaction involved during containment.
- When cement and slag powder are added and hydrated these materials seal the claymineral–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 (holes) in the structure. The fact that such a mix gives a low leachate value in the Toxicity Characteristic Leaching Procedure (TCLP) supports this hypothesis.

Conclusions

In the light of FTIR, DSC, and GC/MS evidence, we have shown that:

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

- (6) Quick lime solidification is not a true solidification/stabilization at all. There are a number of hazards involved in this and hence it is not desirable for organic wastes.

References

- 1 Geosafe Corporation, Application and Evaluation Considerations for In situ Vitrification Technology: A Treatment Process for Destruction and/or Permanent Immobilization of Hazardous Materials, Report April, 1989, Geosafe Corp., Kirkland, WA.
- 2 D.H. Solomon, (Clay Minerals as electron acceptors and/or donors in organic reactions, *Clays Miner.*, 16 (1968) 31-39.
- 3 M.M. Mortland, S. Shaobai and S.A. Boyd, Clay-organic complexes as adsorbents for phenols and chlorophenols, *Clays Miner.*, 34 (1986) 581-585.
- 4 B.K.G. Theng, Clay-activated organic reactions. In *Proc. Int. Conf. on Clays*, 1974, Wiley, New York, NY, 1974.
- 5 L. Heller and S. Yariv, Sorption of some anillines by Mn, Co, Ni, Cu, Zn, and Cd, Montmorillonite, *Int. Clay Conf.*, Tokyo, 1969.
- 6 J.P. Newton, Advanced chemical fixation of organic content waste. *Int. Symp. fixation/Solidification of Chemical and Radiation Waste*, Atlanta GA, May 1987.
- 7 R.M. Silverstein, G.C. Bassler and T.C. Morrill, *Spectrometric Identification of Organic Compounds*, 4th edn., Wiley, New York, NY, 1981.
- 8 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, NY, 1980.
- 9 W.W. Wendland and W.M. Wesley, *Thermal Methods of Analysis*, 2nd edn., Wiley, New York, NY, 1974.