

# Solidification/stabilization study for the disposal of pentachlorophenol

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## Abstract

Solidification/stabilization of toxic pentachlorophenol (PCP) has been studied by using spectroscopic and electrochemical techniques. Portland type I cement was employed to solidify/stabilize PCP. The effects of temperature, pH and ultrasonic waves on setting and curing of the cement in the presence of PCP were investigated. The mechanism of hydration during the early stages of setting of the cement was studied by Fourier transform infrared spectroscopy. Furthermore, UV visible spectroscopy was used to determine the concentrations of PCP and phenol in the mix. Experimental results are discussed in terms of the interaction of hazardous chemicals with cement.

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## 1. Introduction

With recent stringent regulations about alternative methods to mono- or co-disposal of toxic wastes directly to the land, there is a growing interest among waste disposal industries and regulatory agencies in the use of stabilization/solidification (S/S) for disposing toxic wastes [1,2]. Solidification is a process in which materials are added to waste to produce a solid. It may or may not involve chemical bonding between the toxic contaminant and the additive. Stabilization refers to a process by which a waste can be converted into a more chemically stable form. The term solidification includes the use of a chemical agent to transform the toxic component into a new non-toxic compound [3-5].

The S/S technique has been successfully applied

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(i) to improve the handling and physical characteristics of the waste  
(ii) to decrease the surface area across which transfer or loss of contained pollutants can occur  
(iii) to limit the solubility of any pollutant contained in the waste, and  
(iv) to detoxify the contained pollutants. This is in addition to several other factors such as:

- (i) leachability of the waste components to contracting solvent (generally water)
- (ii) physical stability of solidified waste under burial conditions
- (iii) reactivity of waste toward solid matrix
- (iv) susceptibility of the waste toward biodegradation, etc.

Among several waste products pentachlorophenol (PCP) has significant acute toxicity and a number of fatalities have been reported among workers exposed to it [6,7]. PCP and its sodium salt (Na-PCP) are used widely in the United States and are referred to as "biocides" because they are lethal to a wide variety of living organisms. The most important parameters in determining the quality of the S/S products are the extent of immobilization of wastes in the cement and their leaching into water. Leachability of the waste from the solidified product presents a long term threat to ground water contamination. An inherent assumption of these studies is that no chemical interaction occurs between the leachant and the waste which would change the leaching environment with time [8-10].

In the present paper, the hydration behavior of portland cement was studied using the Fourier transform infrared (FTIR) spectroscopy. The ultrasonic wave method was used to study the drastic leaching conditions. Temperature plays an important role in the hydration of cement. The cement can be hydrated very fast at high temperatures so that PCP can be captured quickly and will not permeate outside. Also, the solidified material is ready for land filling in a shorter period of time, leaching to high turnover.

## **2. Experimental**

FTIR spectroscopy is a useful technique to monitor the hydration behavior of portland cement [11-18]. For FTIR studies, an IBM Model 44 spectrophotometer was used ( $400-4800\text{ cm}^{-1}$ ); all powder samples were run as nujol mulls. To improve the signal-to-noise ratio, about 100-500 scans were recorded. To remove any  $\text{CO}_2$  and  $\text{H}_2\text{O}$  from the sample compartment it was flushed with  $\text{N}_2$  gas for about 5 min prior to recording of any spectrum.

A Cary 17 spectrophotometer (Varian Co., Sunnyvale, CA) was used to record the UV visible spectra of phenol and PCP in several different solvents at various concentrations. Since the hydrated cement is too hard to grind with a mortar and pestle, the samples were prepared in nujol mulls rather than in KBr pellets.

### 3. Materials and methods

Portland type I cement (10 g; manufactured by Ideal Cement Company, Denton, TX) was mixed with various amounts of PCP (see Tables 1-6). In order to gain a preliminary understanding of the behavior of solidified phenolic

TABLE 1

Leaching of PCP as a function of setting time (% recovery)

PCP (10 g cement) <sup>a</sup>	Setting time (days)						
	1	2	5	8	11	18	21
10 mg	6.25	3.11	4.33	3.72	4.18	4.90	3.63
1 mg	6.97	—	—	5.70	5.49	5.70	4.89
100 $\mu$ g	46.5	—	—	69.7	59.1	—	—
10 $\mu$ g <sup>b</sup>	38.0	—	—	—	—	—	—

<sup>a</sup>PCP dissolved in 5 ml 0.1 M NaOH then mixed with 10 g cement.

<sup>b</sup>Recovery is larger than 100%, because of background.

TABLE 2

Leaching of phenol as a function of setting time (% recovery)

Phenol (10 g cement) <sup>a</sup>	Setting time (days)						
	1	2	5	8	11	18	21
10.4 mg	66.95	82.62	35.29	57.98	24.81	14.13	17.98
1.04 mg	50.42	—	43.94	27.12	38.75	33.46	31.92
104 $\mu$ g	94.04	—	—	—	—	—	—

<sup>a</sup>Phenol dissolved in 4 ml 0.1 M NaOH then mixed with 10 g cement.

TABLE 3

Comparison of PCP leaching after 3 days from the samples prepared by grinding and without grinding

PCP (g)/ 10 g cement	Recovery after leaching without grinding		Recovery after leaching with grinding	
	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)
0.5	16.47	3.29	40.21	8.04
1.0	31.67	3.17	73.90	7.39

TABLE 4

The effect of various factors on the recovery after leaching of PCP after 3 days

PCP (g)/ 10 g cement	Leaching without A		Leaching without A, B		Leaching without A, B, C	
	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)
0.5	25.75	5.15	13.10	2.62	3.53	0.71
1.0	39.70	3.97	15.63	1.56	4.39	0.44

A: using ultrasonic bath.

B: grinding to fine particles.

C: using 0.1 M NaOH leaching solution.

TABLE 5

Leaching of PCP as a function of setting temperature after 3 days

PCP (g)/ 10 g cement	Recovery at setting temperature					
	0°C		45°C		60°C	
	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)
0.5	34.10	6.28	21.54	4.31	20.27	4.05
1.0	71.37	7.14	43.92	4.39	46.45	4.65

TABLE 6

Leaching of PCP as a function of setting temperature in 0.1 M NaOH after 3 days

PCP (g)/ 10 g cement	Recovery at setting temperature					
	0°C		45°C		60°C	
	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)	Absolute (mg)	Relative (%)
0.5	20.27	4.05	16.05	3.21	18.36	3.67
1.0	22.38	2.24	16.47	1.65	17.74	1.77

compounds, some solidified samples were prepared in a similar manner by using only ordinary phenol.

The cementitious material as prepared in two different ways:

(1) The mixture of phenol and cement was ground to a fine powder; about

5 ml distilled water was added to this mixture and allowed to set at different temperatures.

(2) A given amount of PCP or phenol was added to an alkaline aqueous solution containing 5 ml water; 10 g of cement was added to it and the mixture was allowed to cure at different temperatures for several days.

The exact cure conditions are given in Tables 5 and 6. The leaching of PCP from the solidified samples as a function of time was determined. Curing was done in 2-oz (56.7 g) covered glass vials. After curing, the vials were broken and the samples were ground with a mortar and pestle.

In each case, about 5 mg of the sample was ground to a very fine powder and mixed with paraffin oil to make a mull useful for IR studies. The remaining sample was ground and transferred to a 125 ml bottle to which 100 ml of 0.1 M NaOH solution was added to leach PCP and phenol. This bottle was then placed in an ultrasonic cleaner for 1 hour to increase the rate of mass transfer. Then the leachant was filtered, diluted to an appropriate concentration and analyzed by UV visible spectrophotometry. All samples were stored in the dark prior to leaching to avoid any possible photochemical degradation of either PCP or phenol.

## 4. Results and discussion

### 4.1 The hydration of portland cement

Portland cement is obtained by grinding 4-6% gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{CS}^1\text{H}_2$ ) with the clinker and other constituents present in very small quantities. The four clinker phases are tricalcium silicate ( $\text{C}_3\text{S}$ ), decalcium silicate ( $\text{C}_2\text{S}$ ), tricalcium aluminate ( $\text{C}_3\text{A}$ ) and the ferrite phase. Of these the clinkers which are responsible for setting and developing the strength of the cement are  $\text{C}_3\text{A}$  and  $\text{C}_3\text{S}$ . The early stages of cement hydration depends on the amount of reaction product of  $\text{C}_3\text{A}$  and calcium sulfate hydration. This product is a fine-grained ettringite forming a thin cover on the surface of cement particles and this does not hinder the mobility of cement particles and the paste remains as a slurry. Recrystallization of the ettringite into long needles interlocks the space between cement particles resulting in a hard material. When  $\text{C}_3\text{A}$  hydrates in the presence of  $\text{C}_3\text{S}$ , mono- and trisilico-aluminates ( $\text{C}_3\text{A} \cdot \text{CaSiO}_3 \cdot 12\text{H}_2\text{O}$  and  $\text{C}_3\text{A} \cdot 3\text{CaSiO}_3 \cdot 31\text{H}_2\text{O}$ , respectively) are formed around  $\text{C}_3\text{A}$  by diffusion of silicate ions from  $\text{C}_3\text{S}$ . The  $\text{C}_3\text{S}$  surface reduces the initial retardation of  $\text{C}_3\text{A}$  by sulfate ions by providing additional sites for ettringite crystallization away from  $\text{C}_3\text{A}$  grains.

### 4.2 Spectral results

The IR spectra of four principal clinker phases in Portland cement are displayed in Fig. 1. Because Portland cement is stabilized by the inclusion of foreign ions in its crystal lattice (e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$  and  $\text{Ti}^{4+}$ ),

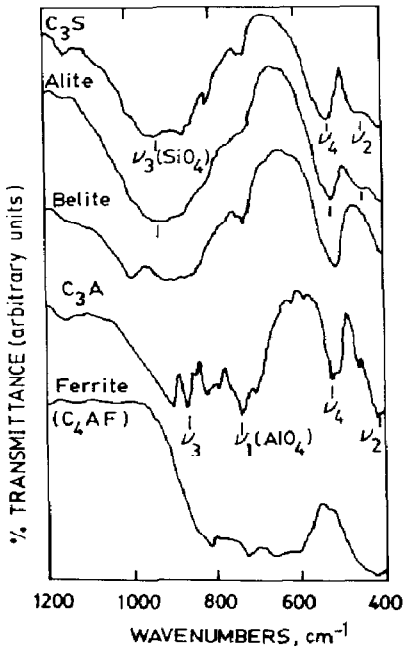


Fig. 1. Nujol mull IR spectra of the main portland clinker phases.

the pure  $C_3S$  has sharper bands than the alite. The wavebands are characteristic of  $SiO_4$  tetrahedra (Table 7). The main absorption centered at  $925\text{ cm}^{-1}$  can be assigned to antisymmetric stretching  $\nu_3$  of  $SiO_4$  and the one at  $525\text{ cm}^{-1}$  can be assigned to its out-of-plane bending of  $\nu_4$  [11,12]. The symmetrical stretching  $\nu_1$  and in-plane bending  $\nu_2$  are weakly IR active. Tricalcium aluminate has a cubic structure. With the spectra of known aluminates [19], the basic units may be  $AlO_4^{5-}$  tetrahedra having a much lower symmetry than  $T_d$ . The strong band at  $740\text{ cm}^{-1}$  may be assigned to symmetric stretching of  $AlO_4^{5-}$  (Table 1) [12]. The wavebands of the minor clinker phases, namely, ferrite and belite, can be seen in Fig. 1.

The IR spectrum of portland cement is shown in Fig. 2. There is considerable overlap, overtone and combination of wavebands of gypsum, four major clinkers and some minor components in the mixtures. Thus, slight changes in absorption bands occur. The IR spectrum of the hydrated portland cement at room temperature is given in Fig. 3. After 12 h, the formation of C-S-H was observed as revealed by the gradual shift of waveband from  $933\text{ cm}^{-1}$ , which after 24 hours shifts to  $973\text{ cm}^{-1}$ . Figure 3(c) shows the formation of calcium hydroxide whose absorption peak appears as a shoulder at  $3640\text{ cm}^{-1}$  due to  $\nu(O-H)$ . The diminution in the absorption around  $800\text{--}1000\text{ cm}^{-1}$  suggests the reaction of the clinker phases. The out-of-plane bending absorption of  $C_3S$ ,  $C_3A$  and some minor clinkers ( $\nu_4$ ) at  $516\text{ cm}^{-1}$  have decreased in intensity and disappeared after one day. The gypsum is gradually converted to

TABLE 7

Assignments of IR bands for principal clinker phases

Alite		C <sub>3</sub> A	
Waveband	Assignment	Waveband	Assignment
450 m	$\nu_2$ , SiO <sub>4</sub>	412 s	$\nu_2$ , AlO <sub>4</sub>
		460 w	a
		470 sh	a
		510 m	
		523 s	$\nu_4$ , AlO <sub>4</sub>
		540 sh	
525 s	$\nu_4$ , SiO <sub>4</sub>	590 vw	a
		620 vw	a
		704 m	a
		740 vs	$\nu_1$ , AlO <sub>4</sub>
		760 m	a
		785 m	$\nu_2$ , AlO <sub>4</sub>
		803 vw	a
		815 m	$\nu_2$ , AlO <sub>4</sub>
830 sh <sup>b</sup>		840 w	
840 sh <sup>b</sup>		860 s	$\nu_9$ , AlO <sub>4</sub>
		895 s	
890 s			
925 vs	$\nu_9$ , SiO <sub>4</sub>		
960 s			

<sup>a</sup>Probably combination vibrations.<sup>b</sup>Probably mixed SiO<sub>4</sub> vibrations.

ettringite and later to monosulfate as indicated by a broadening of the water absorption band and also by conversion of the sharp singlet band at 1153 cm<sup>-1</sup> to a doublet at 1154 and 1169 cm<sup>-1</sup>. At room temperature it took about 12-24 h to bring about such changes. However, at higher temperatures the hydration was much faster. For example, at 45°C, only 6 h are needed for a similar degree of hydration (see Fig. 4). With increasing temperature, the hydration rate of cement also increases due to the facile removal of Ca<sup>2+</sup> from clinker to the surrounding liquid. If cement containing the waste develops its strength in a shorter period of time, then larger amounts of waste can be prepared for disposal in a shorter period of time.

Alkalis in general accelerate the rate of hydration of cement and give high compressive strengths during the early stages, although the final strengths are lower than those of low-alkali cement. The alkali solution will decrease the solubility of Ca<sup>2+</sup> ions, but the Al-O and Si-O linkage networks are destroyed

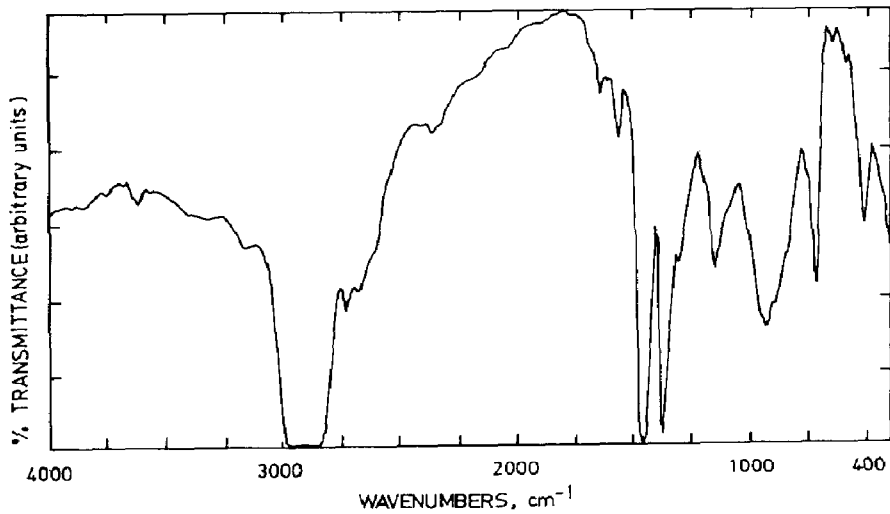


Fig. 2. Nujol mull IR spectrum of portland type I cement.

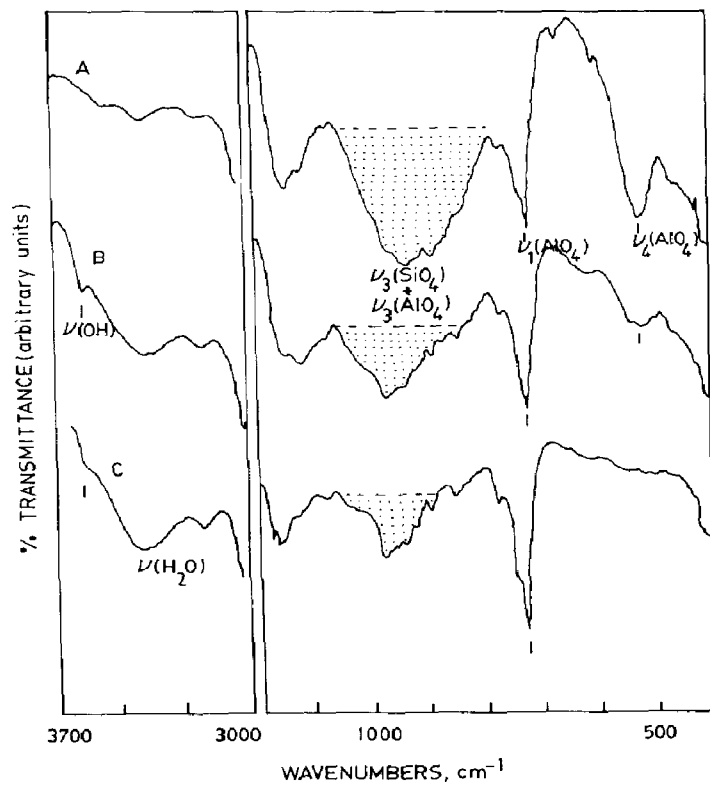


Fig. 3. Nujol mull IR spectra of hydrated portland cement at room temperature after (A) 15 m, (B) 2 h and (C) 24 h.



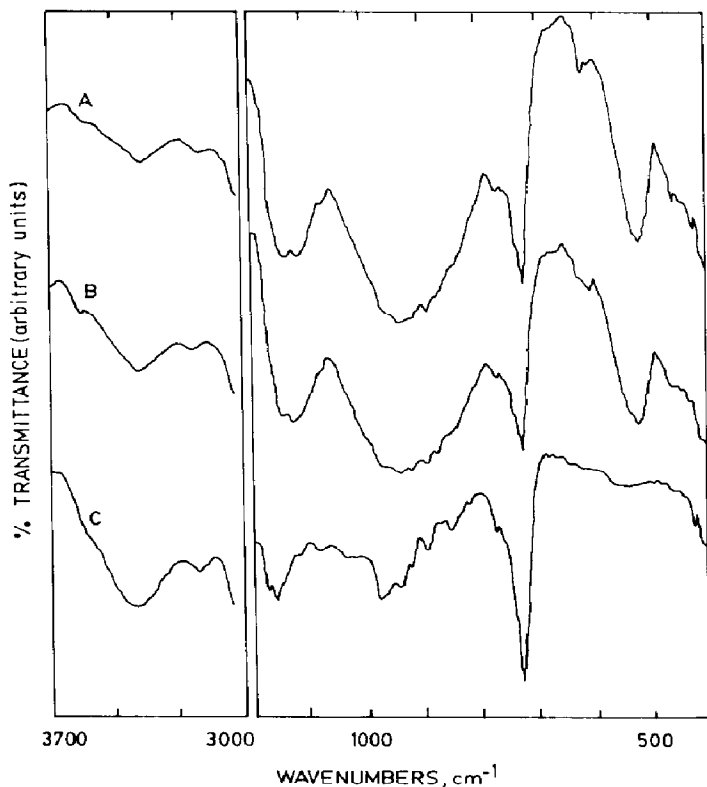


Fig. 4. Nujol mull IR spectra of hydrated portland cement at 45°C after (A) 15 min, (B) 1 h, and (C) 6 h.

at high  $\text{OH}^-$  concentration, resulting in a larger amount of hydrated particles. However, the final strength of the cement is lower. This may be due to the rapid formation of the hydrated particles as shown in Fig. 5. At higher temperatures and in the presence of alkaline solutions the hydration is even faster. In about 1 hour, the hydration structural features start appearing in the spectrum (see Fig. 6). The solubility of  $\text{Ca}^{2+}$  ions increases at higher temperature but, the presence of alkaline solution affects the solubility in the opposite manner.

PCP is a stronger acid than phenol while cement is alkaline. PCP in its ionized form may be adsorbed around clinker particles and thus helps to reduce the removal of  $\text{Ca}^{2+}$  ions from clinkers. However, the hydration reactions might occur at slower rates. Figures 7 and 8 present the IR spectra of cement containing phenol and PCP, respectively. The out-of-plane bending absorption at  $516\text{ cm}^{-1}$  for PCP-containing cement decreased at a slower rate than when phenol was present in the cement. The  $\nu$  asymmetric bands around  $800\text{--}1000\text{ cm}^{-1}$  are still somewhat broad because the major clinker phases of  $\text{C}_3\text{S}$  and  $\text{C}_3\text{A}$  were inhibited to form hydrated products. The ettringite slowly changed

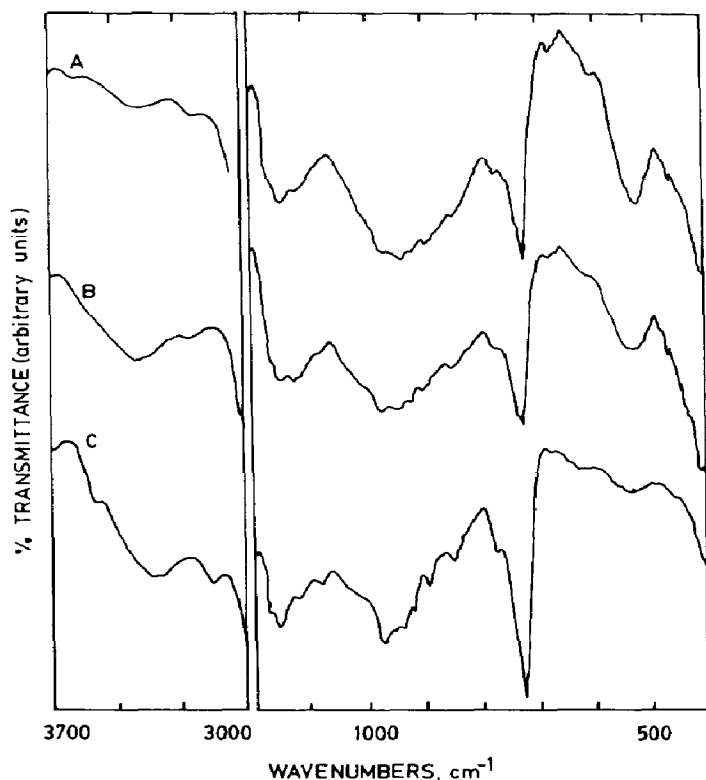


Fig. 5. Nujol mull IR spectra of portland cement hydrated in the presence of 0.1 M NaOH solution at room temperature after (A) 30 m, (B) 60 m and (C) 12 h.

to monosulfate as evident from the growth in the intensity of water waveband and also from the appearance of the doublet absorption bands (located at 1154 and 1168  $\text{cm}^{-1}$ ) after two days.

Organic compounds which contain carboxylic acid, hydroxyl, carbonyl and ionized hydroxyl groups are adsorbed at surfaces containing  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  or  $\text{O}^{2-}$  ions. These mixtures adsorb quite strongly on the hydration products of  $\text{C}_3\text{A}$ . The retarding effect of organic compounds on the hydration of  $\text{C}_3\text{A}$  is closely linked with their adsorption into the structures of the metastable hexagonal calcium aluminate hydrates that are first formed. In paste hydration, sorption inhibits both the crystal growth of the hexagonal hydrates and their conversion to  $\text{C}_3\text{AH}_6$  (cubic hydrate) [20]. Tricalcium silicate adsorbs organic molecules from aqueous solution much less strongly. Although the strong adsorption properties of  $\text{C}_3\text{A}$  will remove most of the admixture from solution some remain associated with  $\text{C}_3\text{S}$  to cause retardation of the hydration process. The self-retarding feature of  $\text{C}_3\text{S}$  hydration is due to the inhibition of nucleation of crystalline calcium hydroxide by soluble silica which adsorb onto the calcium hydroxide nuclei. The organic compounds adsorb on the calcium hydroxide nuclei and position their future growth in the same way as silicate ions do.

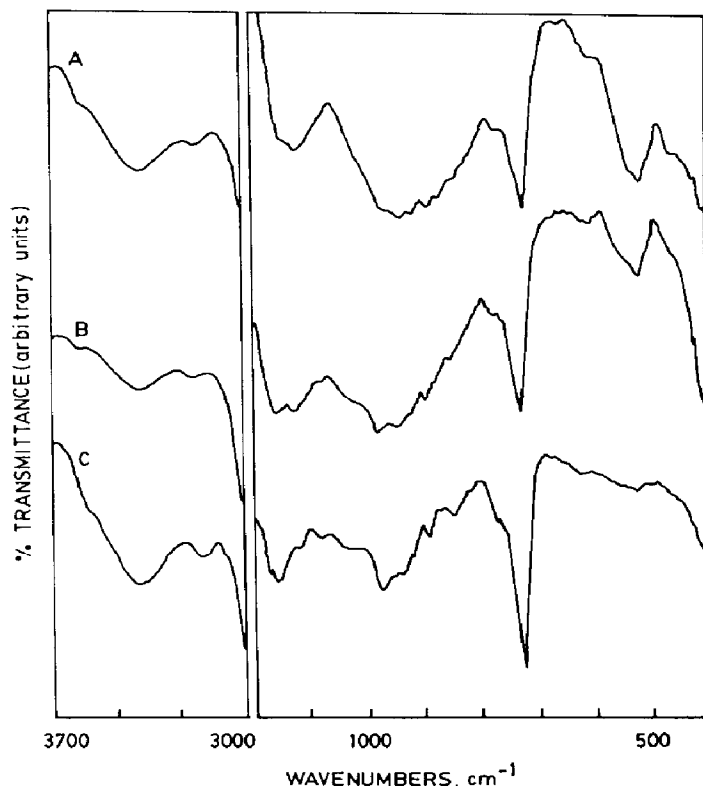


Fig. 6. Nujol mull IR spectra of portland cement hydrated in the presence of 0.1 M NaOH solution at 45°C after (A) 15 m, (B) 60 m and (C) 6 h.

Tables 1 and 2 contain the amount of PCP and phenol leaching out from portland cement as a function of time. When the ratio of the amounts of PCP and cement is low, the recovery (amount leaching) of PCP is high for the samples that were cured for 1 day. Samples cured for longer periods exhibit much lower recovery. The values reported in Table 1 are higher due to different mechanisms. In the present study leaching of the PCP-containing samples were prepared in a different manner. PCP as mixed with cement, the mixture was ground to a fine powder and an appropriate amount of water was added. The cement was allowed to set and cure. Leaching tests were done in two different ways. In the first method, the cure cement block was not ground while in the second, it was ground to a powder before leaching. Table 3 lists the results of these tests which show that a small amount of PCP leaches out from both the types of samples. However, the amounts of PCP leached out are not very different for each other, indicating that PCP is bound to the cement particles rather strongly. In reality, the solidified materials are not ground prior to land filling. Therefore, the PCP recovery of about 3% is closer to the actual situation.

Table 4 presents the combined effects of various factors on the leaching

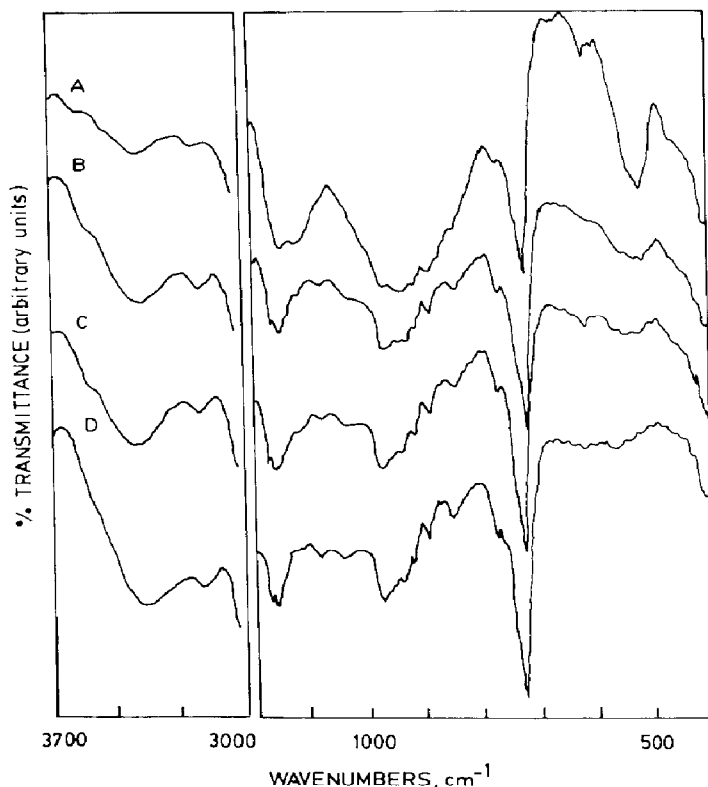


Fig. 7. Nujol mull IR spectra of portland cement hydrated in the presence of an alkaline solution of phenol at room temperature after (A) 30 min, (B) 3 h, (C) 6 h, and (D) 24 h.

behavior of PCP. The samples were prepared by first mixing PCP and cement. After grinding the mixture, 5 ml of water was added and allowed to cure. After three days, one batch of the solidified sample was ground and subjected to leaching tests without employing an ultrasonic vibrator. The second batch of the sample was subjected to leaching where the sample was neither ground nor exposed to ultrasonic waves. Finally, for the third batch of the sample neither NaOH nor an ultrasonic vibrator employed or grinding of the sample was done. As the external perturbations or the surface area decreases, the amount of PCP leached decreased. The leaching tests involving ultrasonic waves represent a more extreme condition, and if the method works in such extreme conditions, then obviously the amount of the toxic PCP that could be leached to the surroundings would be less than the laboratory results presented here. For land filling the solidified toxic waste, laboratory tests should be carried out to ascertain the long-term leaching of the toxic substance and such tests are not feasible. A better approach is to employ as drastic leaching conditions as possible; for this reason, the ultrasonic wave method was used.

The results given in Table 5 illustrate the effect of temperature on the curing

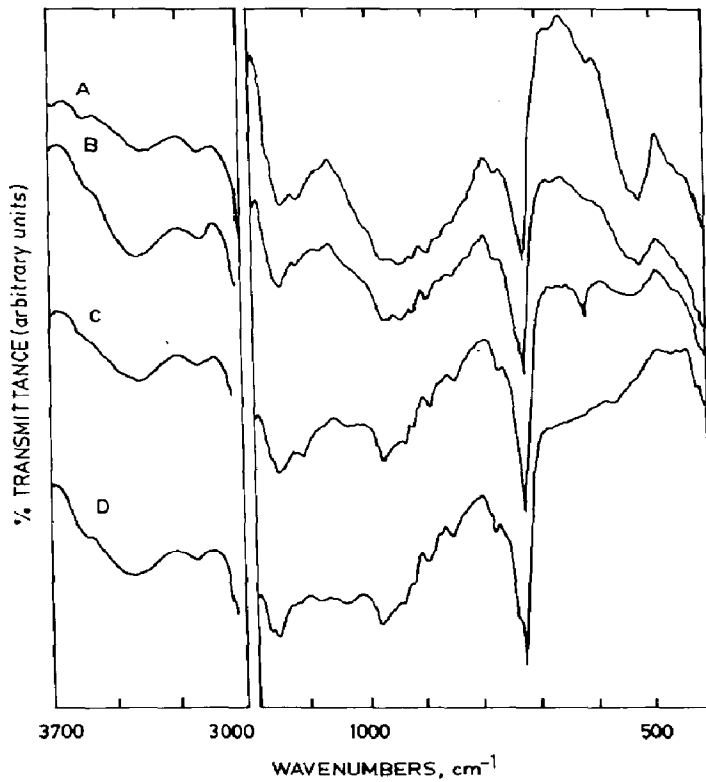


Fig. 8. Nujol mull IR spectra of portland cement hydrated in the presence of alkaline solution of PCP at room temperature after (A) 30 min, (B) 3 h, (C) 6 h and (D) 2 days.

of cement and its leachability. The recovery of PCP decreases as the temperature increases, but the amounts leached (about 4%) at 60°C are not significantly different from those obtained at room temperature (Table 5). Perhaps the porosity of the cement does not decrease significantly at higher temperatures. Even though the amount of waste leaching at higher temperatures is not different, the time saved in the preparation of samples for the disposal is substantial.

When 0.1 M NaOH was added to a powdered mixture of cement and waste instead of water, the percentage recovery of PCP from the samples containing different amounts of PCP were significantly different (see Table 6). However, the samples were not ground before leaching as would be the case with disposal in real life. Nevertheless, the absolute amounts of recovery were almost the same at each temperature suggesting that PCP could be leached out to the leaching solution. The variability in the results of leaching at low concentration of PCP and phenol (Tables 1 and 2) by time-dependent leaching is due to the unequal particle size after grinding which may result in slightly different surface areas. After 21 days, the amount of PCP leaching decreases to about 3.5–5.0%, while the physical strength of cement increases. On the other hand,

phenol under similar conditions showed about 18–32% recovery, indicating its weaker interaction with cement.

## 5. Conclusions

Solidification/stabilization systems have wide applicability in the disposal of hazardous wastes but their applicability is not examined for the disposal of toxic organics. The present work has shown that S/S technology can be employed for the disposal of PCP and phenol which are hazardous substances. The interactions between cement components and the added organics during hydration are still not well understood. Our results indicate that PCP might delay the hydration of cement and thus, it may decrease the strength of hydrated cement resulting in the formation of a more porous matrix.

The leaching tests showed that about 3–4% of PCP can be leached out. Most of the PCP that leaches to the leachant appears to have come from the surface of hydrated cement and some from the pores through which contact of the waste to leaching solution is made. Factors such as the presence of hydrophobic materials, surface tension effects, pH, microorganisms, temperature and UV radiation may cause either the breakdown of the solidified matrix or increase the leachability [21,22].

## References

- 1 L.R. Swann and A. Eschenroeder, Fate of chemicals in the environment, ACS Symposium Series 225 (1983).
- 2 G. Noble, Sanitary Landfill Design Handbook, Technomic, Lancaster, PA, 1976.
- 3 M.E. Tittlebaum and R.K. Seals, State of the art on stabilization of hazardous organic liquid waste and sludges, CRC Crit. Rev. Environ. Control, 15 (1985) 179–211.
- 4 C.C. Wiles, A review of solidification/stabilization technology, J. Hazardous Mater., 14 (1987) 5–12.
- 5 M.J. Cullinane, L.W. Jones and P.G. Malone, Handbook for Stabilization/Solidification of Hazardous Waste, U.S. Dept. of Commerce, NTIS, Springfield, VA 22161, 1986.
- 6 R.J. Fielder, Pentachlorophenol, In: Toxicity Review 5, HMSO, London.
- 7 K.R. Rao, Pentachlorophenol, In: Chemistry, Pharmacology and Environmental Toxicology, Plenum Press, New York, NY, 1978.
- 8 C.S. Poon, A.I. Clark and R. Perry, Permeability study on the cement-based solidification process for the disposal of hazardous wastes, Cem. Concr. Res., 16 (1986) 161–172.
- 9 W. Shively, P. Bishop, D. Gress and T. Brown, Leaching tests of heavy metals stabilized with Portland cement, J. Water Pollut. Control Fed., 58 (1986) 234–241.
- 10 C.S. Poon, A.J. Clark, C.J. Peters and R. Perry, Mechanisms of metal fixation and leaching by cement-based fixation processes, Waste Manag. Res., 3 (1985) 127–142.
- 11 J. Bensted and V.S. Prakash, Some applications of infrared and Raman spectroscopy in cement chemistry, Part 1. Examination of dicalcium silicate, Cem. Technol., 5 (1974) 256–261.
- 12 J. Bensted and V.S. Prakash, Some applications of infrared and Raman spectroscopy in cement chemistry, Part 2. Portland cement and its constituents, Cem. Technol., 5 (1974) 378–382.

- 13 J. Bensted and V.S. Prakash, Some application of infrared and Raman spectroscopy in cement chemistry, Part 3. Hydration of Portland cement and its constituents, *Cem. Technol.*, 5 (1974) 440-442, 444-445, and 448-450.
- 14 J. Bensted, Chloroaluminates and the role of calcium chloride in accelerated hardening of Portland cement, *World Cem. Technol.*, 8 (1977) 171-175.
- 15 J. Bensted, Examination of the hydration of slag and pozzolanic cements by infrared spectroscopy, *Spectroscopia Infrarossa*, 73 (1976) 209-214.
- 16 J. Bensted and S.P. Varma, Infrared and Raman spectroscopy in cement chemistry - miscellaneous applications, *World Cem. Technol.*, 8 (1977) 16-20.
- 17 S.N. Ghosh and S.K. Handoo, Infrared and Raman spectral studies in cement and concrete, *Cem. Concr. Res.*, 10 (1980) 771-782.
- 18 J. Bensted, An infrared spectroscopic examination of high alumina cement and its hydration products, *World Cem. Technol.*, 13 (1982) 85-90.
- 19 P. Tarte, Infrared spectra of inorganic aluminates and characteristic vibrational frequencies of  $\text{AlO}_4$  tetrahedra and  $\text{AlO}_6$  octahedra, *Spectrochim. Acta*, 23A (1967) 2127-2143.
- 20 J.F. Young, A review of the mechanisms of set-retardation in Portland cement pastes containing organic admixtures, *Cem. Concr. Res.*, 2 (1972) 415-433.
- 21 D. Chalasani, F.K. Cartledge, H.C. Eaton, M.E. Tittlebaum and M.B. Walsh, The effects of ethylene glycol on a cement-based solidification process, *Hazard. Waste Hazard. Mater.*, 3 (1986) 167-173.
- 22 M.B. Walsh, H.C. Eaton, M.E. Tittlebaum, F.K. Cartledge and D. Chalasani, The effects of two organic compounds on a Portland cement-based stabilization matrix, *Hazard. Waste Hazard. Mater.*, 3 (1986) 111-123.