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LEACHABILITY OF LEAD FROM SOLIDIFIED CEMENT-FLY ASH BINDERS

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ABSTRACT

Potential of partly replacing cement with class C fly ash to immobilize lead was investigated. Lead nitrate up to a concentrations of 10% (by weight of binder) was solidified with binders such as Type I Portland cement and a cement-fly ash (equal proportion) mixture. Pore fluid analyses indicated that lead increased the calcium and silicon concentration in the pore fluid during the initial period of hydration of cement and cement-fly ash mixtures. Addition of fly ash to cement reduced the initial and final setting times, but with the addition of lead nitrate setting times were increased. The compressive strength of the solidified cement decreased with the addition of fly ash and lead nitrate. Lead leachability from the solidified binder matrix was studied using the Toxicity Characteristic Leaching Procedure (TCLP) recommended by the U. S. Environmental Protection Agency (EPA). The quantity of Pb(II) leached was dependent on the initial lead nitrate concentration and the binder systems adopted. Lead solidified with cement-fly ash mixture showed a slightly less leaching compared to the cement binder. A simple model has been proposed to predict the leachability of Pb(II) from the binder matrix.

Introduction

Cement-based solidification/stabilization (S/S) is one of the most popular technique for treating hazardous waste under the Superfund Innovative Technology Evaluation (SITE) program (EPA/540/5-91/008, 1991). It has been demonstrated that S/S process can be very effective in immobilizing certain inorganic wastes, but wastes such as organics, salts and heavy metals may not be amenable to this treatment (U. S. EPA 625/6-89/022, 1989). Lead, which is listed as a Priority Pollutant by the EPA (EPA code D008), was found in 15% of the uncontrolled hazardous sites (Ellis *et al.*, 1985). Lead has been shown to retard cement hydration. Cartledge *et al.* (1990) have concluded that the poor treatment efficiency of cement in immobilizing lead was due to reactions between hydroxide and sulfate (cement hydration products) with Pb in Pb/cement system. These reactions not only retarded the cement hydration but also reprecipitated Pb on to the surface of cement matrix, thus increasing the leachability of the system. Several additives such as fly ash, silicates, clays and kiln dust are being used in cement-based S/S process to improve the performance with various wastes and have demonstrated measurable degree of success (Sheriff *et al.*, 1989; Shieh, 1990).

An important factor in determining whether a particular S/S process is effective in treating a given waste is the reduction in the leachability of the waste to below EPA limit. Bishop *et al.* (1991) have identified numerous factors which affect the leachability of a waste after S/S treatment. The factors include waste form, binder system, alkalinity, surface-to-volume ratio, porosity, durability, leachant composition, and leachant volume-to-waste ratio. Based on different short term leachability tests of solidified wastes, several researchers (Ren *et al.*, 1987; Godbee *et al.*, 1987; Cheng *et al.*, 1992) have demonstrated that diffusion was a dominant mechanism governing leaching characteristics of waste from the S/S system. Vipulanandan *et al.* (1993) have indicated that initial wash out followed by diffusion controlled leaching of phenol waste from solidified cement matrix during the TCLP test.

Experimental Program

In this study, immobilization of lead with a cement-fly ash (Class C) mixture was investigated. The testing protocol included (a) analyses of pore fluids extracted from hydrating binders up to 12 hours, (b) setting time, (c) leachability of lead by the TCLP test, and (d) compression strength. Lead nitrate concentrations up to 10% (by weight of binder and equivalent to 100,000 mg/kg) were solidified with cement-based binders. For the binder systems, fly ash/cement (by weight) ratios of zero (cement only, C) and one (CF) were used. Lead contaminated water was prepared by adding measured amounts of lead nitrate directly to water and mixed well till all the lead nitrate was dissolved. This contaminated water was used with various binder systems to prepare the test specimens and water/binder ratio of 0.5 was used. Samples were cast in Teflon® molds (38 mm in diameter and 80 mm in height). After extraction from the molds, the samples were stored in air-tight bags in a temperature (72°F) controlled humid (> 96%) room. Tests were done on solidified binders after 7 and 28 days of curing.

Pore fluids were extracted from hydrating pastes during the first 12 hours of setting. The aim of this experiment was to obtain a better understanding of the constituents of the pore fluid and hydration behavior of cementious material in the presence of lead. The apparatus used in the extraction procedure consisted of a glass flask with a funnel stopper to it. A certain amount of cementious paste was placed on a 0.45 μm filter paper contained in the funnel. The amount of sample used was dependent on the ease with which the extraction process could be done by vacuuming the flask. The extracts were analyzed for calcium, silicon and lead concentrations. Analyses of these cations were done according to the EPA Method 6010 (SW 846, 1986), using an Inductively Coupled Plasma (ICP) machine (Perkin-Elmer ICP/5500 with Data Station 10). The estimated detection limits for calcium, silicon and lead were 10, 58 and 42 μg/L, respectively. The initial and final setting times of cementious paste with and without lead were determined according to ASTM C191-74 using a Vicat needle. The unconfined compressive strengths (UCS) of solidified samples were determined according to ASTM recommendations (ASTM 2166). The S/S samples were also subjected to the TCLP test (40 CFR Part 268 App I, 1988). Also a modified version of the TCLP was used and leaching was continued for 7 days with pH corrections. The leachant was not changed during the entire duration of the test while the pH of the leachant was adjusted to the starting value every 24 hour period. The leachates were analyzed for lead at the end of every 24 hours using the ICP.

Test Results and Discussion

The effects of various lead concentrations on the setting time, degree of immobilization, and mechanical properties of cement (C) and cement/fly ash mixture (CF) were investigated. The test results are reported and discussed in the following sections.

Pore Fluid Analysis. The pore fluids extracted from hydrating cement pastes were analyzed for calcium, silicon, and lead. Cement pastes with lead nitrate concentrations up to 10% were studied. The maximum time up to which extraction of pore fluid was possible for any paste was dependent on the amount of contaminant in it (Vipulanandan *et al.*, 1991, 1993; Wang 1993). With the technique adopted in this study, extraction of fluid from control cement paste was possible only up to 4 hours, for cement paste with 10% lead nitrate the maximum extraction time was 20 hours. In Pb/CF systems, the maximum time for extraction of pore fluids were 2 and 12 hours for 0 and 10% lead nitrate concentration, respectively. The addition of fly ash in the binder system accelerated the setting time of cement as discussed later.

Results from the pore fluid studies are shown in Figs. 1 & 2 and each point represents an average of three readings. The concentrations of Ca and Si in pore fluids increased with increase in lead content. The concentrations of Ca and Si ions reached a peak before declining to a constant value. The time required to reach their peak value depended on the amount of lead nitrate contained in the system (Wang, 1993). It can be observed from Fig. 1a that calcium concentration detected in the Pb/C and Pb/CF system with 10% lead nitrate was in the range of 2,500 mg/l. The peak Ca concentration was 1,340 mg/l and the corresponding time was 30 minutes for control cement paste. Silicon concentrations showed a similar trend to that of Ca, but with much lower concentrations. Adding 10% lead nitrate to the Pb/C system doubled the Si in the pore fluid. The maximum Si concentration detected for the 10% Pb/C system was 8.0 mg/l. The Ca and Si concentration in the pore fluid found in Pb/CF system showed similar trends as the Pb/C system with no notable variation. Hence fly ash used in the binder system did not alter the compositions in the pore fluid significantly.

The presence of lead nitrate caused a higher amount of Ca and Si released in the pore fluids which suggests that lead possesses a deleterious effect on cement paste. The possible reaction mechanism is that calcium hydroxide and other (sulfates) salts which are produced during cement/fly ash hydration reacted with the lead and takes the form:

$$\text{Salts} + \text{Ca(OH)}_2 + \text{Pb(II)} \rightarrow \text{Ca}^{+2} + \text{Pb(II) salts} + \text{Entrained Liquids} \quad [1]$$

Since the solubility of Pb(II) salts (sulfate, hydroxide) are very low and they will precipitate out. This precipitation provides the driving force to release more Ca from the binder system and affecting the hydration of the binder. The increasing release of Si into the pore fluids suggested that lead also affected the hydration of calcium silicates. Both cement and cement-fly ash mixture had similar results. The precipitation of Pb(II) salts also provided extra binding sites of the binders to trap more free aqueous salts and the sorption process reached an equilibrium within the first 3 hours (as shown in Fig. 2). The uptake percentage of Pb by the CF binder system was higher than the cement only system. It might due to the increasing of surface area which increased by the addition of finer particles of fly ash in the binder system.

Setting Time. The setting times of the binders with lead nitrate concentration up to 10% were measured. The results are shown in Fig. 3. It is apparent that lead retards the setting process of both Pb/C and Pb/CF systems. The change in initial and final setting times are very much depended on the initial lead nitrate concentration. The control cement (no lead) reached initial set in 3 hours and final set in 4.5 hours. In the presence of 0.5% lead, the initial and final setting times for Pb/C system were 35 and 80 hours, respectively. For the 10% lead nitrate samples, the time to initial set was 100 hours and the time to final set was 260 hours. In the Pb/CF system,

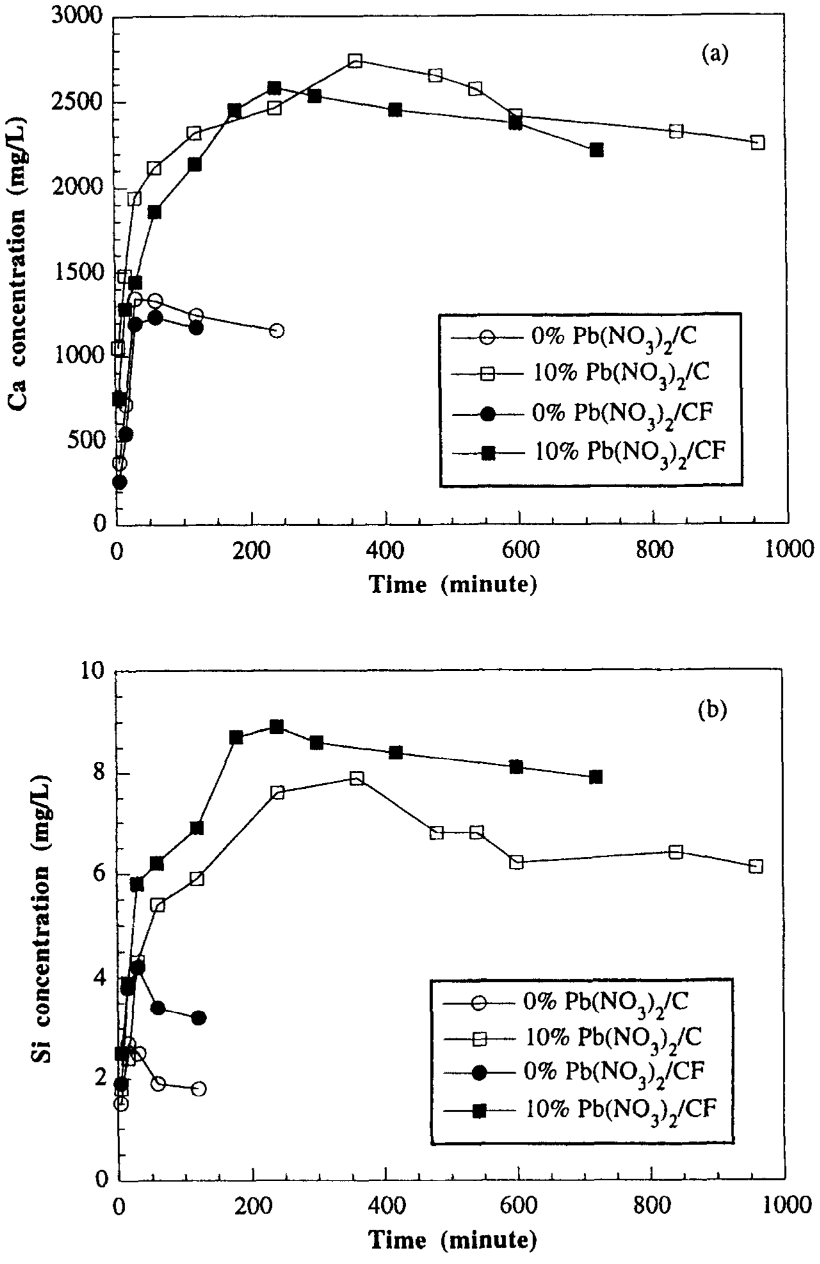

FIG. 1.

Concentration of (a) calcium and (b) silicon in the pore fluids of Pb/binder systems.

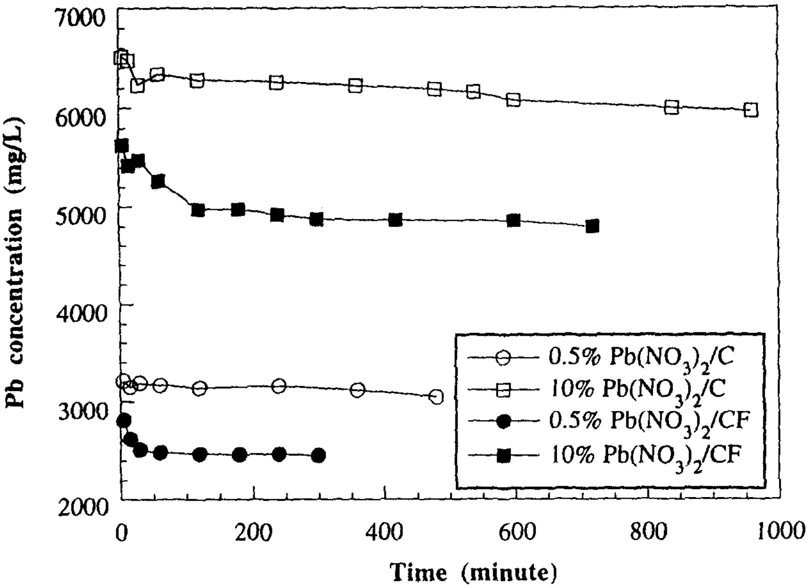

FIG. 2.

Concentration of lead (Pb) in the pore fluids of various Pb/binder systems.

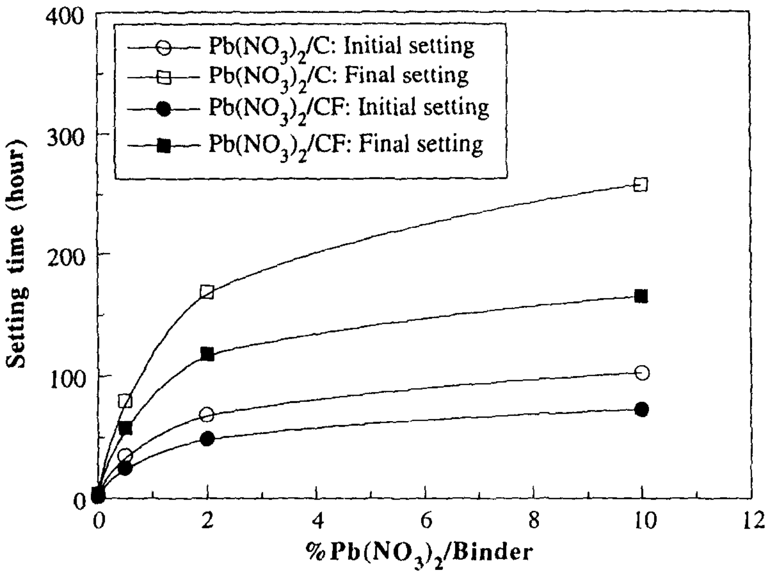

FIG. 3.

Effect of $Pb(NO_3)_2$ on the initial and final setting times of binders using the Vicat Needle (ASTM C191-74).

the control paste reached initial set in 1.5 hours and final set in 3.5 hours. For 0.5% lead contained pastes, the initial and final setting times were 25 and 60 hours, respectively. At the highest lead concentration studied (10%), the time to initial set was 58 hours and the time to final set was 160 hours. Comparing the results from Pb/CF system with the Pb/C system, it is evident that the setting (initial and final) of the Pb/CF system was accelerated by the presence of fly ash used in the binder. Coupled with the results of the pore fluid studies, unambiguous indications of the interference of lead in the hydration of binders can be inferred from the setting time observations.

Mechanical Properties. Cylindrical samples cured for 7 and 28 days, with and without lead (up to 10%) were tested for unconfined compressive strength according to ASTM 2166. The results of the compressive strength tests are shown in Fig. 4. The compressive strength was found to depend upon the amount of lead nitrate added in the binder system. In the Pb/C system, the highest strength (6,000 psi) was observed for control cement cured for 28 days, and the strength (1,900 psi) was exhibited by cement containing 10% lead and cured for 7 days. About 70% reduction in compressive strength was noted for the Pb/C system containing 10% lead nitrate after 28 days of curing. This phenomenon can be attributed to the high inhibition effect of lead on the cement hydration process.

In the Pb/CF system, the highest strength (3,000 psi) was observed for the control sample cured for 28 days, and the lowest strength (500 psi) was exhibited by a sample containing 10% lead nitrate and cured for only 7 days. The addition of 50% fly ash in the binder system caused 50% reduction in the maximum compressive strength of the control samples (no lead nitrate) for both 7- and 28-day curing samples. This effect is even more evident at a high content of lead. After curing for 28 days, the average compressive strength were 3,000, 1,200, and 600 psi for 0, 0.5, and 10% lead nitrate content, respectively. The synchronic deleterious effect of lead and fly ash on the strength of binders can be explained in the light of the interference of cement

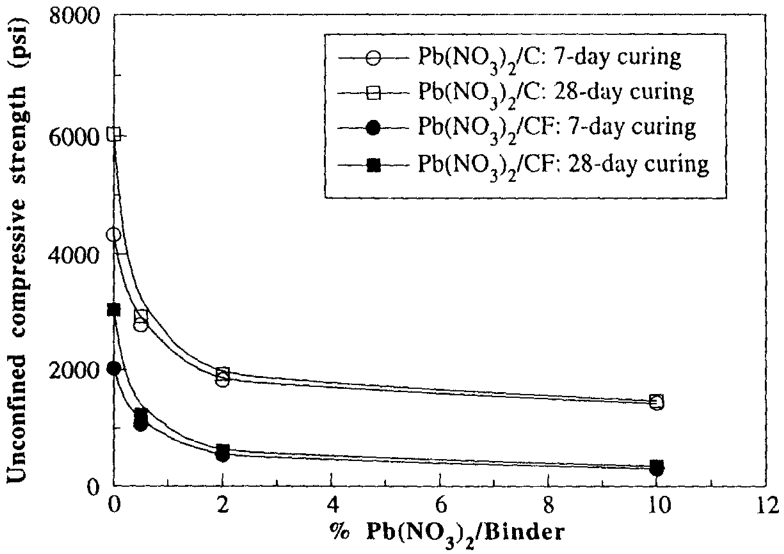

FIG. 4.
Effect of lead and curing time on the unconfined compressive strength of solidified samples.

and fly ash hydration process. The hindrance posed to the development of the hydrated structure causes delay in strength development. This is reflected by greater differences in the strengths between control cement and Pb/CF samples.

Leachability. Samples with lead (up to 10%) were tested for leaching of Pb(II) after 7 and 28 days curing using the extended TCLP test (Vipulanandan *et al.*, 1993). The recovery of lead from TCLP test for various for the lead/binder systems are shown in Figs. 5 and 6 for 28-day cured specimen. The leaching pattern of Pb(II) follows a two stages process (Vipulanandan *et al.*, 1993), where an initial wash out is followed by a diffusion-controlled phase. After the loosely bonded lead was washed out into the leaching solution the leaching solution is gradually saturated with lead and the concentration gradient decreased with time, so a slow-diffusion process was observed and only contributed to small increase of lead in the leachate thereafter.

As shown in Figs. 5 and 6, the recovery of Pb(II) was controlled by the binder system used, the amount of lead nitrate contained in the sample, and the leaching duration. In both Pb/C and Pb/CF system, $Pb(NO_3)_2$ content up to 2% can be treated effectively by the binder systems adopted here to meet TCLP lead limit (5 mg/L). The addition of fly ash in the binder system (Pb/CF system) slightly improved the performance by reducing the amount of lead in the leachate. The CF system reduced the lead leached by an amount of 10% to 30% compared to the cement only binder system. As the $Pb(NO_3)_2$ content was increased to 10%, both binder systems failed to meet the TCLP limit. The highest recovery of lead was from the 10% lead nitrate sample in Pb/C system after 7 days of leaching and with a leachate Pb(II) concentration of 30 mg/L.

Leaching Model. Based on the modified TCLP results, a general mathematical relationship can be used to express the leaching of lead over the test period of 7 days, which takes the form (Vipulanandan *et al.*, 1993)

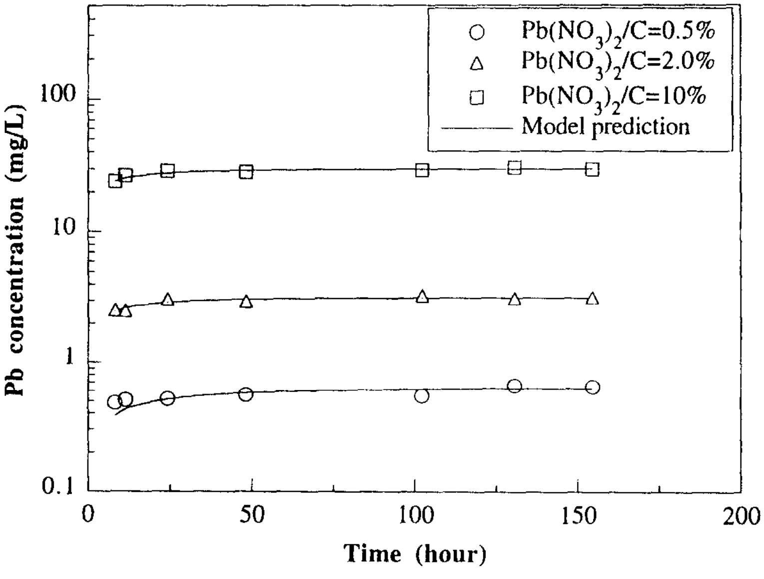

FIG. 5.
The recovery of Pb(II) from solidified cement binder during the TCLP test and the model predictions.

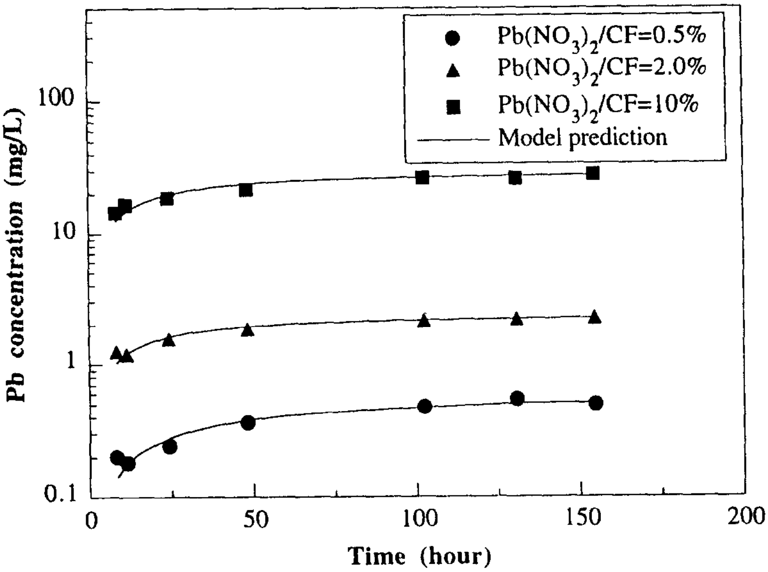

FIG. 6.
The recovery of Pb(II) from the solidified cement-fly ash binder during the TCLP test and the model predictions.

$$C = \frac{T}{A + BT} \qquad [2]$$

where
C = cumulative Pb concentration in leaching solution , mg/l,
T = leaching time, days.

In Eq.[2], A and B are parameters of the binder systems and the amount of contaminant contained in the matrix. In order to find the two constants, the equation can be linearized and rewritten as

$$\frac{T}{C} = A + B \times T \qquad [3]$$

TABLE 1
Summary of 'A' and 'B' Values for S/S System

Curing period	28 days					
Sample	Pb/C			Pb/CF		
Lead content	0.5%	2.0%	10.0%	0.5%	2.0%	10.0%
A	9.40	0.78	7.08 e^{-2}	44.96	4.66	0.39
B	1.52	0.31	3.30 e^{-2}	1.67	0.42	3.48 e^{-2}
R	0.98	1.00	1.00	0.98	1.00	1.00

It can be seen from Eq.[3] that a plot of T/C versus T (Fig. 7) showed a linear relationship with a slope of 'B' and an intercept of 'A'. Note that dC/dT = 1/A at T = 0 and C_{max} = 1/B at T = ∞ under the testing conditions adopted, and C_{max} is the maximum of lead that can be leached from the binder. The values of 'A' and 'B' for Pb/C and Pb/CF systems are summarized in Table 1.

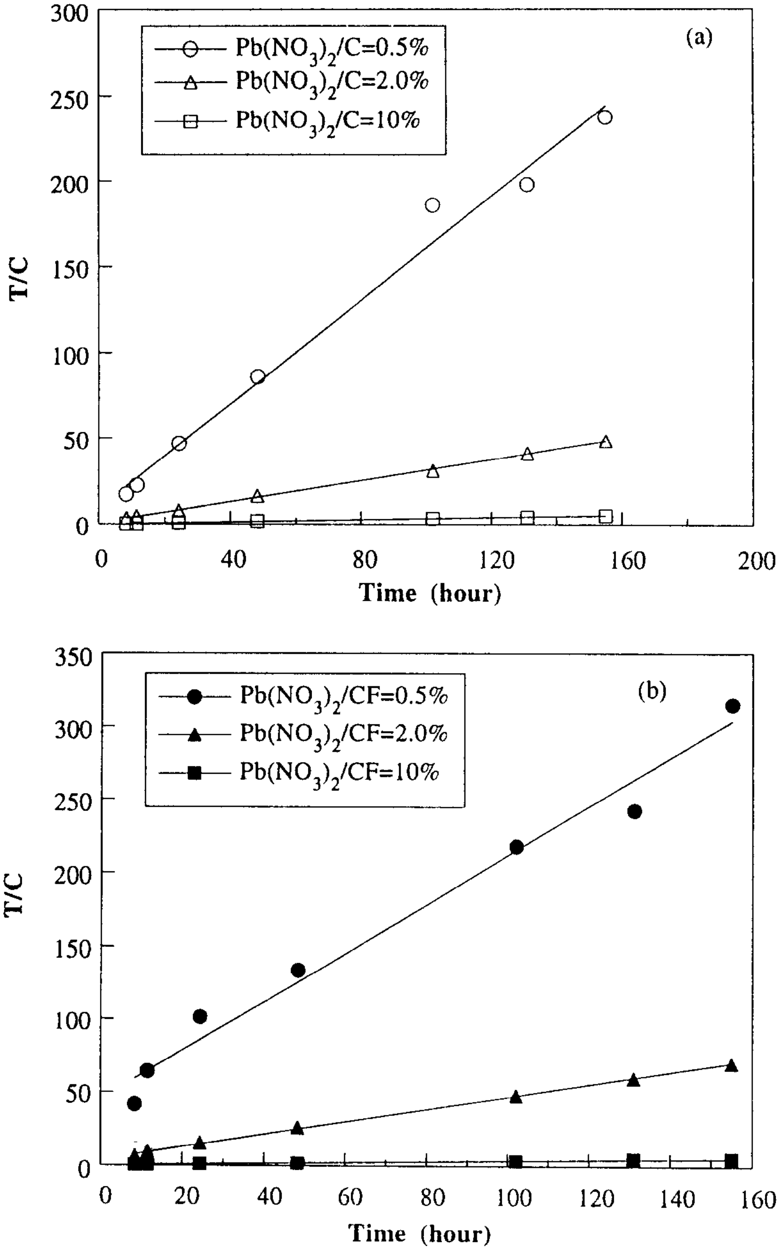

FIG. 7.
The plot of T/C vs. T for the TCLP test results (a) Pb/C system; (b) Pb/CF system.

The fitting of the Eq. [2] to the test results was in Figs. 5 and 6, a good agreement was observed in the model prediction to the test data and the correlation coefficients are all greater than 0.98.

Conclusions

The following conclusions can be advanced based upon this experimental study:

(1) The concentration of Ca and Si in the pore fluid in cement paste increased with lead addition. Replacing cement with equal amount of fly ash (50/50) mix did not significantly alter the pore fluid composition.
(2) Lead retards the initial and final setting of cement by interfering with the normal hydration reactions. The presence of 10% lead nitrate caused the final setting time of cement to 260 hours compared to 9.5 hours for the control cement with a water to cement ratio of 0.5. Addition of fly ash in the cement paste reduced both the initial and final setting times.
(3) The average efficiency for immobilizing lead contained waste by cement only binder system was 98% (for lead nitrate concentration up to 10%). In treating similar waste, the addition of fly ash in cement-based S/S slightly increased the efficiency.
(4) A simple model has been proposed to predict the leaching of Pb from the binder systems during the extended TCLP test with correlation coefficients were all greater than 0.98.

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