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Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: leaching studies

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Abstract

In this research, we investigated the use of an inexpensive thermally regenerated activated carbon as a pre-adsorbent in the solidification/stabilization of phenol-contaminated sand. Our results show that even the addition of very low amounts of regenerated activated carbon (1%–2% w/w sand) resulted in the rapid adsorption of phenol in the Chemical solidification/stabilization (S/S) matrix, with phenol leaching reduced by as much as 600%. Adsorption studies indicated that the adsorption of phenol on the reactivated carbon was found to be partially irreversible over time in the S/S waste form, indicating possible chemical adsorption. Pore-fluid analyses of the cement paste containing phenol suggested the formation of a calcium–phenol complex, which further reduced the amount of free phenol present in the pores. Studies using several micro-structural techniques, including field emission scanning electron microscopy, X-ray diffraction, fourier transform infrared spectroscopy and energy dispersive X-ray spectroscopy, indicated significant morphological changes in the cement matrix upon the addition of phenol and reactivated carbon. The hydration of cement in the presence of phenol was retarded concomitant with formation of amorphous portlandite. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Solidification/stabilization; Organics; Activated carbon; Scanning electron microscopy; Infra-red spectroscopy

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1. Introduction

Chemical solidification/stabilization (S/S) of hazardous wastes is a widely used technology employed for the treatment and disposal of hazardous wastes. S/S systems have been used for about 15 years in the US for immobilization of contaminants in hazardous wastes, industrial sludges, contaminated soils, fossil fuel flyash, and incinerator residues. The USEPA now designates S/S systems as accepted technology, as opposed to an innovative technology [1]. Because of this, they are the most widely used of all hazardous waste management alternatives. However, these processes were designed to manage heavy metals in the waste, not organics. Organics are present to some degree in many predominantly inorganic waste materials, and their leaching can lead to serious public health or environmental problems. Studies involving the use of S/S processes for organic wastes have reported little success in immobilizing the organic constituents. Consequently, there is a great need to develop effective and economic solidification/stabilization systems that can reliably treat hazardous wastes containing organics. Very little information is available on the mechanisms involved with the release, or leaching, of organics from the stabilized waste. A better understanding of the leaching behavior of organics would enable us to predict their fate under 'real-world' disposal conditions.

Stabilization of metals in S/S processes consists mainly of converting the heavy metals into insoluble precipitates. However, this does not happen with most organics. The organics generally do not react with the inorganic binders because many of them are nonpolar and hydrophobic. They are generally sorbed or encapsulated in pores and can leach relatively rapidly, based primarily on their solubility in water and their diffusivity through the waste matrix. Consequently, most experts consider conventional S/S processes to be inappropriate for long-term containment of toxic organics. This is particularly true for volatile organics, but also holds for most semi-volatiles [2].

The main goals of this research were to evaluate the overall effectiveness of regenerated activated carbon in immobilizing organics, determine the appropriate dosages of reactivated carbon required, understand the adsorption characteristics of reactivated carbon in S/S systems, and predict the long-term effects related to the leaching behavior of organics. Phenol was chosen as a representative for polar, highly soluble and commonly used aromatic compounds.

2. Background

There is an increasing interest in understanding and evaluating the limitations of various technologies to treat hazardous organic wastes. As mentioned, solidification/stabilization treatment is viable for most metallic waste streams but it is only emerging for organic wastes [3,4]. One of the main concerns of treating organic wastes with currently available S/S technologies [5], is the interfering effects of organic contaminants on setting and chemical stability of cement. Limited information is available on the effects of organics on the complex setting reactions, which can result in a significantly altered cement matrix [6].

One solution to effectively immobilize organic wastes is to sorb the soluble organics onto a solid sorbent, and then encapsulate the sorbent/sorbate complex in the S/S matrix. In most adsorption systems dealing with water or wastewater treatment, the sorbent is contacted with the contaminants for a specific time period, and then removed. Normally, the process is dynamic, and equilibrium is not achieved. In S/S systems however, the sorbent remains in the waste mixture, and eventually achieves equilibrium with the pore water. As the waste form cures, pH and other changes occur that can alter the immobility of the sorbed material [7]. These changes are not uniform throughout the waste, and have not been well-documented [8].

Several materials have been investigated for use as organic sorbents for solidification/stabilization systems. These include metal oxides, clays, natural materials (peat moss, natural zeolites, vermiculite, etc.), synthetic materials (zeolites, flyash, organic polymers, etc.), and activated carbon. Most current research has focused on organophilic clays. These are typically bentonite or montmorillonite clays in which tetra-alkylammonium compounds are substituted between the clay layers to increase the interlamellar spacing and enhance the adsorption of organic molecules. Initial results indicate that these modified clays may be useful for immobilization of certain organic compounds, but not for others. The long-term stability of the clay-organics complex is in question, though, and they are very expensive.

Activated carbon is widely used in water and wastewater treatment for capture of organics, and can also successfully trap many heavy metals. There are very few citations in the literature concerning use of activated carbon in S/S systems. Conner [7] states that activated carbon may be quite attractive for immobilization of certain organics in S/S waste forms, but he indicates that the cost would probably be too high. It is known that certain commercial S/S vendors use small amounts of activated carbon in their proprietary mixes, but none use enough for them to focus on its use as a binding agent [8]. Sherriff et al. [9] investigated the use of decolorizing charcoal and quarternary ammonium exchanged clays and found them to be effective pre-solidification adsorbents for phenol, 3-chlorophenol and 2,3-dichlorophenol. Leaching from these wastes was substantially reduced compared with solidified wastes without the charcoal. The Wastewater Technology Center in Ontario investigated the use of S/S systems with the addition of activated carbon as well as other additives [10]. They found activated carbon to be the best additive for immobilizing organic contaminants. With the exception of phenol, none of the contaminants tested (acenaphthene, aniline, bis(2-chloroethyl) ether, phenol, benzene, trichloroethylene) were detected in the aqueous leachate.

Activated carbon additives would appear to be an excellent choice if a cost-effective activated carbon could be used. One possibility would be to use thermally reactivated carbon which had previously been used to remove contaminants. Much of this spent carbon is now disposed rather than being reused. Industries using carbon for 'food grade applications' prefer virgin carbon because of the potential for contamination from the previously trapped chemicals. Regeneration and reuse of this carbon as a pretreatment sorbent for S/S systems would remove it from the waste stream, resulting in great cost savings. The cost of this regenerated activated carbon is less than one-fourth that of virgin carbon, making its use more attractive to the S/S industry. It needs to be shown, though, that the regenerated activated carbon will indeed immobilize a wide range of

organic compounds (and possibly certain inorganics) in the solidified waste form, and that it will continue to do so over the life of the material. The question of reversibility of the carbon adsorption also needs to be addressed.

2.1. Leaching of organics

Binding mechanisms for organics in cement are largely unknown. While the chemistry of cement is complex in its own right, addition of hazardous organics to the matrix makes the system even more difficult to study [11]. It is generally not even known where the organic is located [12].

Organic compounds generally seem to retard the hydration of cement, but some initial acceleration may occur. Some mechanisms of retardation include: (1) formation of insoluble calcium compounds, (2) adsorption, and (3) complexation. A common example of an organic retardant is sugar, which combines with the lime in cement to form calcium saccharate. This causes the solubility of aluminum to increase, due to the reduced calcium concentration, leading to a poor alumina silicate gel coating on the cement grains, which severely retards the cement hydration process [13]. Hydration can also be inhibited by hazardous organics, for example, 3-chlorophenol [14,15].

Mixed results have been obtained from studies on the effectiveness of S/S processes for immobilization of organics. Riaz and Zamorani [16] found only a minor release of 1,3,5-trichlorobenzene (TCB) when it was cement-stabilized. Binding mechanisms were not elucidated, but the authors reported that the TCB caused a reduction in pore diameters in the waste form, indicating that the reduced leaching may have been due to pore entrapment. Tittlebaum et al. [5] studied the binding of *p*-bromophenol (PBP), a water-soluble organic compound. They found the contaminant to be present in two distinct phases in the waste form. Some was in the form of grains, the inside of which was cement, with the organics coated on the surface in a concentrated form. The remainder was in the C–S–H (calcium–silicate–hydrate) gel, heterogeneously distributed on a submicroscopic scale. No high concentrations of PBP were found in the pore water, indicating that binding was not due solely to physical entrapment in the pores.

Very little work has been done on developing leaching models for organics in S/S waste forms, partly because little is known concerning binding mechanisms for organics in these materials. In addition, leaching will vary between classes of organic compounds depending on a variety of factors including solubility in water, polarity, presence of functional groups, volatility, etc. Nonetheless, modeling should be relatively straightforward once controlling mechanisms have been identified and quantitatively assessed.

2.2. Activated carbon adsorption in S/S waste forms

The effective use of activated carbon requires: (a) adequate knowledge of the equilibrium adsorption characteristics; and (b) kinetic data for transport of the solutes. These data are generally lacking, especially with respect to multicomponent systems, the systems of importance in waste solidification.

The adsorption of organics on to activated carbon is a complex process that may involve dispersive interactions, hydrogen bonding, chemisorption, and surface poly-

merization. Recent work [17] on phenol adsorption on a non-ashing carbon has demonstrated that the mechanism of adsorption is influenced by the degree of bonding with surface carbonyl groups, the degree of water adsorption, and dispersive interactions. Furthermore, if the carbon has a significant ash content, surface polymerization of adsorbed phenol groups can also be present [18]. Because of the complex nature of the adsorption process, solution pH affects adsorption behavior in a complex manner through its influence on dissociation and its influence on the surface interactions.

3. Experimental

3.1. Activated carbon characterization and isotherms

The activated carbon used in the study was thermally regenerated F-400 carbon (powdered and granular) manufactured by Calgon Carbon (Pittsburgh, PA). The adsorption isotherms for adsorption of phenol on this reactivated carbon were determined using the Bottle point method, following ASTM standards (ASTM D3860-89a). Different amounts of carbon were weighed into 50 ml bottles, with solution volumes ranging from 14 ml to 50 ml. Three bottles were prepared for each point on the isotherm and the average of these measurements was used. The temperature was held constant at $23^{\circ}\text{C} \pm 1^{\circ}\text{C}$ and pH was controlled at 3.0, 7.0, 9.0 and 12.0 using different buffer systems. The buffers used were $\text{Na}_2\text{HPO}_4/\text{H}_3\text{PO}_4$ (for pH 7.0), HCl/NaOH (for pH 3.0) and KCl/NaOH (for pH 9.0 and 12.0). A UV- spectrophotometer (Shimadzu, UV 160U) was used to measure the adsorbate concentration in the solution after equilibration; the time for equilibration was 14 days for granular reactivated carbon, and 24 h for powdered reactivated carbon. The wavelength used for the analysis of phenol was 270 nm.

3.2. Mix formulations

Powdered, regenerated, activated carbon (F-400, regenerated) was used to prepare the contaminant batches. Small batches of various mix formulations using Type I ordinary Portland cement (OPC) as binder were prepared and cured using standard ASTM procedures (ASTM, C 192-88). Representative samples were tested for unconfined compressive strengths using a 60 kips Tinius-Olsen (PA, USA) universal testing machine. The average compressive strength was typically about 2500 psi. In most S/S applications, a minimum of only 25–50 psi unconfined compressive strength is required. A water/cement ratio of 0.5 and sand/cement ratio of about 2.0 were found to be optimum to obtain the required strength, reasonable time of curing and proper setting of the waste forms, and hence these ratios were used in this study.

3.3. Preparation of contaminated soil

Contaminated soils for use in S/S waste forms were prepared according to currently acceptable practices. These techniques are based on previous attempts to create large

batches of standardized contaminated soil, such as the EPA SARM program [19]. A variety of soil types are being evaluated in this research program. This paper will focus on the use of sand, the least adsorptive and therefore the most conservative component of soil. The type of sand used in this study was cube test sand (CT 190A — ELE International, Lake Bluff, IL). To simulate naturally contaminated soils, phenol solutions (1000 mg/l and 5000 mg/l) prepared in de-ionized water were spiked to the sand, and the sand was initially allowed to ‘age’ for up to 30 days for adequate adsorption of phenol onto the sand particles. Preliminary results using phenol and sand indicated that there was no appreciable adsorption on sand particles. Most of the phenol (about 99%) remained in the solution. Hence, it was decided to age the soils for only 4–5 days in zero headspace glass jars (ELE International).

3.4. Addition of regenerated powdered activated carbon

After aging the soils for 4–5 days, an appropriate amount of regenerated powdered activated carbon (RPAC) was added to the contaminated sand. This amount was initially based on the equilibrium adsorption isotherms developed. However, after preliminary leaching tests using phenol-contaminated sand, it was found that a higher quantity of carbon was required to counterbalance the mass transfer limitations on adsorption. Different amounts of RPAC (0.5%, 1.0%, 2% and 5% with respect to weight of soil) were used in the study to determine their effect on leaching.

A calculated amount of OPC, based on a water/cement ratio of 0.5 or 1.0, was added to the mix. After mixing with a hand mixer, the cement–sand–phenol slurry was put into 2 in. by 4 in. (5 cm by 10 cm) PVC cylinders (Jatco), covered with a lid to produce a zero-headspace and allowed to cure. Samples cured for different periods were tested for leaching and unconfined compressive strength.

3.5. Pore-fluid analysis

To better understand the complex cement setting reactions in the presence of phenol, samples of the pore-fluid within the first 2 h, when the cement paste had not yet hardened, were taken. Pore-fluid is defined as the excess water that does not participate in the hydration reactions of cement and remains entrapped in the cement pores. A measured quantity of the paste was put into a Nalgene (115 ml) vacuum filter, (filter size 0.45 μm), and samples of the pore-fluid were drawn at periodic intervals by using a vacuum. These samples were again filtered through 0.22 μm filters and analyzed for phenol by UV-VIS spectrophotometry (Shimadzu, UV-160U) at a wavelength of 270 nm, and for calcium by inductively coupled plasma spectroscopy (ICP, Perkin-Elmer ICP/5500).

3.6. Leaching procedure

After the S/S waste forms were allowed to cure for 7, 14, or 28 days, they were tested by the Toxicity Characteristic Leaching Procedure [20] and also by a modified version of this procedure. Alteration to the procedure involved using a liquid to solids

ratio of 10:1 to obtain easily measurable levels of phenol in the leachate. Following the leaching procedure, the samples were filtered through a Nalgene 0.22- μm membrane filter, preserved and analyzed by a UV-VIS spectrophotometer for phenol and by inductively coupled plasma spectrometry for calcium.

3.7. Phase and microstructural analyses

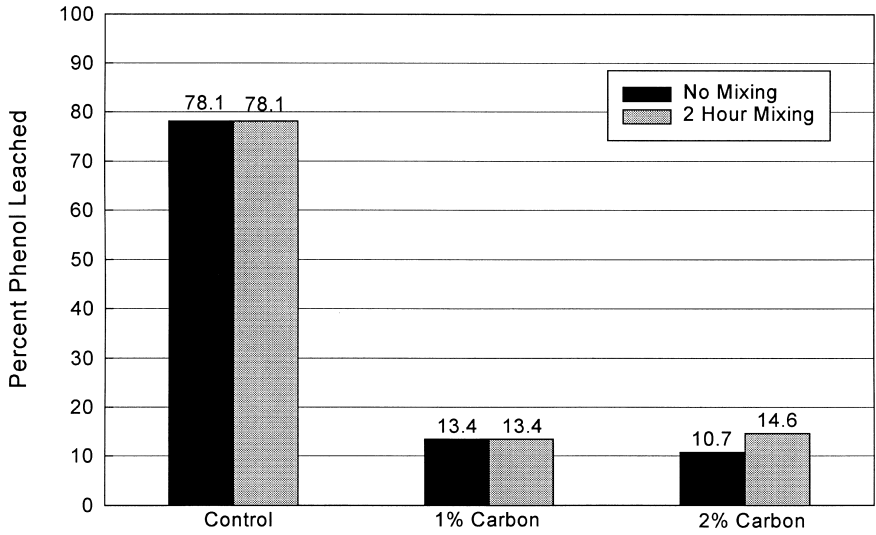
Solid S/S specimens, cured for different periods, were fractured or ground and dried in a vacuum dryer for 1 day. To analyze the crystalline and amorphous phases in the cured cement, X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and fourier transform infrared spectroscopy (FT-IR) techniques were used. Powder diffraction analysis (PDA) was performed using a Philips PW 1729 X-ray diffractometer. The range of 2θ was 10–65° with scan speed of 0.02°/s. XRD was set at 40 kV and 20 mA. The IR analysis was carried out on Bio-Rad FTS 40 spectrophotometer in the wave number range of 3200–4000 cm^{-1} using the KBr disc technique. The morphology of hydrated phases was examined using a Hitachi field emission scanning electron microscope. Specimens for FESEM analysis were coated with gold to prevent charging. The acceleration voltage was 20 kV at a working distance of 15 mm. The precipitated phase and hydrated phase in the S/S samples were characterized by energy dispersive X-ray spectroscopy (EDX).

4. Results and discussion

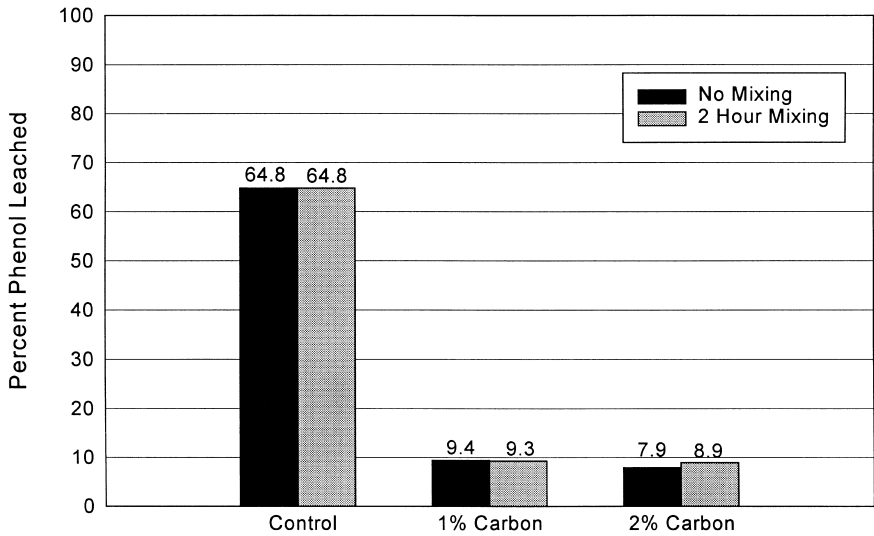
4.1. Sequence of addition of activated carbon and cement

The pH of the phenol contaminated sand was approximately 7.0, but this quickly increased to about 12 after addition of cement. Equilibrium isotherm results for phenol indicated that the adsorptive capacity of the reactivated carbon is lower at a pH of 12.0 as compared to a pH of 7.0 (Arafat et al., in press). In this research, it was found that adsorption of phenol on carbon granules virtually stops after they are coated with cement. Thus, the timing of addition of reactivated carbon seemed important. Two sets of mixing schedules were carried out. In one set of experiments, the reactivated carbon was added and mixed with the phenol-contaminated sand at the same time that cement was added. In the other set, cement was added 2 h after the addition of reactivated carbon to the phenol-contaminated sand. The rationale behind this mixing schedule was to compare the effects of adsorption of phenol at two different pH values. Cement-based S/S systems produce large amounts of $\text{Ca}(\text{OH})_2$, which precipitates in the pores, creating a significant source of alkalinity and a high pore water pH (about pH 12). In the first set, since cement was mixed at the same time as reactivated carbon, the pH rose rapidly to about 12. Hence, reactivated carbon adsorption was expected to occur at an alkaline pH. In the second set, reactivated carbon was first mixed with the phenol-contaminated sand while cement was not added until 2 h later. This enabled the adsorption of phenol to proceed at a neutral pH.

However, preliminary leaching test results (Fig. 1) indicated that there was no appreciable difference in the amount of phenol that leached out under these two sets of



(a)



(b)

Fig. 1. TCLP leachate analysis of phenol (1000 mg/l) from 7-day cured solidified/stabilized soil samples for different PAC loadings. (a) $L/S = 20:1$; (b) $L/S = 10:1$.

mixing conditions for 7-day cured specimens. Similar results were obtained for specimens cured for 14 and 70 days. This indicated that the adsorption of phenol on reactivated carbon proceeded at a much faster rate than the hydration of cement and complexation reactions of calcium with phenol, with about 95% of the phenol adsorbed in the first 15 min. Hence, even when cement was added to the contaminated soil at the same time as reactivated carbon, most of the adsorption took place before the pH could rise to 12. Another possibility for this result is that the carbon has excess adsorption capacity at both pH 7 and 12. This result indicated that all ingredients (contaminated sand, reactivated carbon and cement) can be added at once, making processing much easier.

4.2. Reversibility of adsorption

The solidification/stabilization process using reactivated carbon as adsorbent would not be effective if the adsorption of phenol was reversible; that is, if the phenol desorbed under the alkaline conditions resulting after addition of cement. To evaluate this, adsorption isotherms were generated at two pH values – 7.0 and 12.0. A pH of 7.0 represented the pore-water pH in the contaminated soil, while a pH of 12.0 represented the pore water pH after addition of cement to the soil (Fig. 2). As stated earlier, the adsorptivity of the reactivated carbon was lower at a pH of 12 than at a pH of 7. After

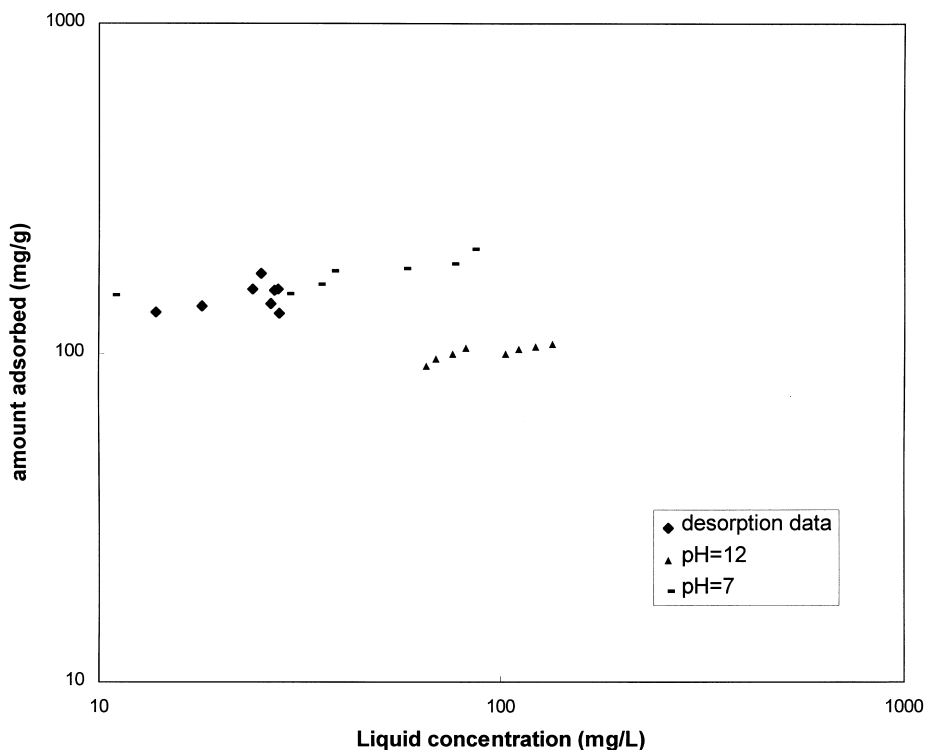


Fig. 2. Desorption test for phenol on F400 reactivated carbon.

the phenol was adsorbed at a pH of 7, the pH of these samples was increased to 12. This represents what would happen when cement is added to the mix. As can be seen in Fig. 2, the capacity did not change with the change in pH, indicating that the adsorption was irreversible.

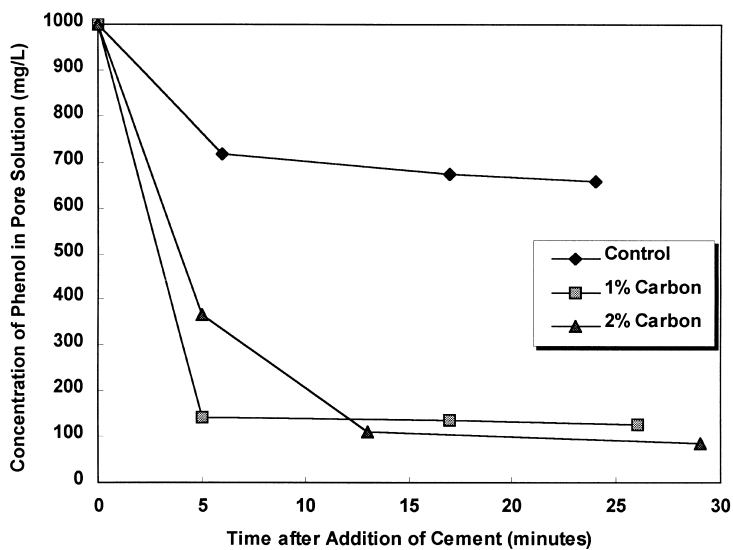
4.3. Pore-fluid analyses

The results of the pore fluid extraction analyses for the cement–phenol system are shown in Figs. 3 (a and b) and 4 (a and b) for the various w/c ratios and phenol concentrations. The concentration of phenol in the pore-fluid decreased with time, due to adsorption onto the reactivated carbon, for all combinations. The phenol concentration reached a minimum after about 10 min of curing. It can be noticed that calcium ions were present in high concentrations, in the range of 600–900 mg/l, depending on the amount of carbon added and the age of the paste. The calcium concentration was generally higher in pastes containing greater amounts of phenol. The lowest amounts were in the pastes containing the maximum amount of carbon (2% w/w of soil). The calcium ion concentrations showed a local peak before gradually declining. The time for the concentrations to peak (about 10–15 min) suggests a dependence on the amount of phenol present in the pore water. The results of this study agree with Thomas and Double [21], who investigated the pore-fluids of Portland cement in the presence of oxalic acid and EDTA, and also with Vipulanandan and Krishnan [3].

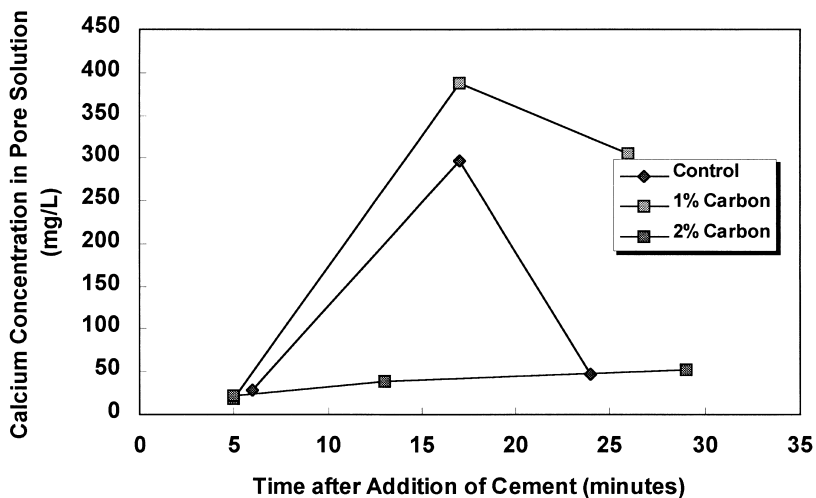
The increase in the calcium ion concentration in the pore fluid with increase in phenol content suggests a possible complexation reaction between phenol and calcium ions. A similar reaction has been observed by Scouten and Dougherty [22], who suggested that the reaction of calcium hydroxide and phenol at room temperature formed a calcium–phenol complex, hydroxycalcium phenoxide. The reaction is as follows:



The results also corroborate the membrane theory of cement hydration [23]. Initially, when OPC is dispersed in water, calcium ions are rapidly leached from the solids to form a solution mainly of calcium hydroxide, leaving behind silica-rich cement grains. The aqueous Ca(OH)_2 is thought to react with silicic acids on the surface of the cement to form a gelatinous semi-permeable membrane of C–S–H gel around the cement particles. The water that passes through this semi-permeable membrane causes the hydration of cement grains enclosed by the membrane. Since this membrane allows the transport of water across the membrane, and is not permeable to calcium ions, the hydrates are contained within the membrane until the build-up of osmotic pressure causes the rupture of the membrane, releasing the hydrated ions. Based on our results, the calcium released by the initial dissolution of cement reacts with phenol in the pore water and thus is made unavailable for the formation of C–S–H gel, which in turn impedes the formation of the osmotic membrane. This causes the hydration products to enter the solution, causing a local peak in the concentrations of Ca^{2+} ions. When the solution is saturated with Ca-phenol complex, the calcium released subsequently starts to complex with the silicate hydrates to form C–S–H gel. These complexation reactions occur simultaneously with adsorption reactions of phenol on activated carbon. The presence of a second peak may indicate a similar phenomenon occurring again, until the

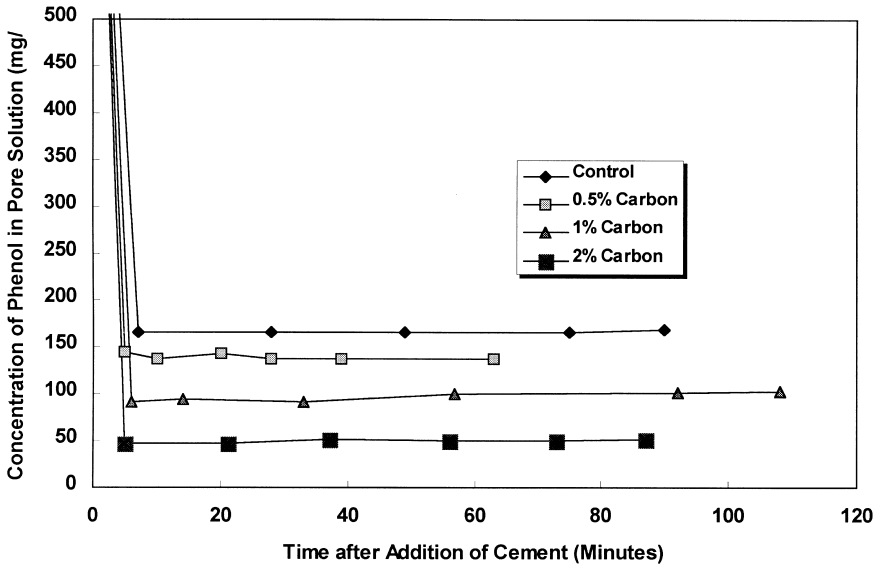


(a)

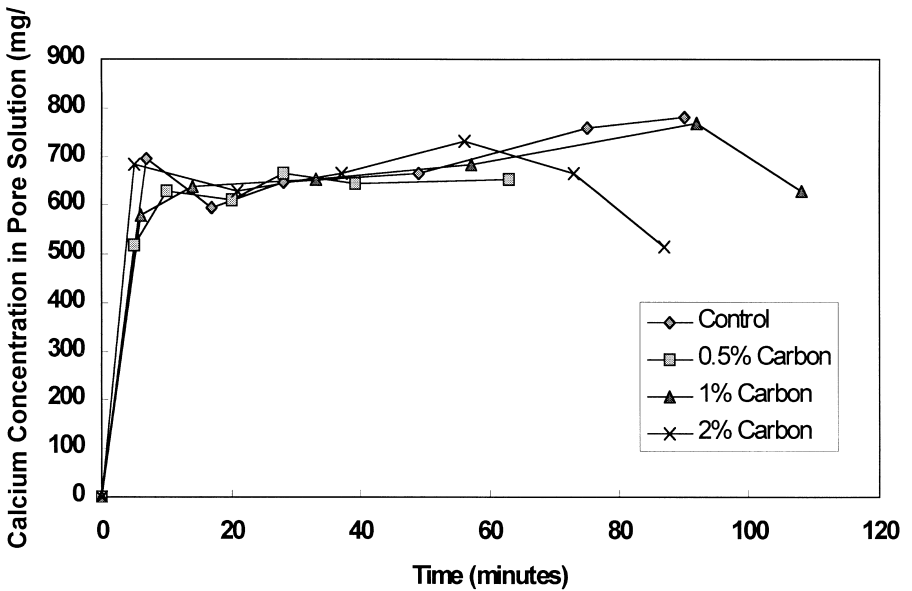


(b)

Fig. 3. Pore fluid analysis for a solidified/stabilized soil (water:cement = 0.5) at various times after addition of cement. (a) Phenol concentrations (initial concentration = 1000 mg/L); (b) calcium concentrations.



(a)



(b)

Fig. 4. Pore fluid analysis for a solidified/stabilized soil (water:cement = 1.0) at various times after addition of cement. (a) Phenol concentrations (initial concentration = 1000 mg/l); (b) calcium concentrations.

concentration of phenol decreases to a very low value due to adsorption on activated carbon.

4.4. Micro-structural analyses

Investigation of the microstructure of the solidified/stabilized specimens, containing organics, showed some interesting results. FT-IR and XRD analyses were performed on S/S specimens that contained phenol, regenerated powdered activated carbon, and sand, and that were cured for 7 days. Fig. 5 presents their FT-IR spectrum and XRD patterns. A $\text{Ca}(\text{OH})_2$ band centered at 3640 cm^{-1} was clearly observed in the FT-IR spectrum. A much stronger peak, corresponding to the OH stretch of $\text{Ca}(\text{OH})_2$, was noted in the control samples than in samples containing activated carbon. As the phenol concentration in the S/S specimens increased from 1000 mg/l to 5000 mg/l, the intensity of OH stretch due to the presence of $\text{Ca}(\text{OH})_2$ in the FT-IR spectrum increased while the XRD peak of $\text{Ca}(\text{OH})_2$ decreased. From these observations it was deduced that the ratio of amorphous $\text{Ca}(\text{OH})_2$ to crystalline $\text{Ca}(\text{OH})_2$ increased as a function of phenol concentration. A small amount of crystalline $\text{Ca}(\text{OH})_2$ phase and a much lesser amount of amorphous $\text{Ca}(\text{OH})_2$ was detected in samples containing reactivated carbon compared to the control samples. The formation of amorphous portlandite, as well as a complex formation between calcium and phenol, seems to contribute to retarding the formation of the C–S–H gel.

The microstructures of the control specimens (containing 1000 ppm and 5000 mg/l phenol, but no reactivated carbon), as well as specimens with reactivated carbon added and cured for 7 days, are shown in Fig. 6. Significant morphological differences were revealed in control specimens compared to carbon-added specimens. The control specimens had large particles of C–S–H on the cement grains. The well-developed needle-like shape of ettringite crystals was observed in specimens containing reactivated

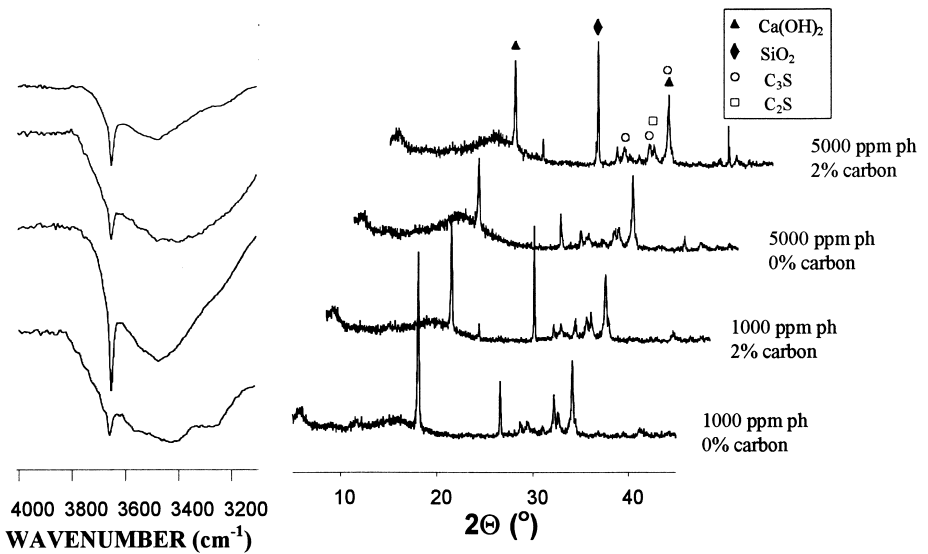


Fig. 5. FT-IR spectra(left) and XRD spectra(right) of cement block cured for 7 days.

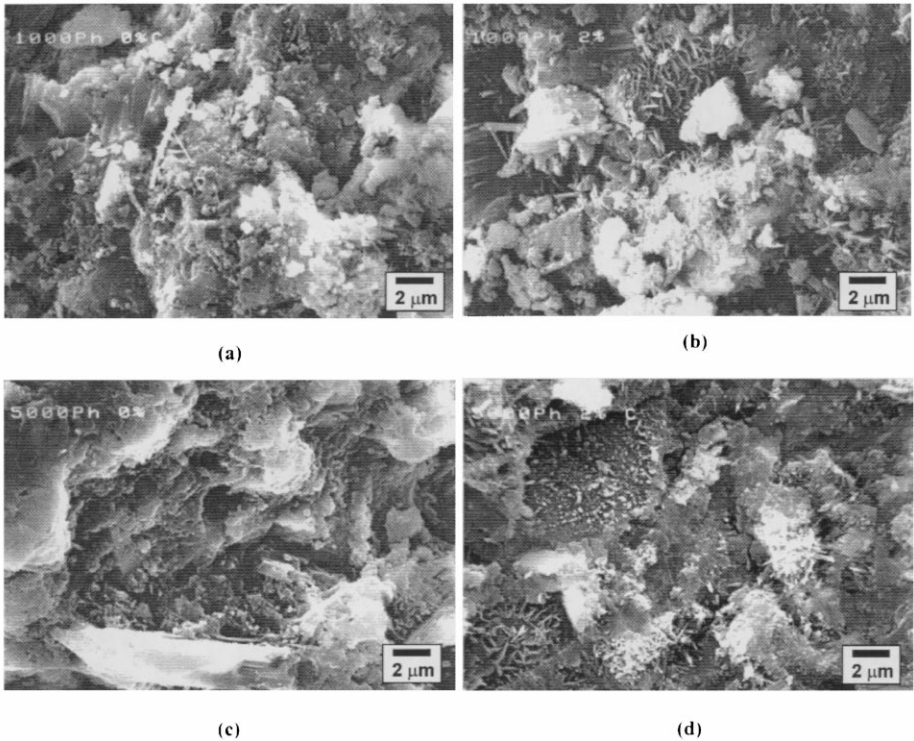


Fig. 6. SEM photos of cement block surfaces cured for 7 days, (a) control sample (1000 ppm phenol), (b) 2% carbon and 1000 ppm phenol, (c) control sample (5000 ppm phenol), and (d) 2% carbon and 5000 ppm phenol.

carbon, but was confined mainly to porous regions. Very few Aft crystals were observed in the control samples. More porous areas, that were not covered by ettringite or C–S–H, were noted in the control samples. Not only gel-like C–S–H but also the plate-like shape of tobermorite crystals (which was confirmed by EDX) were observed in certain pores, but only for carbon-added specimens. Striated calcium hydroxide crystals were observed in carbon-added specimens, but more gel-like calcium hydroxide was frequently observed in the control specimens. This seems to be caused by enhanced dissolution of Ca^{2+} ions from cement clinkers and increased solubility of calcium in an amorphous colloidal gel layer on the surface of cement grains with the presence of phenol.

Microstructural differences were also observed with the extended curing time. Fig. 7 represents the microstructures of four different specimens cured for 40 days. The most dramatic microstructural differences were revealed in the 40-day cured reactivated carbon-added specimens as compared with 7 day-cured specimens. Much larger and more numerous ettringite crystals were observed in carbon-added specimens cured for 40 days. The control samples exhibited cement grains with particle-like, not as fibrous, C–S–H on the surface, and still lesser ettringite crystals as compared to the carbon-added specimens. The hydration layer on the cement grains of carbon added specimens

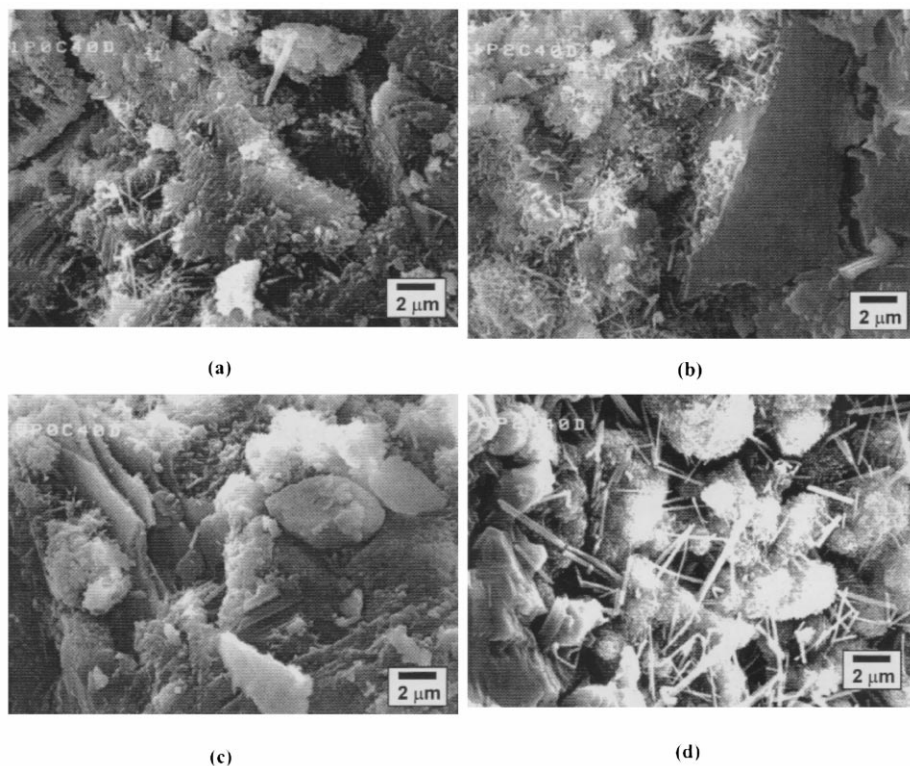
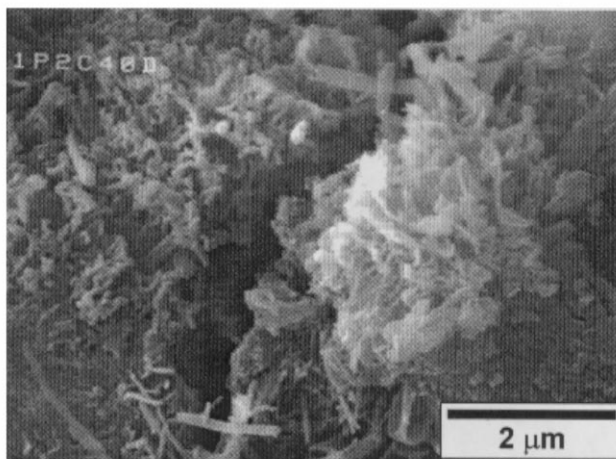
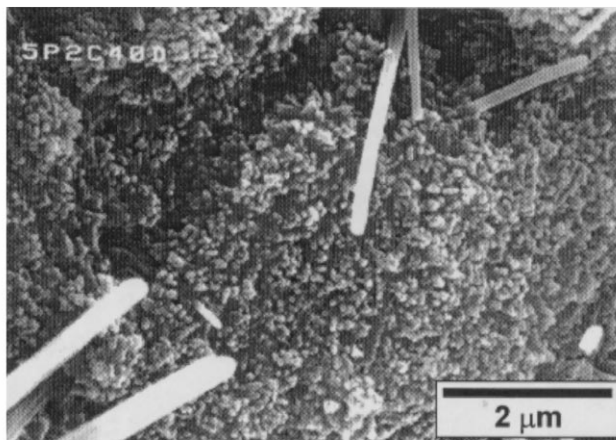


Fig. 7. SEM photos of cement block surfaces cured for 40 days. (a) control sample (1000 ppm phenol), (b) 2% carbon and 1000 ppm phenol, (c) control sample (5000 ppm phenol), and (d) 2% carbon and 5000 ppm phenol.

showed a reticulated and fibrous morphology. A more fibrous structure was observed in the proximity of the reactivated carbon particles, as shown in Fig. 8. Fig. 8 shows a high magnification SEM micrograph of cement grains in the carbon-added specimens. The cement grains were covered with C–S–H (about 10 nm in size) in the carbon-added specimens with 5000 ppm phenol, while more fibrous C–S–H connected the cement grains in the carbon-added specimens with low phenol content (1000 ppm). The 2% carbon-added specimen with 1000 ppm phenol showed a morphology similar to that usually observed in well-matured S/S specimens with no phenol added. From this observation, it is evident that the hydration process of the control specimens is different from hydration in the carbon-added specimens. The presence of reactivated carbon in the S/S matrix immobilizes and traps the phenol, allowing for normal or even accelerated hydration of the cement. The efficiency of this hydration decreased as the phenol concentration increased for the same reactivated carbon content. Another interesting observation was the pozzolanic effect due to the presence of sand. Fig. 9 shows the crystal development around the surface of sand. Silicon rich C–S–H crystals grew out from the surface of the sand. Even though this pozzolanic effect is expected to be small



(a)



(b)

Fig. 8. High magnification SEM photos of cement grains in the specimens designated as (a) and (b) in Fig. 7.

because of the small surface area of the sand, it will affect the Ca concentration of pore fluid and hence the crystallization of $\text{Ca}(\text{OH})_2$.

4.5. TCLP leaching studies

The leaching of phenol from the S/S matrix appeared to depend on several factors. These include: amount of reactivated carbon, liquid/solids (L/S) ratio, curing period,

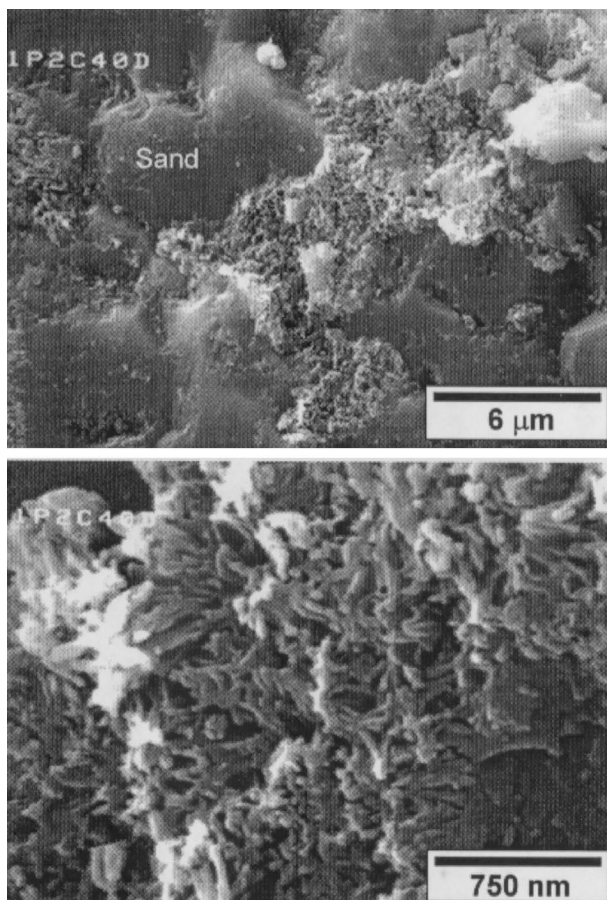


Fig. 9. Pozzolanic effects on the sand grain (top) silica rich crystals on sand grain and (bottom) high magnification of silica rich crystals in the top.

concentration, and presence of other organic constituents. These effects are discussed in detail in the following paragraphs.

4.5.1. Effect of amount of reactivated carbon

The amount of reactivated carbon added to the S/S mix was the most important factor in the leaching behavior of phenol. Two concentrations of phenol were used in the study – 1000 mg/l and 5000 mg/l. To study the effect of reactivated carbon, S/S specimens were prepared with no reactivated carbon, 1% and 2% (w/w sand) of reactivated carbon. Fig. 10(a) and (b) indicate that for phenol (5000 mg/l) specimens with a L/S ratio of 20.0, as high as 87% of the phenol (w/w initial phenol present in the S/S matrix) leached out when no reactivated carbon was added. However, when reactivated carbon was added, the leaching reduced drastically. This clearly demonstrated the effectiveness of reactivated carbon in the S/S process. The leachate phenol

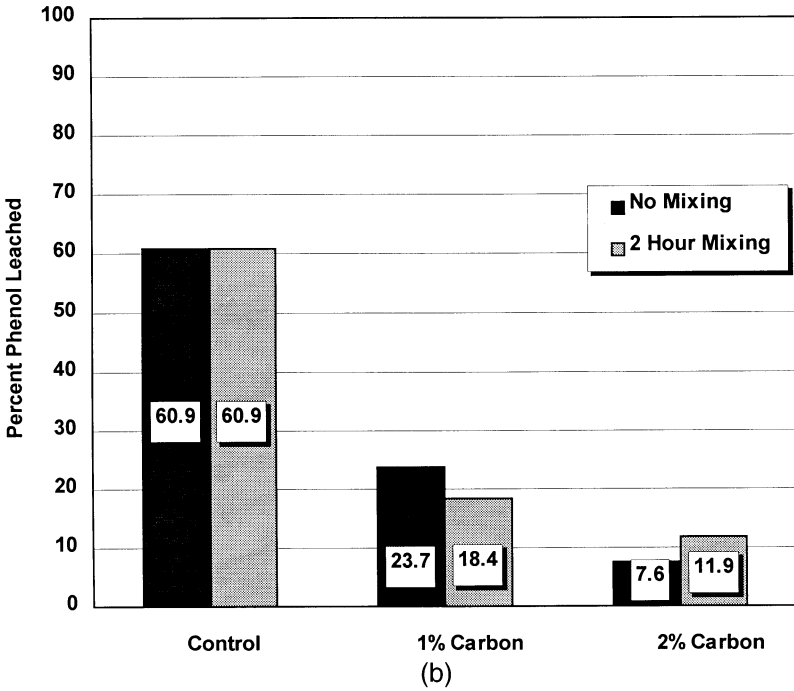
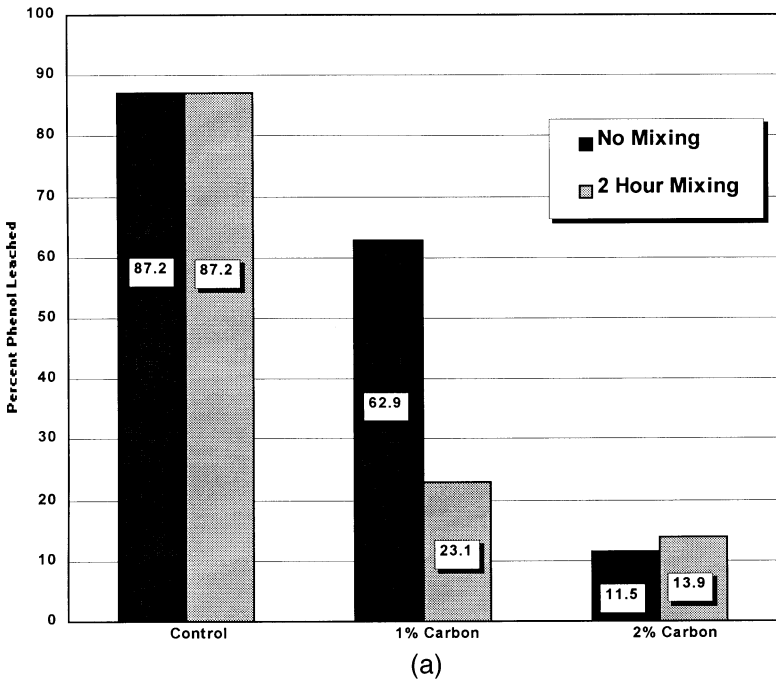


Fig. 10. TCLP leachate analysis of phenol (initial concentration = 1000 mg/l) from 7-day cured solidified/stabilized soils with different PAC loadings. (a) $L/S = 20:1$; (b) $L/S = 10:1$.

concentrations from the solidified specimens with 5000 mg/l phenol exceeded the regulatory TCLP limit of 14 mg/l in all the specimens without reactivated carbon. However, the TCLP limit for specimens with reactivated carbon was exceeded only for the specimens containing 1% reactivated carbon (w/w sand) and cured for only 7 days. All other specimens containing reactivated carbon showed leaching much below the regulatory TCLP limits. As the amount of reactivated carbon required is very small in comparison to the total mass involved, this process can prove to be very economical to solidify/stabilize soils contaminated with phenolic wastes.

4.5.2. Effect of liquid / solids ratio

Two different L/S ratios were used in the TCLP leaching test – 20.0 (conventional) and 10.0 (modified). Figs. 1 and 10 show the leaching observed for different L/S ratios. For the phenol (1000 mg/l) specimens cured for 7 days, about 78% of the phenol leached out from the control (no reactivated carbon) specimens using a L/S ratio of 20.0 [Fig. 1(a)]. The leaching was reduced to about 65% when a L/S ratio of 10.0 was used [Fig. 1(b)]. The higher L/S ratio (20.0) produces a greater driving force for the leaching of the contaminant from the solid into the solution phase. Whereas, a L/S ratio of 10.0 produces a greater amount of leachate for better measurement, a L/S ratio of 20.0 causes more leaching (with respect to the original amount of phenol present in the solid) to take place, but lower concentrations in the leachate.

4.5.3. Effect of curing period

As mentioned, hydration of cement is a continuing process. Since the C–S–H gel is continually formed in the S/S matrix, the fixation of a contaminant is a function of curing time. Comparing Fig. 10(a) for phenol (1000 mg/l; $L/S = 20:1$) specimens indicates that leaching from the TCLP test after 50 days curing was reduced to about 62% of the initial amount present, as compared to about 87% after 7 days curing. As the curing time increased, the leaching of phenol decreased. A possible explanation of this may be the encapsulation of phenol in the C–S–H gel matrix in the cement. As curing time progressed, phenol may actually have chemically bonded with the cement constituents and also adsorbed on the reactivated carbon.

4.5.4. Effect of initial concentration

Two different concentrations of phenol (1000 mg/l and 5000 mg/l) were used in this study. Figs. 1, 10 and 11 indicate that the concentration of phenol in the leachate increases with an increase in the original amount of phenol present in the S/S matrix. However, the overall percentages of phenol leached from the 1000 mg/l and 5000 mg/l were nearly the same.

By comparing the results from phenol pore-fluid [Fig. 3(a)] and leaching analyses [Figs. 1(a,b) and 10(a,b)], it can be seen that the phenol which leached out in the TCLP tests was the fraction which was not adsorbed on the reactivated carbon, but rather was present in the pore-water. In Fig. 3(a), about 70% phenol (w/w of the initial amount present) remained in solution in control specimens (containing no reactivated carbon) whereas only 10% of the initial phenol leached out in S/S specimens containing 2%

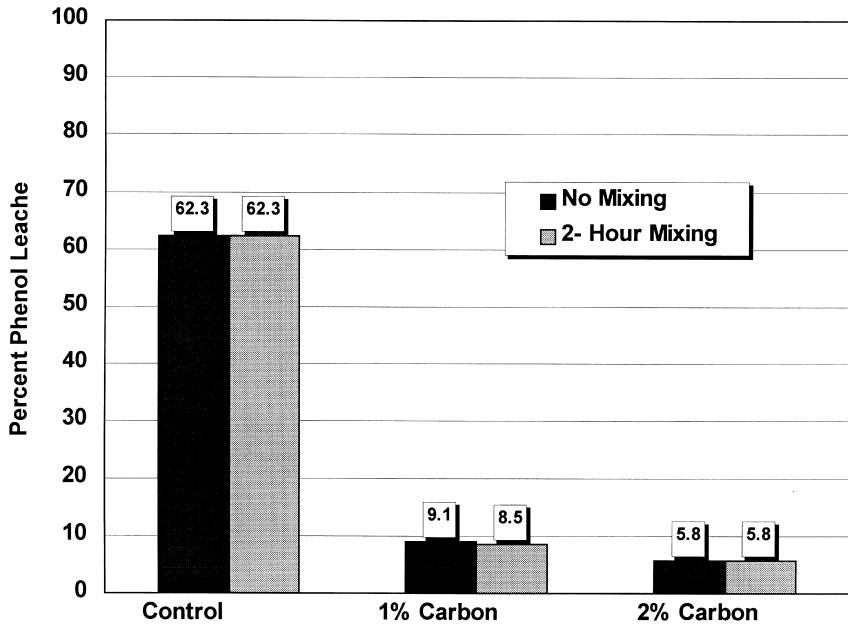


Fig. 11. TCLP leachate analysis of phenol (initial concentration = 5000 mg/l; L/S = 20:1) from 7-day cured solidified/stabilized soils with different PAC loadings. (a) L/S = 20:1; (b) L/S = 10:1.

reactivated carbon (w/w sand). In Fig. 10(a), approximately 80% of the phenol (w/w initial phenol) leached out in control specimens, while about 15% leached in the specimens containing 2% reactivated carbon. This suggests that phenol, which is unadsorbed and remains in solution, is the fraction that leaches in TCLP leaching tests.

5. Conclusions

The leaching behavior of phenol from solidified/stabilized wastes was investigated. The following conclusions can be derived from this study.

- The use of regenerated powdered activated carbon in the S/S process reduces the leaching potential of phenol by as much as 600% compared to when no reactivated carbon is used. Even very low amounts of reactivated carbon added to the mix (1% w/w of soil) efficiently adsorb most of the phenol and prevent it from leaching.
- The adsorption of phenol to carbon is essentially irreversible when the pH is varied from 7 (contaminated soil) to 12 (stabilized soil with cement) and back to 7 again (S/S waste form after $\text{Ca}(\text{OH})_2$ leaching).
- The expected requirement for a mixing period of about 2 h after addition of reactivated carbon to the soil but before the cement is added to the mix is not justified by leaching results, and hence cement can be added at the same time as the reactivated carbon.

- Phenol (especially at higher concentration – 5000 mg/l) affected the hydration reactions, with formation of amorphous portlandite, but to only a moderate extent. Hence, the S/S process can be safely used for phenol up to these concentrations.
- Some of the phenol remaining in the pore water forms an insoluble complex with the calcium ions released from the cement, and is the fraction that is available for leaching. This calcium–phenol complex may resolubilize when subjected to acidic leachants.
- Phenol present at these concentrations (1000 mg/l and 5000 mg/l) does not cause any noticeable reduction in the unconfined compressive strength of the cured waste forms.
- Regenerated activated carbon, because of its low cost, appears to be an attractive choice for use in solidification/stabilization of wastes containing organics. However, its effectiveness with other compounds needs to be investigated.

Acknowledgements

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