Cement/activated-carbon Solidification/stabilization Treatment of Phenol-containing Soil

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Abstract—In this research, the cement/activated-carbon solidification/stabilization (S/S) technology was used to treat contaminated soil with 500ppm phenol, choosing ordinary portland cement (30% or 50% w/w of contaminated soil) and activated carbon (0%-10% w/w of contaminated soil) as binder and additive respectively. The leaching test, long-term leaching test, and pore size distribution analysis of the solidified/stabilized samples were carried out to investigate the S/S effect. The results showed that under the natural curing conditions, the phenol-contaminated soil could be effectively treated by the cement/activated-carbon S/S technology; very low amounts of activated carbon (less than 3% w/w of contaminated soil) could significantly improve the fixation ratios of phenol; the cumulative leaching ratio of 28 days cured samples were much lower than that of 7 days cured samples in the long-term leaching test; the adding of activated carbon had a strong effect on the porosity of the solidified/stabilized samples, increasing the total porosity, which might lead to easily leaching out of phenol; and careful balancing between the adding amount of activated carbon and cement was necessary to obtain the minimum phenol release and better economic feasibility.

Keywords—phenol; solidification/stabilization; cement; activated carbon; contaminated soil

I. INTRODUCTION

Cement based Solidification/stabilization (S/S) is a widely used technology employed for the treatment and disposal of hazardous wastes, especially hazardous wastes containing heavy metals. Although the applications of S/S to treat organic contaminants are much less, due to the detrimental effect on the properties of cement caused by organic compounds which make the organic contaminants easily leach out, the S/S technology is still a good choice to treat organic contaminants in some scenarios, like soil remediation, emergency respond et al. Unlike heavy metals, the properties of organic compounds are much more complex. As a rule of thumb, organic compounds that are volatile, water soluble, and with a pKa value below 12 are likely to readily leach from cement based binder systems [1]. According to such hypothesis, as a highly soluble and with a pKa value of 10.02 organic, phenol is quite a challenge to be treated by S/S. However, phenol is a widely used aromatic compound, so the generation of phenol-containing waste which is listed in the National Catalogue of Hazardous Wastes (NCHWs) is unavoidable during the producing and using period. At the same time, the phenol spilling accidents happen sometimes in China. In the first half year of 2008, four phenol spilling accidents happened in China, generating phenol-containing soils, sediment, water which were need to be treated quickly and properly. In such scenarios, the S/S can be chose as an emergency responding technology.

Vipulanandan concluded from leaching studies that phenol reacted with cement and that up to 400ppm phenol could be treated effectively using cement based S/S, which resulted in less than 15 ppm of phenol in the leachate solution during the TCLP [2]. From the result, a phenol leaching ratio of 75% could be calculated, which indicated that such a S/S method was not likely to be used in immobilizing phenol. Later, Arafat et al. reported that the use of regenerated powdered activated carbon in the S/S process reduced the leaching potential of phenol by as much as 600% compared to when no reactivated carbon was used. Even very low amounts of reactivated carbon added to the mix (1% w/w of soil) efficiently adsorbed most of the phenol and prevented it from leaching [3].

In the former studies, the curing of the solidified/stabilized samples were done under controlled conditions of constant temperature and humidity, and the TCLP procedure was adopted to estimate the leachability of phenol, which could not reflect the real conditions of the wild. Firstly, the curing conditions in the wild were quite different from that which was used in lab. Secondly, the TCLP procedure, which is based on leaching potential that may occur in a sanitary landfill does not represent conditions present at the particular location where the phenol-containing waste is being treated. In this study, cement and activated carbon were chose as binder and additive to treat the phenol-containing soil. To simulate the real conditions, the solidified/stabilized samples were cured under natural conditions in the lab. Leachability of phenol was studied using a leaching test developed base on actual rainfall conditions and a long-term leaching test. The pore size distribution of the solidified/stabilized samples was also studied.

II. EXPERIMENT
A. Sample preparation

The soil was taken from the Tsinghua University, which could be classified as sandy loam (SL) according to the Unified Soil Classification System (USCS). Phenol solution (2000 mg/l)
prepared in de-ionized water was spiked into the soil to obtained a simulated contaminated soil with 500ppm phenol.

Then a calculated amount of ordinary Portland cement, based on a cement/soil ratio of 0.3 or 0.5, and different amounts of activated carbon (0%-10% with respect to weight of soil) were added to the simulated contaminated soil. A water/cement ratio of 0.4 was used in this study. After mixing with a hand mixer, the fresh paste was put into cylindrical moulds. Samples cured under the natural conditions in the lab for different periods (7 days or 28 days) were tested for leaching. And pore size distribution analysis was carried out for the 28 days cured sample.

B. Leaching test

The Chinese regulation standard method, sulphuric acid & nitric acid method (HJ/T 299-2007) which was based on actual rainfall conditions for that particular region of China, was adopted to estimate the leachability of phenol in the 28 days cured solidified/stabilized samples. Following the leaching test, the samples were filtered through a 0.45 μm cellulose nitrate membrane filter, acidified and analyzed by a UV-VIS spectrophotometer (Shanghai Jingyan Technology Co.,Ltd., UV757CRT) for phenol at a wavelength of 270 nm.

C. Long-term leaching test

To understand the long-term leaching behaviour of phenol in the acid rain scenario, a dynamic leach test modified from UNICEN 8798(see UNICEN 8798 in the references) was adopted. The fresh pastes were cast into cylindrical moulds (3.2 cm height and 2.2 cm diameter), sealed and cured for 7 days or 28 days under the natural conditions in the lab. Then the cured solidified samples were smoothed, cleaned and each of them hung in a 500 ml jar filled with leaching fluid, completely immersed and maintained at 24 °C without agitation. The leaching fluid was chosen based on the acid rainfall in China, which was obtained using a mixture of 2/1 H2SO4/HNO3 (by weight) to achieve the appropriate pH 3.20±0.05. And the solid/liquid ratio was 1 to 10. Leaching fluid was periodically renewed according to the procedure: once per day the first week, twice the second week, once per week up to the sixth week, then once per month. These operations were performed for a number of progressive extractions up to 123 days. Concentrations of phenol in the leaching fluid were determined at each leaching fluid renewal. The leaching fluid was separated, filtered through a 0.45 μm cellulose nitrate membrane filter, acidified, and then analyzed by a UV-VIS spectrophotometer for phenol at a wavelength of 270 nm.

D. Pore size distribution analysis

The test was concerned with the differences of pore size distribution caused by the addition of activated carbon, and also by the long-term leaching test. The pore size distribution analysis was carried out by means of N2 adsorption/desorption at 77 K with a Quantachrome's Autosorb-I-C using the BJH(Barrett, Joyner and Halonda) method, which assumed that all the pores were cylindrical, slit-shaped and based on the Kelvin equation.

III. RESULTS AND DISCUSSION

A. Comparison of the fixation effect in leaching test

The fixation ratio (FR) of phenol during leaching test was adopted to indicate the S/S efficiency of different mixing formulations, which was calculated as follows:

$$\text{FR} \% = \frac{\text{the addition amount} - \text{the amount leaching}}{\text{the addition amount}} \times 100\%$$

The leaching test results (Fig. 1) showed that the increasing of cement adding amount could elevate the fixation ratio of phenol, but the improvement was not so remarkable as which caused by the increasing of activated carbon adding amount. Actually, when the cement/soil ratio increased from 0.3 to 0.5, the FR of phenol had just been raised by 7.4% on average.

![Figure 1. Leaching test of solidified/stabilized soil samples for different adding amount of activated carbon.](image)

As shown in Fig. 1, according to the S/S efficiency changing, the improvement process caused by the increasing adding amount of activated carbon could be divided into 3 phases as follows:

Phase I: remarkable improvement state. A small amount (<3% w/w of soil) of activated carbon added could significantly improved the immobilization of phenol. The FR
of phenol could reach 80%, while the FR of phenol was less than 30% without activated carbon added, which indicated that the S/S treatment was not effective for immobilizing phenol in the absence of activated carbon. These results were similar to the ones obtained by Hebatpuria et al.[6]

Phase II: slowly continuous improvement state. The FR growth slowed down as the adding amount of activated carbon increased. When the adding amount of activated carbon increased to 6% after Phase I, the FR of phenol had just raised by about 10%.

Phase III: technical limits state. When the adding amount of activated carbon was higher than 6%, the S/S efficiency could not be continuously improved. The FR of phenol fluctuated around 90% and 93% for 30% (w/w of soil) and 50% (w/w of soil) cement added specimens respectively. In other words, the technology had approached its limit.

Activated carbon could be used as adsorbent for the S/S of phenol, but the use of activated carbon in S/S treatment would increase the cost at the same time. Nevertheless, as well as the activated carbon performed in this research, it might be an attractive option in the emergency scenario to immobilize the phenol. Among these three phases, the cement/activated-carbon S/S technology was much more economic and technically feasible in phase 1 due to the low activated carbon addition, which might be considered firstly in practice. Careful balancing between the adding amount of activated carbon and cement was necessary to obtain the minimum phenol release and better economic feasibility. And future studies, like optimizing the mixing formula, modifying the curing conditions, should be made to improve the S/S efficiency in Phase I.

B. Long-term Leaching Behaviour

As shown in Fig. 2, during the leaching period of 123 days, more than 90% of phenol released occurred in the first 2 weeks. The leaching process could be seen to be an initial leach-out period followed by a slow diffusion controlled leach-out period. In general, phenol increasingly leached out with time at a decreasing rate. Similar phenol leaching patterns had been identified and reported in a modified TCLP test for cement-clay solidified/stabilized soil [2].

The total phenol released cumulated in the end of the long-term leaching test were shown in Table I. As expected, for samples cured for 28 days, the total amounts of phenol released decreased as the amount of activated carbon increased, and the total amount of phenol released was never greater than about one fifth of the total amount originally contained in the contaminated soil. But for samples cured for 7 days, the total amount of phenol released was higher than one third of the total amount originally contained in the contaminated soil, which could reach as high as 47%. And the total amount of phenol released of 1% activated carbon addition sample was more than the other two samples, which might be caused by the pore structures differences related to the adding of activated carbon. The matrix of cement without full hydration was difficult to retain phenol. Base on this phenomenon, it was very important to prevent the solidified/stabilized soil from acid rain exposure in the initial curing period.

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C. Pore Size Distribution

Fig. 3 showed the characteristic curves of the pore size distribution of 0%, 1% and 2% activated carbon addition specimens. It was possible to observe that the curves typically exhibited one peak in the diameter range of 38–40 Å. And the higher the activated carbon was added, the sharper was the peak. For 0%, 1% and 2% activated carbon addition specimens, the average pore diameters were 48.21nm, 22.62nm and 16.75nm respectively, which decreased as the adding amount of activated carbon increased. The differences of the pore size
distribution could explain part of the S/S efficiency improvement caused by the activated carbon.

![Figure 3. Pore size distribution of the solidified/stabilized soil (cement/soil ratio=0.5).](image)

Actually, phenol in the solidified/stabilized samples was generally adsorbed or encapsulated in the product matrix. On the one hand, the adding of activated carbon enhanced the phenol adsorbing and was beneficial for phenol immobilizing. On the other hand, the adding of activated carbon had a strong effect on the porosity of the solidified/stabilized samples, increasing the total porosity, which might lead to easily leaching out of phenol, because the most rapid diffusion of phenol in hydration cement matrices was through the pore network as a direct pathway.

Pore size distribution of the solidified/stabilized soil with cement/soil ratio of 0.5 and activated carbon addition of 2% before and after the long-term leaching test was also studied. As shown in Fig. 4, the leaching procedure influenced the pore size distribution, which increased the small pores (diameter =30-70 Å) and decreased the large pores (diameter>70 Å).

![Figure 4. Pore size distribution of the solidified/stabilized soil before and after the long-term leaching test](image)

The changes of the pore size distribution before and after the long-term leaching test might be caused by the reopening of the sealed pores formed in the S/S process during the leaching procedure, which was shown in Fig. 5. How this changes affect the leaching behavior of phenol in the long-term leaching test still need a further study.

![Figure 5. Schematic representation of the pore changes of solidified/stabilized soil before and after the long-term leaching test](image)

IV. CONCLUSIONS

The results showed that under the natural curing conditions, the phenol-containing soil could be effectively treated by the cement/activated-carbon S/S technology; very low amounts of activated carbon (less than 3% w/w of contaminated soil) could significantly improve the fixation ratios of phenol; the cumulative leaching ratio of 28 days cured samples were much lower than that of 7 days cured samples in the long-term leaching test, which indicated that it was very important to prevent the solidified/stabilized soil from acid rain exposure in the initial curing period; the adding of activated carbon had a strong effect on the porosity of the solidified/stabilized samples, increasing the total porosity, which might lead to easily leaching out of phenol; and careful balancing between the adding amount of activated carbon and cement was necessary to obtain the minimum phenol release and better economic feasibility.

REFERENCES