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Stabilization/solidification of nitrobenzene contaminated soil based on hydrophobilized CaO

S.Yu[a], R.Xu[a], L.Hou[a], M.Song[a], J.Liu[a,] *

[a]*School of Environment, Tsinghua University, Beijing, 100084, China*

Abstract

Lime, one of the common binders used in Solidification/Stabilization (S/S), is not adequate to immobilize toxic organic compounds of high-concentration released into soil by accidents in petrochemical and chemical industries. CaO, the main composition of lime, was hydrophobilized with stearic acid (SA) and silane coupling agent (KH570) to improve its fixation of nitrobenzene in S/S remediation of contaminated soil in present work, and the effect of hydrophobilized CaO on toxic organic compound encapsulation was evaluated through leaching and volatilization tests. Results showed that the binder composed of 20% SA hydrophobilized CaO together with 10% original CaO could reduce nitrobenzene's volatilization ratio to 0.096% and leaching ratio to 8.79%, while the nitrobenzene's volatilization ratio is 0.413% and leaching ratio is 35.48% with 30% original CaO as the binder.
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Keywords: Calcium oxide; hydrophobic modification; toxic organic compounds; contaminated soil; Solidification/Stabilization;

1. Introduction

With the rapid development of China, Sites are prone to be contaminated by high-concentration toxic organic compounds because of frequent pollution accidents in petrochemical and chemical industries. The common

* Corresponding author. Tel.: +86-010-6278-2029; fax: +86-010-6278-2029.
E-mail address: jgliu@tsinghua.edu.cn

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pollutants in soil include phenol, petroleum, polycyclic aromatic hydrocarbon(PAH), organic pesticide[1] To prevent compounds from doing harm to air, river and underground water after emergency, rapid immobilization is demanded to control their migration.

Solidification/Stabilization (S/S) is one of most widely used soil remediation methods[2,3]. Ordinary S/S usually uses lime, whose main element is CaO, as binder and focuses on heavy metal[4,5]. However, encapsulation of original CaO is not adequate to immobilize toxic organic compounds from polluted soil. It cannot ensure the long-time stability or prevent the volatilization of toxic organic compounds because of different chemical polarity between CaO and toxic organic compounds. Organic compounds are lipophilic and are hard to combine tightly with CaO, which results in the low fixation ratio in S/S of toxic organic compounds contaminated soil. Hydrophobic modification of CaO has been taken to enhance the ability to capture and fix toxic organic compounds as the surface modification makes CaO powder hydrophobic and lipophilic.

Hydrophobic modification has been studied for a long time[6] over the world and those studies concentrated mainly on chemical catalyze domain[7]. Hiromi Matsuhashi prepared solid base catalysts composed of CaO covered with 5-20% of Al_2O_3 by decomposition of $Al(OCH(CH_3)_2)_3$ over an $Ca(OH)_2$ surface in an ethyl acetate solution for a retro-aldol reaction to convert diacetone alcohol into acetone[8]. Sneha E. Mahesh modified CaO powder into hydrophobic using potassium bromide as catalysts for extracting biodiesel from waste cooking oil[9]. Kamegawa Takashi achieved hydrophobic modification of sulfonic acid-functionalized meaoporous silica for improvement of the catalytic performance in Fiedel-Crafts alkylation[10].In the present work, we investigated wet processes for hydrophobic modification of CaO powder with stearic acid (SA) and silane coupling agent (KH570).

In this work, hydrophobic modification technology, which is used in chemical catalyze domain widely，was applied to Solidification/Stabilization to enhance organic compounds’ adsorption, in order to improve the fixation of toxic organic compounds in soil in emergency treatment after accidents. A systematic S/S experiment using hydrophobilized CaO and original CaO together to immobilize the high-concentration nitrobenzene, which was selected as a representative of toxic organic compounds, has been taken to study the effects of hydrophobic CaO in S/S. Three indicators, including volatilization ratio, leaching ratio and fixation ratio, have been thought to evaluating the effect of immobilization.

2. Materials and methods

2.1. Materials

In this work, the main materials including CaO(AR), SA(AR), KH-570(AR), Nitrobenzene(AR), Methyl tertiary butyl ether (MTBE)(GR), Concentrated nitric acid(AR),Concentrated sulfuric acid.

The hydrophobilized CaO was produced in our lab experiment before, using SA or KH570 as a modifier. The optimum conditions for SA modification of CaO is 5% of SA (mass fraction) at 30 ℃ and with 30min, and the optimum conditions for KH570 modification of CaO is 0.02mL KH570 / g CaO at 30 ℃and with 40min.

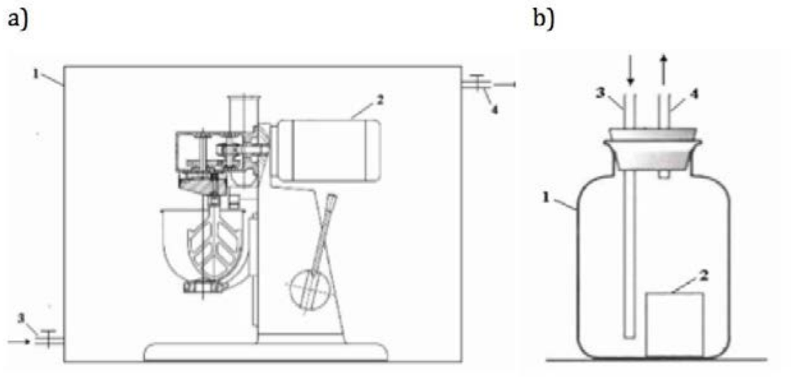
We used the soil from Tsinghua university campus, after 105℃ drying, screen-through 2 mm sieve. In this work we chose 10000mg nitrobenzene/kg soil as the experiment concentration, which is 100 times of standard for Class B in “Standard of Soil Quality Assessment for Exhibition Sites”(HJ350-2007). Nitrobenzene acetone solution, which is prepared at a certain amount, was poured into the drying soil. The mixture of soil and nitrobenzene acetone solution was putted in fume hood for 48h after what all acetone was volatilized. The contaminated soil sample was transferred to the brown bottle. Testing the concentration of nitrobenzene in soil before the experiment, the result is the initial concentration of nitrobenzene of contaminated soil sample

2.2. Equipment

Cement mixer (JJ-5, China); GC-MS (QP2010Plus, Shimadzu Japan); Air sampler (QC-1S, Beijing China); XRD (D8-Advance, BRUKER Germany); SEM (MERLIN VP Compact, Carl Zeiss Jena); FTIR (VERTEX 70v, BRUKER Germany).

2.3. Solidification/Stabilization experiment

Weighed quantities of soil sample, CaO and water were homogenized in blender. The prepared mixture was poured into seal bottle preparing for the test. Our study aims to control toxic organic compounds in soil for emergency, so we tested volatilization ratio, leaching ratio and fixation ratio of mixture after 3 days curing to evaluate the effect of immobilization. The equipment for stir and curing are arranged as Fig.1. Three factors were studied in our work as summarized in Table 1 and we arranged the materials following it.



1-seal box；2-blender；3-air in；4-air off 1-sea bottle；2-mixture；3-air in；4-air off

Fig. 1. (a) Equipment for stir; (b) Equipment for curing

Table 1. Factorial design experiment

No.	Mass of Soil (g)	Modifier	CaO Modified (mass %)	CaO (mass %)
S-1			10	20
S-2		SA	20	10
S-3			30	0
K-1	300		10	20
K-2		KH570	20	10
K-3			30	0
N		-	0	30
B		-	0	0

2.4. Evaluation test

The volatilization ratio (VR) of nitrobenzene came from both stir process (VR_1) and curing process (VR_2) in a S/S experiment. In this work, the volume of the seal box is 260L(not including the blender) and the volume of the seal bottle, which is used for curing, is 1L. The air sampler is used to collect the air for test. MTBE was chosen as absorption liquid in the absorption bottle, which is connected to the air sampler. In our work, the flow rate is settled 1L/min. This sampling lasted 10min for stir process and 20 min for curing process. The absorption liquid was measured both before and after the sampling and was transfer to seal plastic bottle to be kept at 4℃ and to be test by GC-MS in 72hours.

$$\mathrm{VR} = \mathrm{VR}_1 + \mathrm{VR}_2 \tag{1}$$

$$\mathrm{VR}_1 = \frac{\text{Mass of the organic compounds volatilized in stir process}}{\text{Mass of total organic compounds in the soil}} \times 100\% \tag{2}$$

$$\mathrm{VR}_2 = \frac{\text{Mass of the organic compounds volatilized in curing process}}{\text{Mass of total organic compounds in the soil}} \times 100\% \tag{3}$$

According to "Solid waste-Extraction procedure for leaching toxicity-sulphuric acid & nitric acid method"(HJ/T299-2007), selection of leaching liquor pH was 3.20±0.05 nitric acid solution, liquid solid ratio (L leaching liquid/kg solidified soli) was 10:1, and reverse oscillation time was for 18±2h. In this work, leaching liquor need go through 0.45μm membrane and be determined of MTBE before it entered GC-MS for testing. Leaching ratio (LR) is as the equation below.

$$\mathrm{LR} = \frac{\text{Mass of the organic compounds in the leaching liquid}}{\text{Mass of total organic compounds in the soil}} \times 100\% \tag{4}$$

Fixation Ratio （FR） means the amount of nitrobenzene immobilized in S/S experiment and is calculated like：

$$\mathrm{FR} \approx 100\% - \mathrm{VR} - \mathrm{LR} \tag{5}$$

3. Results and Discussion

3.1. Effect of Hydrophobilized CaO on nitrobenzene immobilization

The results of the testing before S/S experiment are shown in Table.2. There is 8093mg nitrobenzene/kg soil in our sample.

Table 2. Initial concentration of nitrobenzene

No.	Nitrobenzene (mg/kg soil)
1	8110
2	8080
3	8090
Average	8093

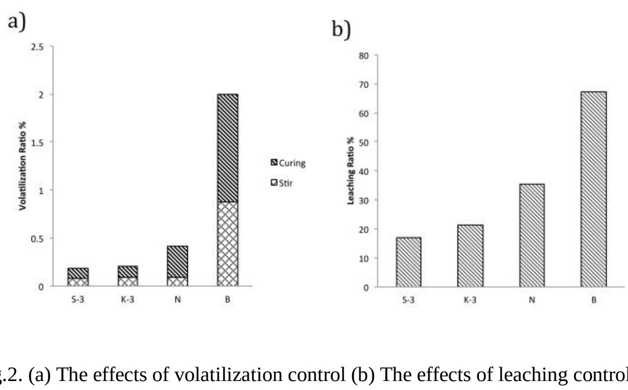


Fig.2. (a) The effects of volatilization control (b) The effects of leaching control

Hydrophobilized CaO has better effect on reducing volatilization and leaching of nitrobenzene than original CaO. Fig. 2 summarizes the results of S/S using hydrophobilized CaO. Compared to the group using original CaO (group N), whose VR was 0.413% and LR was 35.48%, using CaO modified by SA reduced VR to 0.1819% and LR to 16.91% and using CaO modified by KH570 reduced VR to 0.2083% and LR to 21.23%. Among the groups, group S-3, using CaO hydrophobilized by SA, had highest fixation ratio 82.91%. Also, CaO hydrophobilized by SA was more efficient than CaO hydrophobilized by KH570 in S/S experiment， whether in volatilization ratio or leaching ratio.

It proved that better immobilization ability came from hydrophobic surface characteristic of hydrophobilized CaO. As is known, original CaO immobilizes pollutant by its encapsulation. However the organic compounds like nitrobenzene are nonpolar so that they cannot bond with CaO tightly. After hydrophobic modification of CaO powder, organic groups are adsorbed to the surface of powder， and the hydrophobic surface can get better with nonpolar organic compounds leading to better immobilization effects.

3.2. Effect of Hydrophobilized CaO +Original CaO on nitrobenzene immobilization

Although hydrophobilized CaO could increase fixation ratio to 82.91%, it still let about 20% nitrobenzene get into other soil, water or air. Using hydrophobilized CaO with original CaO together can immobilize more nitrobenzene than only using hydrophobilized CaO.

Fig.3 summarizes the results of S/S experiment using original CaO together with CaO modified by SA. Hydrophobilized CaO addition reduced volatilization and leaching ratio than only using original CaO. The fixation ratio would change with different ratio between hydrophobilized CaO with original CaO. It is shown that 20% hydrophobilized CaO and 10% original CaO addition worked best, and could immobilize over 91.11% of nitrobenzene of our sample, which was over three times of group B’s soil itself. Compare to group N, only using original CaO, 75% nitrobenzene who can escape from S/S using original CaO would been controlled by hydrophobic CaO together with original CaO.

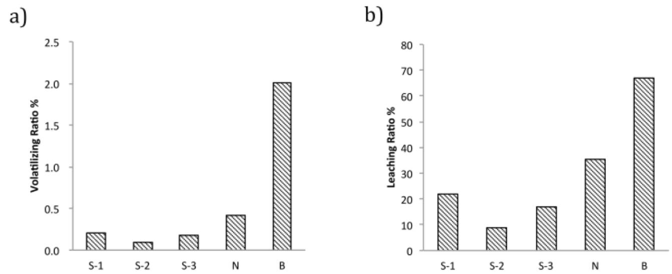


Fig.3. (a) The effects of volatilization control (b) The effects of leaching control

Fig.4 summarizes the results of S/S experiment using original CaO together with CaO modified by KH570. Compare with group B and group N, using original CaO together with hydrophobilized CaO reduced volatilization and leaching more effectively. The best is group K-2 consist of 20% hydrophobilized CaO and 10% original CaO, which is almost the same ratio as CaO modified by SA. This group’s fixation ratio was 89.19%, only 2% lower than S-2.

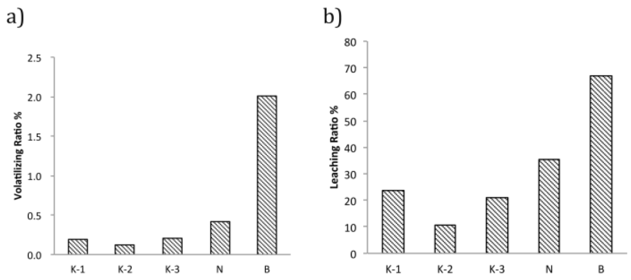


Fig.4. (a) The effects of volatilization (b) The effects of leaching

It is believed that hydrophobilized CaO and original CaO have different mechanism in immobilizing organic compounds. As we all know, CaO is a widely used binder because CaO can encapsulate contaminated soil to prevent toxic organic compounds from volatilizing or leaching. However the mechanism of hydrophobilized CaO is quite different. It is mentioned before hydrophobilized CaO is cover with organic groups from modifier over its surface. When we put hydrophobilized CaO with contaminated soil, the organic compounds would be adsorbed to surface of CaO with organic groups covered. The encapsulation of original CaO is a macro fixation while the adsorption of hydrophobilized CaO is a micro one. The cooperation of those two fixation mechanisms ensured the high fixation ratio in S/S experiment. And we suppose that the ratio between hydrophobilized CaO with original CaO is linked to the high concentration of nitrobenzene in soil.

4. Conclusion

In this work, S/S experiments of organic compounds contaminated soil based on hydrophobilized CaO were studied to find out the effects of hydrophobilized CaO. Hydrophobilized CaO can significantly strengthen the fixation of nitrobenzene in S/S remediation of contaminated soil. The volatilization ratio of nitrobenzene with 30% SA hydrophobilized CaO addition and 30% KH570 hydrophobilized CaO addition are 0.1819% and 0.2083% respectively and the leaching ratio of these two are 16.91% and 21.23, which shows the better effects of SA as the modificator. And the binder composed of 20% SA hydrophobilized CaO together with 10% original CaO could reduce nitrobenzene's volatilization ratio to 0.096% and leaching ratio to 8.79%, while the nitrobenzene's volatilization ratio is 0.413% and leaching ratio is 35.48% with 30% original CaO as the binder. The advantage of this combination comes from the cooperation of macro-fixation and micro-adsorption. Hydrophobilized CaO can be used in emergency cases for Solidification/Stabilization (S/S) of high concentrations of toxic organic pollutants contaminated soil.

5. Acknowledge

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