In Situ Chemical Stabilization of Arsenic-contaminated Soils Using Ferrous Sulfate

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Abstract — In this paper, a probe into the stabilization effects of ferrous sulfate (FeSO₄) came from two aspects-stabilization efficiency and leachate content. Fe/As molar ratio, arsenic pollution intensity, soil pH, reacted time interval, competitive ions, such as sulfate(SO₄²⁻), phosphate(PO₄³⁻) and zinc ion(Zn²⁺), were studied in order to discuss their effects on the stabilization of arsenic. Results show that, to all different levels of arsenic contaminated soils , when Fe/As molar ratio reaches 6, arsenic stabilization efficiency exceeds 90%, and arsenic concentration in leachate could also reduce to less than 5 mg/L; in the soil pH range from 8.10 to 8.57, ferrous sulfate has obtained the preferable results, and pH=8.23 is the optimum value; because of existing of competitive actions, the exogenous adding of SO₄²⁻, PO₄³⁻ and Zn²⁺ could lead to much poorer performance for FeSO₄.

Keywords- soils; arsenic; ferrous sulfate; stabilization efficiency; leachate content

1. INTRODUCTIONS

Arsenic is an element that is widely distributed in the earth's crust. It ranks twentieth among the elements in abundance in the earth's crust and is a major constituent of no fewer than 245 mineral species [1-2]. Arsenic and its compounds have been widely used in the productions of alloy, dyes, pesticides, preservatives and so on [3]. With the development of arsenic industries, leakage - fire - explosion of chemicals containing arsenic may happen at times, which would easily induce serious environmental pollution accident. Once it happens, environment and people may suffer a lot. Due to the high toxicity of arsenic, it’s necessary to adopt emergent measures to control pollution after the accident. At the same time, contaminated sites also need to be quickly remedied, so as to reduce the pollution degree and pollution range to the minimum.

At present, major technologies for remediation of heavy-metal contaminated soils include physicochemical method and biological method. In situ chemical solidification/stabilization (S/S) belongs to the former, which has two aspects. One hand, chemical ways are used to decrease the solubility and extractability of heavy metal in the soil; on the other hand, physical ways are used to make the contaminated soils embedded in a hard matrix [4]. Chemical stabilization can be considered a part of the S/S method. Because of cost-effective and time-feasible, chemical stabilization is given much attention. The choice of immobilizing amendments depends on the type of soil contaminants, affinity with soils usually considered as the major factor [5-6]. In the aspect of arsenic stabilization, many researches pay their attention to the water area, sludge and waste residue, and choose iron compounds as stabilizing agents. A study by Krause and Et al showed that arsenic can form relatively insoluble ferric iron compounds, which have solubility products on the order of 10⁻²⁰ to 10⁻²⁴ [7]. Carlson et al. revealed that the mobility of arsenic can be reduced by the formation of amorphous iron (III) arsenate (FeAsO₄ • H₂O) and/or insoluble secondary oxidation minerals, e.g. scorodite (FeAsO₄ • 2H₂O) [8]. It is generally believed that iron (III) and arsenate As (V), may be the most stable for arsenic existing [9].

On the base of the previous studies, this experiment chose ferrous sulfate as the immobilizing amendments for As. Simultaneously, Fe/As molar ratio, arsenic pollution intensity, soil pH, reacted time interval, competitive ions, such as sulfate, phosphate and zinc iron, were studied in order to discuss their effects on the stabilization of arsenic.¹

2. MATERIALS AND METHODS

2.1. Experimental Materials

First-level experimental soils were collected in Haidian District of Beijing. After pretreatment, et al. air-dried, removal of sundries and crushed, the samples were thoroughly homogenized by hand and passed through a 100 mesh sieve. Some properties of soils are displayed in Table1. Second-level

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experimental soils were prepared by the exogenous adding of sodium arsenite (NaAsO$_2$) to the first-level, which had the mean concentration of available arsenic 1196 mg/kg.

<table>
<thead>
<tr>
<th>Collected area</th>
<th>Type of soils</th>
<th>pH(CaCl$_2$)</th>
<th>TOC(%)</th>
<th>CEC(cmol·kg$^{-1}$)</th>
<th>Total amount of clay minerals (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haidian District</td>
<td>brown soil</td>
<td>7.85</td>
<td>1.40</td>
<td>7.74</td>
<td>21.3</td>
</tr>
</tbody>
</table>

2.2. Study Methods

1) Experimental methods

a) Stabilization experiment: Beaker test was adopted. Contents of reagent chemical FeSO$_4$ was decided according to the total soil arsenic concentration, which chose the type of Fe/As molar ratio. Each experiment was performed at a soil:solution ratio of 0.5, using 1 day of cure time.

b) Preparation for leachate: According to moisture content of samples, experiment was conducted by mixing 150g samples of contaminated soil containing stabilizing agents with leaching solution (prepared by concentrated sulfuric acid and concentrated nitric acid, having a mass ratio of 2:1, then added deionized water to adjust pH value at 3.20±0.05) in 2 liter polypropylene bottles. Oscillate the bottles on the rotating oscillator with a speed at 30±2 r/min, time at 18±2 h. Detailed methods of preparation for arsenic leachate was according to 《Identification standards for hazardous wastes-Identification for extraction toxicity》 (GB 5085.3-2007).

2) Analysis and determination methods

First, arsenic leachate passed through a device called arsine generator, which could be seen in Figure 1. Second, Arsenic content in leachate was determined by Ag-DDC spectrophotometry.

3) Standard testing for stabilizing agent

Two standards had to be met, one was that the stabilization efficiency must reach 90% above, the other was arsenic concentration in leachate must be kept 5 mg/L(GB 5085.3-2007) below.

3. Results and Discussion

3.1. Effect of Fe/As Molar Ratio on Stabilization of Ferrous Sulfate to Arsenic

Figure 2 shows the variation of stabilization efficiency (SE) and leachate content (LC) with Fe/As molar ratio. With the increasing of Fe/As molar ratio, the stabilization effects of ferrous sulfate become better. Especially, when Fe/As<6, stabilization efficiency can rise to 94.67% from 62.02% quickly. At the same time, leachate content displays a sharp drop, with the value at 20.93mg/L dropping to 2.94 mg/L. When Fe/As≥6, the increasing/decreasing tendency becomes no obvious. When Fe/As molar ratio reaches 20, compared to Fe/As=6, stabilization efficiency / leachate content just has changed 3.53% or 1.95 mg/L respectively. Therefore, as for the slightly or moderately contaminated brown soils with pH at meta-alkalescence conditions, Fe/As = 6 will meet the two standards. But considering the real soils, Fe/As molar ratio should be adjusted appropriately depending on the soil type and pollution intensity.

3.2. Effect of Pollution Intensity on Stabilization of Ferrous Sulfate to Arsenic

Curved lines in Figure 3 indicate that with the increasing of arsenic pollution intensity, FeSO$_4$ stabilization efficiency and arsenic content in leachate both show no regularities. Though the arsenic concentration in soils is as 100 times as the limit of the China Soil Environmental Quality Standard III (upland soils,40mg/kg), after the adding of FeSO$_4$(Fe/As=6), stabilization efficiency can reach 99.71%. At the same time,
value of arsenic content in leachate is only 1.22mg/L. As for the pollution intensity of 1187mg/kg, under the same conditions, stabilization efficiency and leachate content can only reach 97.22% and 3.30mg/L, respectively. Thus, a conclusion can be drawn that Fe/As = 6 may meet the demand that different concentrations of arsenic contaminated soils need. Because of differences in soil type, soil structure and soil pH et al., during the real application demonstration project, all the factors mentioned would be considered. Hence, it is common that Fe/As molar ratio has to be changed moderately.

3.3. Effect of Soil pH on Stabilization of Ferrous Sulfate to Arsenic

Soil acid-base conditions play an important part on stabilization course. In this experiment, soil pH was adjusted by the change of amount of quicklime, i.e. Ca/As molar ratio. The relations between Ca/As molar ratio and soil pH are showed in Figure 4. It shows that, under the condition of only having quicklime, soil pH increases continuously with the increasing Ca/As molar ratio. Effect of soil pH on stabilization of ferrous sulfate to arsenic can be observed in Figure 5. In terms of Figure 5, when keeping Fe/As=6, in the soil pH range from 8.10 to 8.57, arsenic stabilization efficiency could exceed 90% completely, and arsenic concentration in leachate could also reduce to less than 5 mg/L simultaneously. 8.23 was the optimum pH value. Ferrous sulfate had obtained the best results at pH=8.23.

3.4. Effect of Reacted Time Interval on Stabilization of Ferrous Sulfate to Arsenic

In order to better evaluate the effectiveness and stability of the stabilization reagent ferrous sulfate, it is necessary to check effect of reacted time interval on chemical stabilization process, which can be illustrated by Figure 6. During the 30 days' observation, there were undetectable changes in two evaluation index in chemical stabilization treatment. In the second day, stabilization efficiency and leachate content both obtained the satisfied results, with 99.42% and 0.70mg/L, respectively. Though the results of the 15th day showed somewhat poor, stabilization efficiency and arsenic content in leachate both met the requested standards. All above observed indicates that insoluble arsenic-bearing phases formed just in one day's time. Another point which can also be illustrated is that the newly formed insoluble Fe-As compounds have higher stability.

3.5. Effect of Competitive Ions on Stabilization of Ferrous Sulfate to Arsenic

1) Effect of sulfate on stabilization of ferrous sulfate to arsenic

Total sulphur content in China is about 100~500mg/kg, but most of the soil soluble sulfate is below 25% of total sulfur. Surface soil may have about 10% or even less. In this study, SO\textsubscript{4}\textsuperscript{2-} was added in the form of Na\textsubscript{2}SO\textsubscript{4}. Under the conditions of Fe/As=6, effect of exogenous SO\textsubscript{4}\textsuperscript{2-} on stabilization of FeSO\textsubscript{4} is shown in Figure 7. Within the sulfate content 50mg/kg, stabilization efficiency falls to 98.61% from 99.49%.
At the same time, leachate content goes up to 2.71 mg/L from 1.02mg/L. Under the conditions of higher exogenous $\text{SO}_4^{2-}$ concentrations, though stabilization efficiency and leachate content show no regularities, the existing of $\text{SO}_4^{2-}$ has already affected the stabilization effects of FeSO$_4$. Which can be explained by the competitive adsorption between $\text{SO}_4^{2-}$ and HnAsO$_4^{n-3}$ in the soil.

2) Effect of phosphate on stabilization of ferrous sulfate to arsenic

Exogenous $\text{PO}_4^{3-}$ was added in the form of Na$_3$HPO$_4$. Figure 8 shows that with the increasing of phosphate concentration, the stabilization effects of FeSO$_4$ decline gradually. If $\text{PO}_4^{3-}$ concentration kept higher, then stabilization efficiency of FeSO$_4$ becomes lower. Compared with condition of no exogenous $\text{PO}_4^{3-}$, when $\text{PO}_4^{3-}$ concentration reaches 5000mg/kg, stabilization efficiency can fall to 98.61% from 99.49%. At the same time, arsenic content in leachate rises to 3.59 mg/L from 1.09mg/L. In calcareous soils, $\text{HPO}_4^{2-}$ has already affected the stabilization effects of FeSO$_4$. Which can be explained by the competitive adsorption between $\text{SO}_4^{2-}$ and $\text{HPO}_4^{2-}$.

3) Effect of zinc ion on stabilizing of ferrous sulfate to arsenic

Exogenous zinc was added in the form of ZnCl$_2$. Different concentration levels of $\text{Zn}^{2+}$ bring negative influence on the stabilization effects, which can be shown in Figure 9. With the growing of $\text{Zn}^{2+}$ concentration, stabilization efficiency and arsenic content in leachate go to the adverse direction. Especially, when the $\text{Zn}^{2+}$ concentration is 20mg/kg, stabilization efficiency and leachate content have the lowest and highest value of 96.67% and 3.98mg/L. Similar to Fe(Ⅱ)/Fe(Ⅲ), $\text{Zn}^{2+}$ can combine with As(Ⅲ)/AsO$_4^{3-}$ competitively.

4. CONCLUSIONS

(1) Ferrous sulfate is a kind of relatively effective amendment for arsenic. It would have obvious effects on the soils with different pollution intensity, only when Fe/As molar ratio is appropriate. With the increasing of Fe/As molar ratio, the stabilization effects of FeSO$_4$ become better. Generally, Fe/As=6 can meet the two standards simultaneously. But considering the real soils, Fe/As molar ratio should be adjusted appropriately according to the soil type and pollution intensity, so as to meet the demand of technology and economy.

(2) The optimum soil pH is 8.23, corresponding to Ca/As molar ratio of 1.5. The chemical immobilizing effects become more effective on this condition. The meta-alkalescence conditions are beneficial to stabilization in this experiment, when keeping Fe/As=6, in the soil pH range from 8.10 to 8.57, he fairly good stabilization effects of FeSO$_4$ have been obtained.

(3) As the stabilization reagent for arsenic contaminated soils, after about one day, chemical stabilization reaction between different types of arsenic in the soil and Fe(Ⅱ)/Fe(Ⅲ) had already achieved, with stabilization efficiency 99.28% and leachate content 0.86mg/L. During the 30 days' observation, though experiment results had slight fluctuations, which remained above 98% and beneath 1mg/L respectively. Therefore, a conclusion can be drawn that ferrous sulfate is a kind of effective stabilization reagent for arsenic.

(4) The exogenous adding of $\text{SO}_4^{2-}$, $\text{PO}_4^{3-}$ and $\text{Zn}^{2+}$ could lead to much poorer performance for FeSO$_4$. Especially, as for $\text{PO}_4^{3-}$, it can limit the action of stabilizing agent, because of the formation of Ca-P and Fe-P compounds. With the increasing of $\text{PO}_4^{3-}$ concentration, the stabilization effects of FeSO$_4$ decline gradually. In this study, the arsenic immobilizing efficiency decreases from 99.4% to 98.16% as the concentration increases from 0mg/kg to 5000mg/kg. Meanwhile, arsenic content in leachate increases from 1.09mg/L to 3.59mg/L.

5. SUGGESTIONS

During the study of stabilization of arsenic contaminated soils, besides the factors e.g Fe/As molar ratio, soil pH, competitive ions et al, mixing intensity between stabilization reagent and contaminated soils, reasonable ratio of solid to liquid are also worth considering. These factors mentioned above may play an important part in the real application demonstration project. In addition, soil pollution is not only a single kind of heavy metal pollution, but refers to mixed metal...
or metal-organic combined pollution. Therefore, composite stabilizer has to be given special attention in future.

REFERENCES


