Remediation of As and Cd contaminations by composite material additives in smelting site soil

Xuewu Hu1,2,3,4,5,a, Juan Zhong1,3,4,b, Xingyu Liu1,3,4,e, Xinglan Cui1,3,4,d, Mingjiang Zhang1,3,4,e, Ying Lv1,2,3,4,5,f, Daozhi Ma 1,3,4,g, Xiao Yan1,3,4,h

1National Engineering Laboratory of Biohydrometallurgy, GRINM Group Co., Ltd., Beijing, 100088, China
2School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing, 100083, China
3GRINM Resources and Environment Tech. Co., Ltd. Beijing, 101407, China
4General Research Institute for Nonferrous Metals, Beijing, 100088, China
5GRIMAT Engineering Institute Co., Ltd., Beijing 101407, China
aemail: huxuewu9@163.com, bemail: zhongjuan9574@163.com,
demail: cxl-cxl0521@163.com, eemail: zmj0630@163.com,
eemail: lvying940904@163.com, femail: 1046433955@qq.com,
gemail: yx1443349211@163.com

*Corresponding author’s cemail: liuxy@grinm.com

Abstract: Arsenic (As) and cadmium (Cd) in soil is a serious environmental issue. Exploring an efficient method for simultaneous immobilization of As and Cd in soils is of great significance. In this study, three types of composite material additives were selected to test their ability to immobilization of As and Cd simultaneously in soil of smelting site through leaching toxicity. Results showed that Fe-based composite material additives (SD) significantly reduced concentrations of As and Cd in solutions from SD1 and SD2 treated soils, signifying that certain Fe-based composite material potentially immobilization heavy metals in soil. While Ca-Mg-Si based composite material additives (C) and Si-Mg-Al based composite material additives (S) have a side effect in As immobilization. The conclusions were that Fe-based composite material may be used as effective in situ amendments to immobilization As and Cd simultaneously in soils.

1. Introduction
Soil heavy metal contamination always caused seriously hazard to ecological environment and human health, among which arsenic (As) and cadmium (Cd) are the most toxic heavy metals/metalloids[1]. Long-term Cd exposure to humans have been widely reported to induce adverse health diseases, such as liver cancer, kidney failure, and retardation of bone metabolism. As poisoning can also cause serious damage to most multicellular lives[2]. Therefore, reduction of As and Cd concentrations in soil is important for human health.

Arsenic and cadmium frequently coexist in the environment, and often found released together into...
the surrounding environment in mining and smelting process. Both of them will be deposited and accumulated in the soil, resulting in extremely high concentrations in soil sites. The solubility and bioavailability of As and Cd in soil mainly depend on soil Eh and pH. Arsenic is usually existed in the form of negatively charged HAsO$_{4}^{2-}$ and HAsO$_{2}^{3-}$ in soil, while the predominant form of Cd is Cd$^{2+}$. With the increased of soil pH value, the adsorption amount of As in the soil is decreased, solubilized As is vigorously increased$^{[3]}$. While the solubility of cadmium showed an opposite trend. Previous research found that the addition of some soil amendments increased the pH values and decreased the zinc, cadmium, copper, and lead concentrations while increasing the arsenic concentrations in solutions$^{[4]}$. Thus, it is difficult to reduce the mobility of these two elements simultaneously by changing the soil pH with a single chemical agent. It is essential to develop composite remediation materials for arsenic and cadmium contaminated soil.

Although normally amendments, such as amorphous Al oxides, Fe/Mn oxides or oxyhydroxides, lime, silica, phyllosilicates have been widely applied to the remediation of heavy metal contaminated soils. However, their drawbacks are also obvious. Lime can increase soil pH and decrease heavy metal solubility. However, continuous application of lime could damage the soil aggregate structure, and cause soil hardening, ultimately affect the growth of crops$^{[5]}$. Researchers found that the application of composite material additives have a higher immobilization effect on reducing soil heavy metal availability than sole amendment$^{[6]}$. In this study, three types of composite material additives were selected to test their ability to immobilization of As and Cd simultaneously in soil of smelting site. The primary objectives of this study were (1) to obtain a composite material with higher immobilization efficiency for As and Cd contamination, and (2) to analyze the immobilization mechanism of the composite material additives for As and Cd in soil.

## 2. Materials and methods

### 2.1. Experimental materials

The heavy metal contaminated soil was collected from the smelting site of Qingshuitang Industrial Zone, Zhuzhou City, Hunan Province. The soil was naturally air-dried and mixed evenly through a 2mm nylon sieve for remediation experiments. The soil amendments used in this study were the following: Fe-based composite material additives (SD), Ca-Mg-Si based composite material additives (C), and Si-Mg-Al based composite material additives (S).

### 2.2. Soil Analysis

Soil pH was measured using a calibrated pH meter at a ratio of 1:2.5 (W/V)$^{[7]}$. Soil heavy metal content was determined by inductively coupled plasma mass spectrometry (ICP-MS). The leaching toxicity of heavy metals in soil was detected by sulfuric acid and nitric acid method.

### 2.3. Experimental design

The experiment scheme of the soil was presented in Table 1. The experiment was conducted in

| Groups | Soil (g) | SD(wt/%) | C(wt/%) | S(wt/%) |
|--------|----------|----------|---------|---------|
| SD1    | 50       | 0.8      | 0       | 0       |
| SD2    | 50       | 0.16     | 0       | 0       |
| SD3    | 50       | 0.24     | 0       | 0       |
| C-1    | 50       | 0        | 0.4     | 0       |
| C-2    | 50       | 0        | 0.8     | 0       |
| S-1    | 50       | 0        | 0       | 0.4     |
| S-2    | 50       | 0        | 0       | 0.8     |
| CK     | 50       | 0        | 0       | 0       |
conical flasks at 30 °C for 7 days. The contaminated soils were amended with different composite material additives and deionized water to maintain the soil with a saturated moisture content. All treatments and control (CK, without amend with composite material additives) were performed in triplicate. After curing for 7 days, soil samples were taken for further analyze the leaching toxicity of As and Cd.

2.4. Statistical analysis
Statistical analysis was performed using the software package OriginPro 2017. Multiple comparisons between individual means were determined using Tukey’s test (P < 0.05).

3. Results and discussion
The soil used in this study was highly polluted (Table 2), with total concentrations of As, Cd and Pb between 5 and 24 times higher than baselines proposed by China. According to the current Chinese national standards for groundwater quality, the leaching concentration of As and Cd exceeds the groundwater Ⅳ standard, in which As exceeds 40.2 times and Cd exceeds 22 times.

|                 | As   | Cd   | Cr   | Cu   | Pb   | Sb   | Zn   |
|-----------------|------|------|------|------|------|------|------|
| Total concentrations (mg/kg) | 1421.09 | 340.23 | 50.42 | 1503.14 | 7513.36 | 97.05 | 13204.13 |
| Leaching contents (mg/L)     | 2.01  | 0.22 | L    | L    | L    | 1.28 |      |

After 7 days of reaction, the pH value of the soil was shown in Figure 1. The pH value of all the remediation groups presented a increasing trend and increased from 6 to approximately 7.0, while in the control group pH was remained at about 6.0 all the time. The results indicated that the addition of these composite materials did not lead to soil acidification.

The leaching concentrations of Cd and Cu in soil were clearly affected by the addition of composite material amendments (Figure 2). The addition of Fe-based composite material additives promoted the immobilization of As and Cd in solution. The concentrations of As in the leaching solution decreased with the increased dosage of SD (0.8~2.4 wt%), and SD3 treatment showed the maximum immobilization rates of 66.04% with the addition of 2.4 wt% SD. When added lower levels of SD can
promote the immobilization of Cd in the solution, but further increased of SD concentration, the immobilization rate of Cd decreased greatly. In order to achieve better efficiency of simultaneous immobilization of As and Cd, the optimal addition amount of SD is 1.6 wt%, and the immobilization rate of As and Cd is 56.7% and 22.62%, respectively. The C and S treatment groups showed a difference tendency in immobilization of As and Cd from SD. With the increase of the addition amount of the two materials, the concentration of As in the leached solution increased greatly and was much higher than that in the control group, which indicated that C and S had adverse effect on the immobilization of As. However, C and S exhibited good immobilization effects on Cd. The optimal immobilization efficiency in C1(0.4 wt%) and S2(0.8 wt%) treatment was 52.51% and 65.17%, respectively.

Hartley et al. [8] suggested that iron oxides can oxidize As(III) to As(V) and adsorb As(V) on its surface in the form of complexes, thus reduced concentrations of As in treated contaminated soils. However, higher levels of Pb and Cd were also observed in treated soils. This is similar to our research results, Fe-based composite material additives have a better effect on As immobilization. However, our study found that lower levels of SD can reduce the leaching concentration of Cd, which may be due to the adsorption effect of the SD material on Cd. With the increase of SD additive amount, the cationic adsorption sites on the surface of soil particles were occupied by Mg2+, Ca2+ and other cations in the SD, which resulted in the poor immobilization effect on Cd2+ adsorption.

![Figure 2. Soil leaching concentrations of As and Cd after remediation](image)

**4. Conclusions**

Three different composite materials were prepared to explore the remediation effect of heavy metal contaminated soil in smelting site, results showed that the Fe-based composite material SD can immobilization As and Cd in the heavy metal contaminated soil at the same time. With the increase of SD additive amount, the concentrations of arsenic in solutions was reduced and the concentrations of Cd was increased. In order to achieve a better effect of simultaneous immobilization of As and Cd, the optimal content of SD was 1.6 wt%, and the immobilization rates of As and Cd were 56.7% and 22.62%, respectively. Ca-Mg-Si based (C) and Si-Mg-Al (S) based composite materials significantly reduced concentrations of Cd in solutions while increased As mobility in treated soils. The optimal immobilization efficiency in C1(0.4 wt%) and S2(0.8 wt%) treatment was 52.51% and 65.17%, respectively.
Acknowledgments
This research was funded by the National Natural Science Foundation of China [grant numbers 51974279, U1402234, and 41573074], the National Key Research and & Development Program of China [grant numbers 2018YFC18018, 2018YFC18027, 2019YFC1805903], KeJunPing [2018] No. 159, the Guangxi Scientific Research and Technology Development Plan [grants number GuikeAB16380287 and GuikeAB17129025], GRINM Science and Development [grants number2020 No 75].

References
[1] Maity, J., Nath, B., Kar, S., Chen C.Y, Banerjee, S., Jean, J.S., Liu, M.Y., Centeno, J.A., Bhattacharya, P., Chang, C.L., Santra, S.C. (2012) Arsenic-induced health crisis in peri-urban Moyna and Ardebok villages, West Bengal, India: an exposure assessment study. Environ Geochem Health 34: 563-74.
[2] Moitra, S., Ghosh, J., Firdous, J., Bandyopadhyay, A., Mondal, M., Biswas, J.K., Sahu, S., Bhattacharyya, S., Moitra, S. (2018) Exposure to heavy metals alters the surface topology of alveolar macrophages and induces respiratory dysfunction among Indian metal arc-welders. Toxicol Ind Health 34: 908-921.
[3] Gu, J.F., Zhou, H., Tang, H.L., Yang, W.T., Zeng, M., Liu, Z.M., Peng, P.Q., Liao, B.H. (2019) Cadmium and arsenic accumulation during the rice growth period under in situ remediation. Ecotoxicol Environ Saf 171: 451-459.
[4] Gonzalez, V., Garcia, I., Del Moral, F., Simon, M. (2012) Effectiveness of amendments on the spread and phytotoxicity of contaminants in metal-arsenic polluted soil. J Hazard Mater 205-206: 72-80.
[5] Gong, L., Wang, J., Abbas, T., Zhang, Q., Cai, M., Tahir, M., Wu, D., Di, H. (2021) Immobilization of exchangeable Cd in soil using mixed amendment and its effect on soil microbial communities under paddy upland rotation system. Chemosphere 262:127828.
[6] Friesl-Hanl, W., Platzer, K., Horak, O., Gerzabek, M.H. (2009) Immobilising of Cd, Pb, and Zn contaminated arable soils close to a former Pb/Zn smelter: a field study in Austria over 5 years. Environ Geochem Health 31: 581-94.
[7] Liu, Y.R., Wang, J.J., Zheng, Y.M., Zhang, L.M., He, J.Z. (2014) Patterns of bacterial diversity along a long-term mercury-contaminated gradient in the paddy soils. Microb Ecol 68: 575-83.
[8] Hartley, W., Edwards, R., Lepp, N.W. (2004) Arsenic and heavy metal mobility in iron oxide-amended contaminated soils as evaluated by short- and long-term leaching tests. Environ Pollut 131: 495-504.