# Preparation of one-part geopolymers for heavy metal immobilization from waste leachate concentrate

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Geopolymer solidification/stabilization (S/S) technology has rapidly developed in recent years as an effective remediation method for heavy metal-contaminated soil (Ji and Pei, 2019). However, geopolymers typically exhibit low efficiency in fixing anionic heavy metals due to their electronegativity and alkali-activation characteristics. To overcome this limitation, a one-part geopolymer system was constructed using landfill leachate concentrate (LLC) as a source of Cl and humic acid to immobilize cationic (Cd, Cu, Hg, Pb, and Zn) and anionic heavy metals (Sb and As) simultaneously in antimony mine soil (AMS). With the addition of LLC, the fixation rates of anionic heavy metals (Sb and As) increased from 92%~94% and 82%~86% to over 99%, respectively, achieving a fixation rate of over 99% for all heavy metals in AMS. LLC improves the chemical stability and physical encapsulation of Sb/As by inducing the formation of Friedel's salt, humic acid complexing/chelating, and promoting geopolymerization. Wet curing is more conducive to forming Friedel's salt in the geopolymer, increasing the 28-day compressive strength by 38.5% compared to dry curing. The results demonstrate a harmless treatment method for co-disposing LLC and industrial byproducts, and enhance the efficiency of geopolymers in complex heavy metal S/S.

## Materials and methods

LLC is a nanofiltration concentrate obtained from treating leachate from a domestic waste landfill in Tianjin, China (Table 1). Resin separation results revealed that the primary components of dissolved organic matter (DOM) in LLC are hydrophobic fulvic acid (FA) at 64.3%, humin (HS) at 17.0%, and humic acid (HA) at 14.2% (Fig. 1a). LLC shows a strong fluorescence peak in zone III (fulvic acid-like) (Fig. 1b). AMS is sourced from the top 10 cm of soil around an antimony mine in Guizhou province, China, and contains significant amounts of extractable As, Cd, Cu, Hg, Pb, Sb, and Zn (Fig. 1c and 1d). One-part geopolymer (SBGP-LLC) is produced by using ground blast furnace slag activated by powder sodium silicate and sodium hydroxide, with LLC as the only solvent (Zhang et al., 2021). Compared to traditional geopolymer, one-part geopolymer avoids the use of corrosive and viscous alkali solutions and enhances the treatment capacity of LLC with a high water-solid ratio of 0.45~0.60.

Table 1. Characterization results of landfill leachate concentrate.

| Parameters | LLC (mg $L^{-1}$) | Parameters | LLC (mg $L^{-1}$) |
|---|---|---|---|
| $COD_{Cr}$ | 3873.6 | Cd | N.D. |
| $BOD_5$ | 382.0 | Pb | N.D. |
| TOC | 814.3 | Cr | 0.081 |
| $NH_3$-N | 72.4 | As | 0.044 |
| TDS | 89300 | Hg | N.D. |
| $Cl^-$ | 5759.2 | Cu | 0.024 |
| $SO_4^{2-}$ | 276.3 | | |

N.D. represents sample concentration below the detection limit.

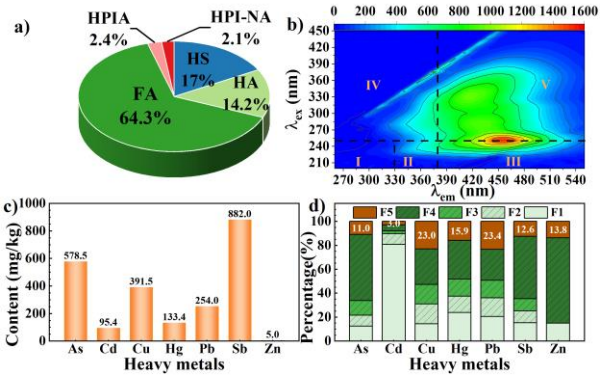


Figure 1. Characterization of (a-b) landfill leachate concentrate and (c-d) antimony mine soil.

## Results and Discussion

*Strength and characteristics of the prepared geopolymers.* Adequate compressive strength guarantees the subsequent treatment of geopolymers. Proper AMS content (10%~30%) increases the unconfined compressive strength (UCS) of SBGP-LLC (17.1 MPa), which is attributed to the skeleton support of $SiO_2$ in AMS, but the excessive AMS adversely affects the UCS (Fig. 2a). As high-salinity wastewater, LLC contains a considerable amount of Cl, which promotes the formation of Friedel's salt and enhances the strength of the geopolymer. By adding LLC, the UCS of SBGP increased by 13.8%~27.6% (Fig. 2b). The wet curing process is more conducive to formation of Friedel's salt and further improves the UCS of geopolymer by 38.5%~50.2% (Fig. 2c). The microscopic characterization proved that hydrated calcium silicate (C-S-H) and hydrated aluminium calcium silicate (C-A-S-H) gels were formed in the prepared geopolymer, and the peak of Friedel's salt is more obvious under wet curing (Fig. 2d).

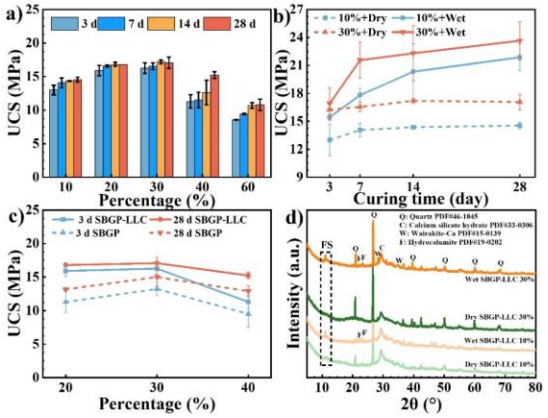


Figure 2. Strength and characteristics of the prepared geopolymers.

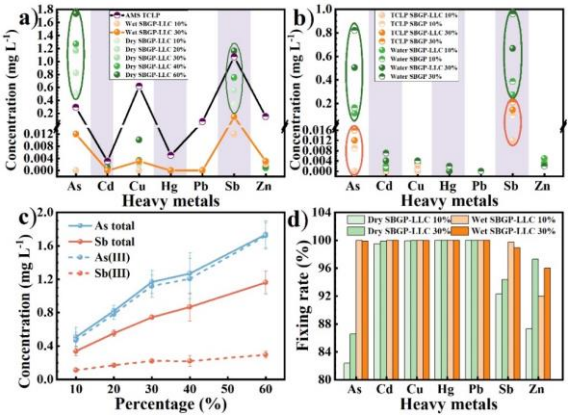


Figure 3. Leaching test results of the prepared geopolymers.

*The heavy metal immobilization efficiency of the prepared geopolymers.* Stability is another factor in determining the disposal method of solidified geopolymer blocks. The leaching test results showed that LLC and AMS can be efficiently co-disposed by the geopolymer system (Fig. 3). The addition of 30% AMS has resulted in the optimum UCS and heavy metal fixation rates. The fixation rates of Cd, Cu, Hg, Pb, and Zn under dry or wet curing conditions are more than 99%, demonstrating the excellent passivation effect of the geopolymer on cationic heavy metals. More importantly, the addition of LLC significantly improved the fixation rates of anionic heavy metals (Sb and As). The fixation rates of Sb increased from 92%~94% to 99~100%, while As increased from 82~86% to 99%~100%.

*The immobilization mechanism of Sb and As by the prepared geopolymers.* To investigate the reaction behavior between Friedel's salt and Sb/As, Friedel's salt was prepared by co-precipitation under alkaline conditions (Zhang et al., 2011). Kinetic and isothermal adsorption experiments have demonstrated that Friedel's salt can quickly immobilize Sb and As on the surface through chemical adsorption (Fig. 4a and 4b). In addition, after adding alkali ($NaOH/Ca(OH)_2$), Sb/As and humic acid precipitate synchronously in LLC, resulting in alkali-promoted ternary complexation (Fig. 4c and 4d). Therefore, when Sb/As in AMS dissolves under alkali conditions, the Friedel's salt formed in the prepared geopolymers and the humic acid in LLC can form stable compounds with them. These stable compounds can be further physically encapsulated in the dense geopolymer structure.

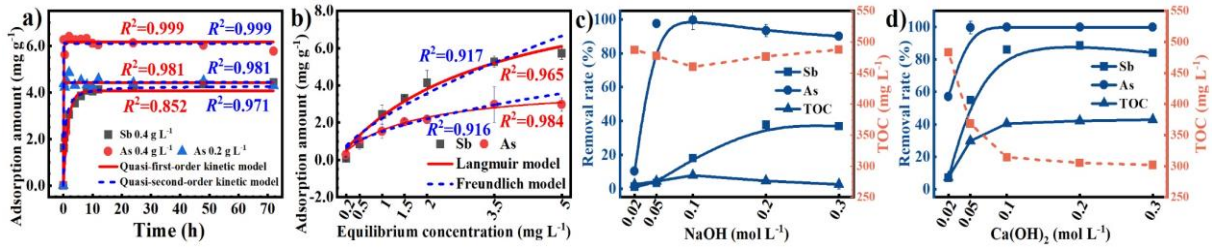


Figure 4. The results of Friedel's salts adsorption (a, b) and humic acid complexation (c, d) of Sb/As.

## Conclusions

The addition of LLC could induce the formation of Friedel's salt in the geopolymer system, thereby enhancing the immobilization efficiency of anionic heavy metals (Sb and As), and enabling the synergistic immobilization of both anionic and cationic heavy metals.


## Acknowledgements

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## References


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