Supporting Information

Sustainable Immobilization of Zn, Pb, and As in Lead Smelting Slag via Fe-S(II) Microencapsulation for Heavy Metal Recycling and Environmental Remediation

1. Elemental and Mineral Composition of Lead Refining Waste

The samples were taken from a waste slag dump in the city of Gejiu, Yunnan Province, which is the lead smelting waste slag from the blast furnace, located at the top of the foothill terrain area, covering an area of 46,775.40 m^2, with a stockpile volume of about 1,260,000 t, and has been stockpiled for nearly 20 years in an open environment with no vegetative cover. The area where it is located is about 2000 m above sea level and belongs to the humid monsoon type of subtropical mountains, with an average annual temperature of 15.9℃ and an average annual rainfall of 1080 mm. With this kind of stockpiling method, location, and regional environmental characteristics, the heavy metals in lead slag are very easily released and migrate to the soil–water body downstream of the slag pile under the effect of rainfall and leaching, resulting in a series of environmental pollution risks. Separate samples were collected from different slag heaps, impurities such as stones and plant debris were removed, and samples were mixed and prepared for natural drying at room temperature in the laboratory.

The collected lead smelting slag is a massive dry slag with a relatively well-balanced crystalline structure and the presence of some amorphous vitreous structures. The lead refining waste slag is a complex non-homogeneous aggregate, and the background of the XRD pattern is elevated between 20° and 40° 2theta, which corresponds to the amorphous phase formed during the smelting process in the blast furnace. The main minerals in the waste slag include silicate minerals such as yellow feldspar, pyroxene, and olivine, sulfide minerals dominated by sulfurous iron ore, the carbonate mineral chalcopyrite, and magnetite and gypsum.

The micro-morphological changes in the lead smelting slag itself, as well as after leaching and stabilization by drenching, were analyzed by scanning electron microscopy (SEM), and the changes in the major elements on the surface were further analyzed by an EDS–SEM model ZEISS Gemini 300, energy spectrometer model OXFORD Xplore, and gold-sprayed target material: gold–palladium alloy. The chemical morphology of the elements on the surface of the particles was analyzed using the following XPS instrument model: Thermo Scientific K-Alpha X-ray source, excitation source: Al Kα-rays (hv=1486.6 eV), beam point: 400 μm vacuum in the analysis chamber was better than 5.0E-7 mBar, operating voltage: 12 kV, filament current: 6 mA, full-spectrum scanning: passing energy of 100 eV in steps of 1 eV, combined energy correction: C1s = 284.80 eV using the combined energy as the energy standard. Waste slag particles endowed with minerals were determined by XRD under the following test conditions: a Cu target was used as a source of Kα radiation (λ = 1.5405 Å), the tube voltage was set to 40 kV, the tube current was set to 300 mA, the scanning range 2θ was set to 10–90°, the scanning speed was set to 2–5°/min, and the instrument model Mini-Flex 600 was used. The heavy metal concentrations in the leach solution of the Pb–slag concentration were determined by ICP-MS (Agilent Technologies, Inc., 7500CX, USA).

Table S1 Results of the XRF analysis of lead smelting waste slag %

O	Na	Mg	Al	Si	P	S	Cl	K
23.3844	0.8623	0.853	3.4112	11.126	0.0599	3.8191	0.086	1.8795
Ca	Ti	**Cr**	Mn	Fe	**Cu**	**Zn**	**As**	Se
8.0659	0.5863	**0.117**	1.3925	31.211	**0.3572**	**4.3818**	**0.242**	0.0032
Rb	Sr	Zr	Mo	Sn	Sb	Ba	W	**Pb**
0.0143	0.2304	0.03	0.0083	0.1185	0.0194	0.2687	0.035	**1.612**

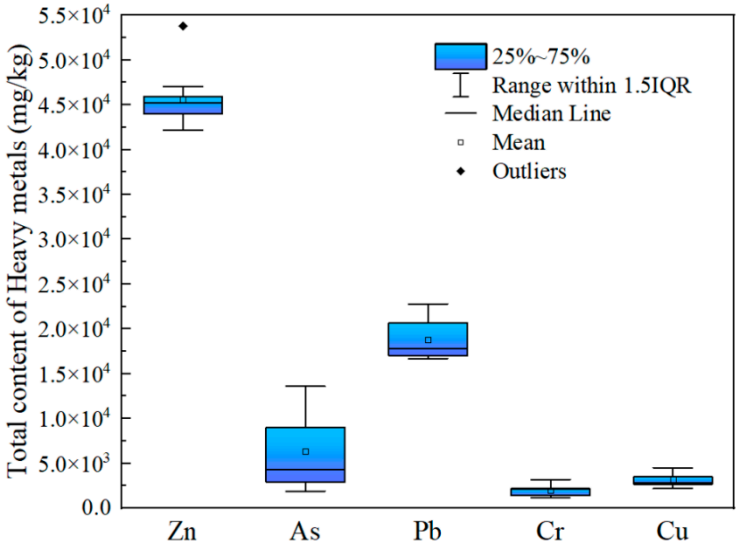


Figure S1 Analysis of the total amount of heavy metals in lead smelting slag

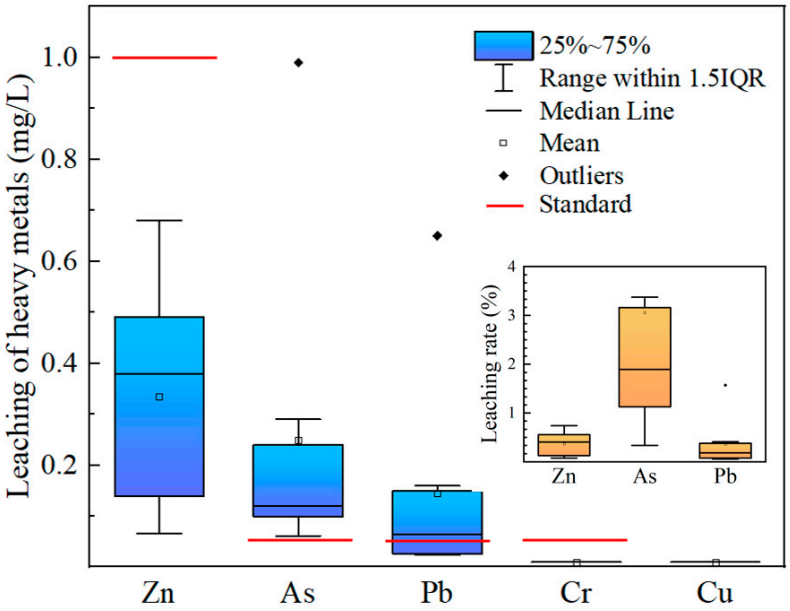


Figure S2 Heavy metal leaching toxicity of lead smelting waste (horizontal shock method)

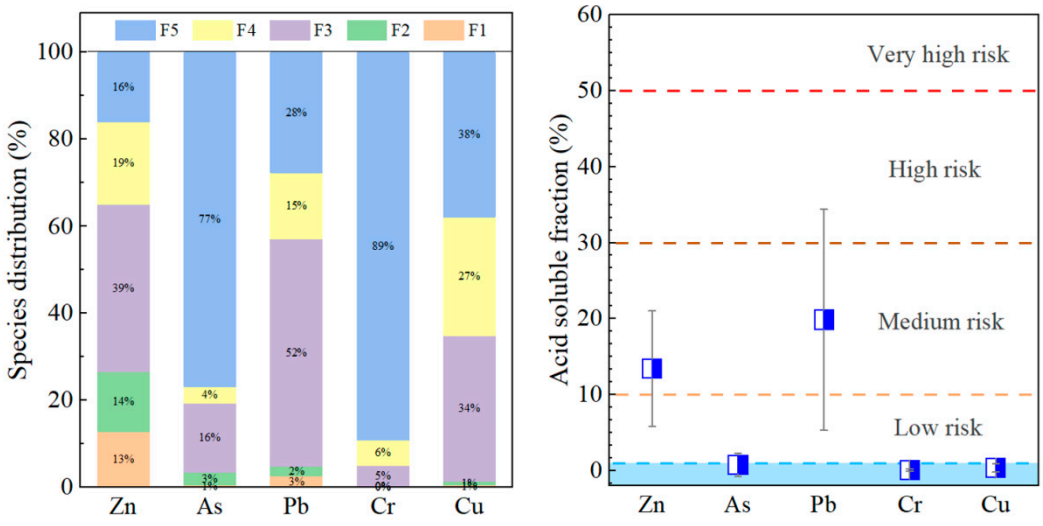


Figure S3 Results of the morphological analysis of heavy metals in lead refining waste (left) and the associated environmental risks (right) (exchangeable (F1), carbonate-bound (F2), iron/manganese oxide-bound (F3), organics/sulfide-bound (F4) and residue (F5))

The waste residue is composed of 23 minerals, and the vein minerals are mainly yellow feldspar, olivine, and pyroxene, with contents of 58.15%, 11.88%, and 5.77%, respectively. Some amorphous materials in the ore have similar chemical compositions to those of yellow feldspar, which are also counted as yellow feldspar. The independent minerals of zinc have three kinds of sulfur–zincite, silicon–zinc–alumina, and zinc–iron spinel, with contents of 1.67%, 0.14%, and 3.06% respectively. The independent minerals of lead have five kinds of lead metal, lead alumina, white lead ore, lead Ferro alumina and galena, with contents of the first four kinds of 0.72%, 0.23%, 0.41% and 1.35%, and galena is less. The independent minerals of arsenic have arsenopyrite and stinking onyxitis, two kinds of arsenic, and the content is 0.18% and 0.14%, respectively. The other metal minerals are mainly sulfurous iron ore and magnetite, with contents of 8.82% and 4.37%, respectively.

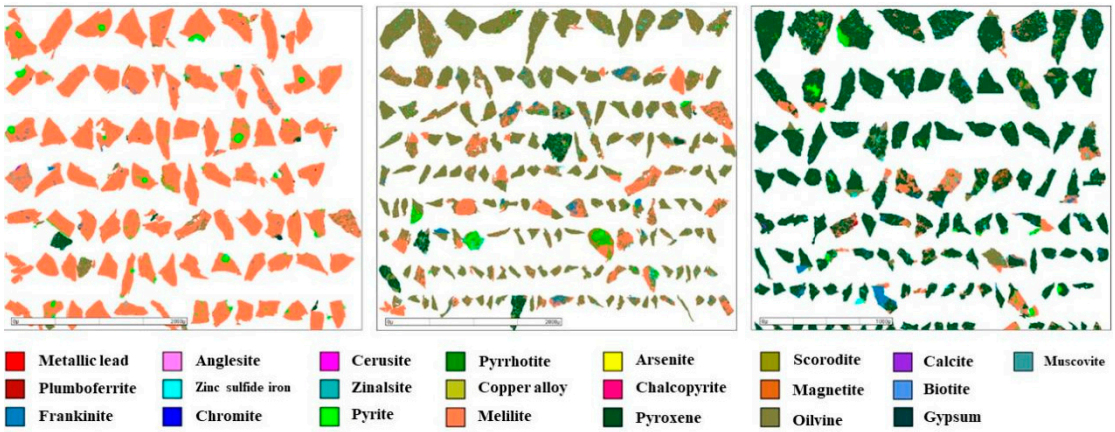


Figure S4 Mineral grain analysis of yellow feldspar (left), pyroxene (center), and olivine (right)

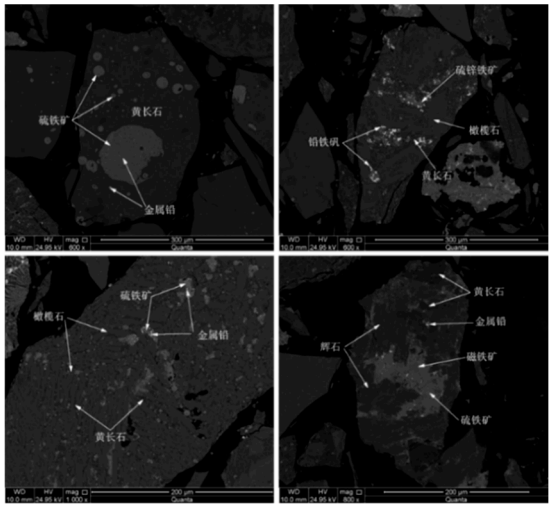


Figure S5 Characteristics of the silicate mineral embedded in lead smelting waste slag

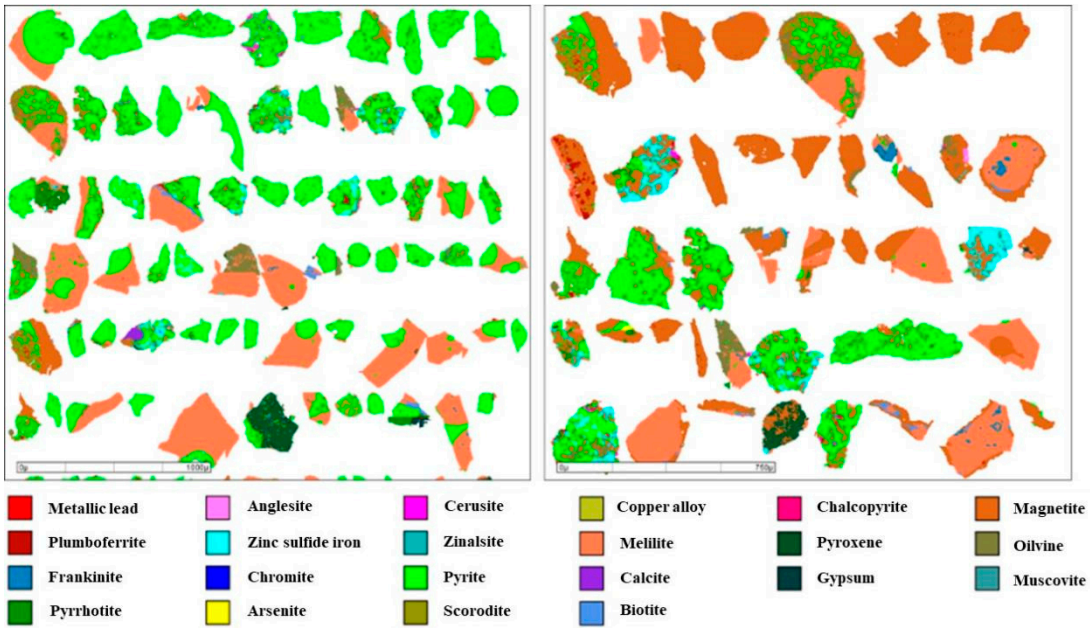


Figure S6 Mineral particle analysis of sulfide (left) and magnetite (right)

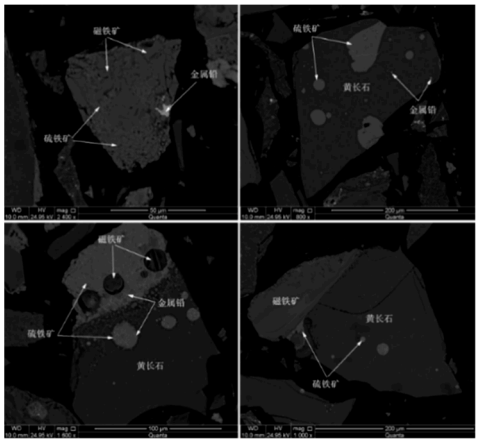


Figure S7 Characteristics of the sulfurous iron ore and magnetite embedded in lead smelting slag

2. Mechanisms for the Release of Zn and Pb

A large amount of Zn leaching occurred at the beginning of the experiment (1~3 days), and what was released at this stage was mainly free Zn, and the concentration of Zn in the leaching solution at the late stage of the experiment decreased gradually with the increase in the time as a whole, which was consistent with the trend of the change of the TDS, indicating that the release of Zn in the lead smelting waste slag was mainly controlled by the dissolution of the soluble minerals, such as carbonate and alkaline silicate weathering products.

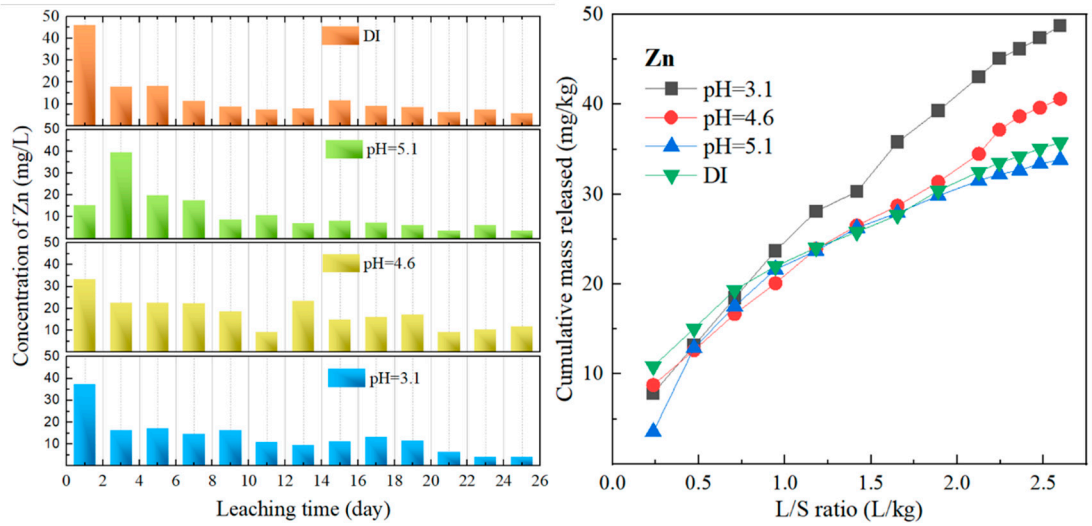


Figure S8 Single leach release (left) and cumulative release (right) of Zn from lead slag

The release of Pb can be divided into three stages. The first stage is mainly the release of free Pb^{2+} under the action of leaching, and the decrease in the leachate pH

will also lead to the dissolution of metal Pb and white lead $PbCO_3$, increasing the release of Pb^{2+}, some of which exists in the form of contiguous lead, which is susceptible to the direct influence of the environment. The second stage of the lead slag for the release of Pb appears to be internal stabilization mechanism, and the reaction between metal Pb and acid will produce hornblende, covering the surface of the metal lead, preventing its further dissolution; in addition, with the percolation of the leachate, the pH value gradually increases to about 8, $PbCO_3$ tends to stabilize and no longer dissolve, and free Pb^{2+} will also react with CO_3^{2-} to produce $PbCO_3$ precipitate, so the Pb release gradually decreases. The release of major Pb in the third stage is controlled by the dissolution of sulfide minerals, and with the oxidative dissolution of the pyrite material, the encapsulated lead-bearing minerals are directly exposed to the leachate, leading to a significant increase in Pb^{2+} release in the later stages of the leachate.

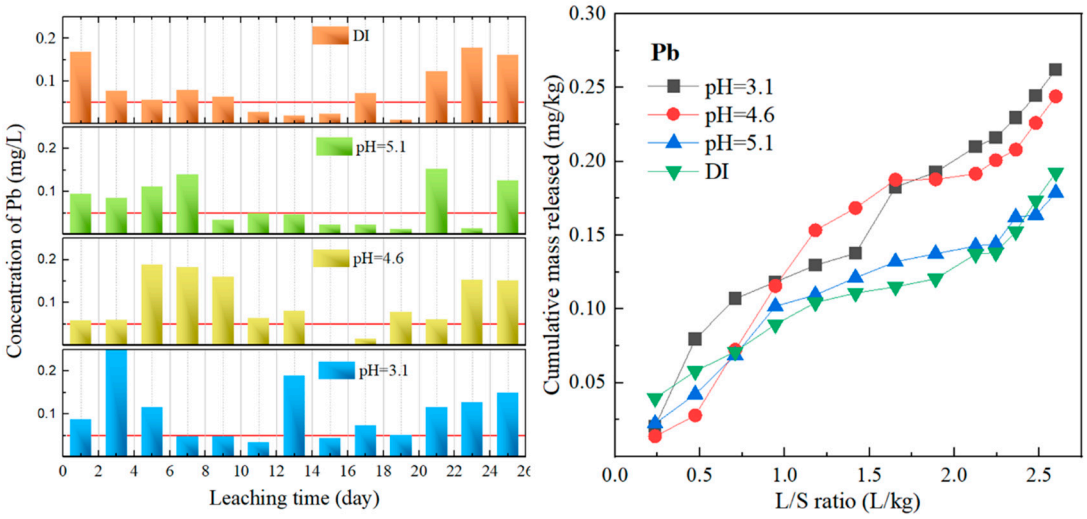


Figure S9 Single leach release (left) and cumulative release (right) of Pb from lead slag

The release of As increased with time, which was different from the trend of the TDS, indicating that similar to Pb, the release of As was not controlled by the dissolution of soluble minerals. The free As mainly exists in the form of arsenate, and at the early stage of leaching, the Fe, Mn, and Al oxides in the lead refining slag will capture the arsenate ions through adsorption and slow down the release of As. With increasing time, the saturation of adsorption or further oxidative dissolution of Fe, Mn, and Al oxides results in the increased release of As. In addition, a long-term decrease

in the redox potential of arsenic-bearing minerals in an aqueous environment can promote the conversion of As(V) arsenate (AsO_4^{3-}) to the more migratory As(III) arsenate (AsO_3^{3-}).

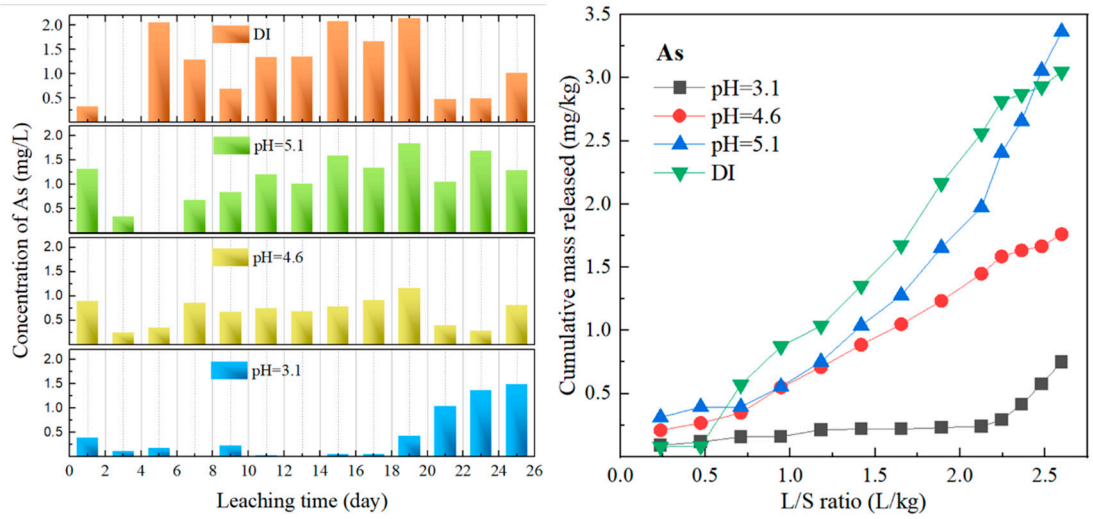


Figure S10 Single leachate release (left) and cumulative release (right) of As from lead slag

In a real environment, passivated materials are often affected by pH changes in the environment, thereby releasing heavy metals into the environment again, especially in some acid rain areas. The stability of the passivated material after 2 days of immersion in different pH environments was further investigated and the results are shown in Figure x. From the figure, it can be seen that the re-release of heavy metals is very low under alkaline conditions, which may be attributed to the fact that the S outer layer of the encapsulated material has very good stability in alkaline environments and its internal pH is mainly maintained at a slightly alkaline environment of 7.5–9 during the passivation process of the material. There is a certain degree of heavy metal release under acidic conditions, but the leaching toxicities of the released heavy metals Zn, As and Pb concentrations are below 0.2 mg/l, which are all lower than the concentration limit of a Class III water body in the Environmental Quality Standard for Surface Water (GB3838-2002). From the above study, we can see that the material has a certain stability after the passivation of heavy metals, both in weakly acidic and weakly alkaline environments, and can remain stable in the real environment.

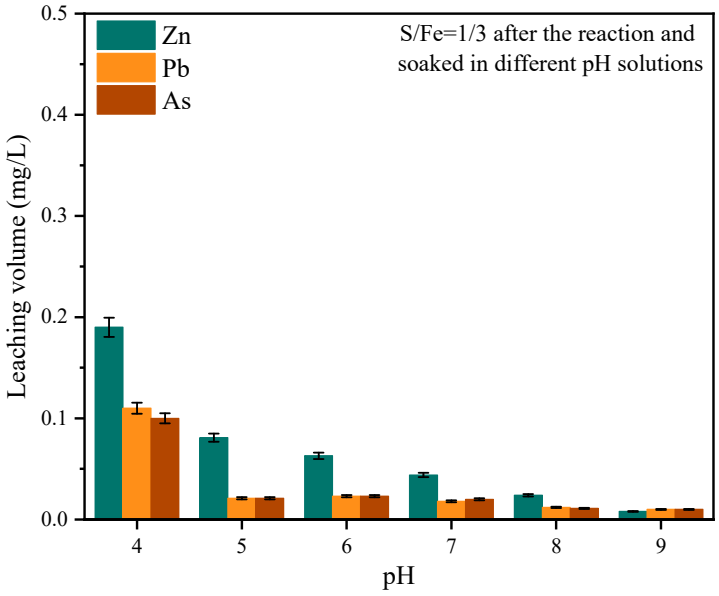


Figure S11 Stabilization of heavy metals by materials under different pH conditions

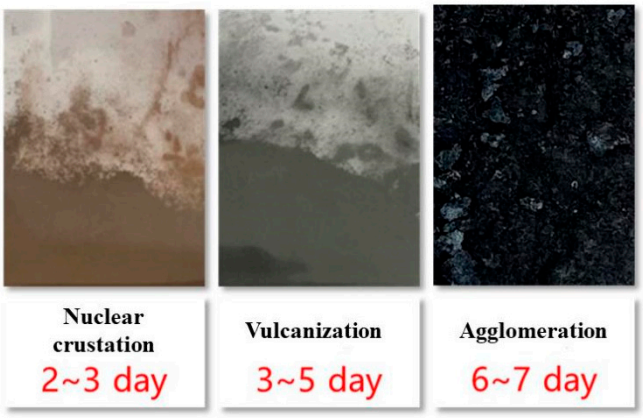


Figure S12 Changes in the appearance of lead slag during the simultaneous stabilization of Fe^0 and Na_2S

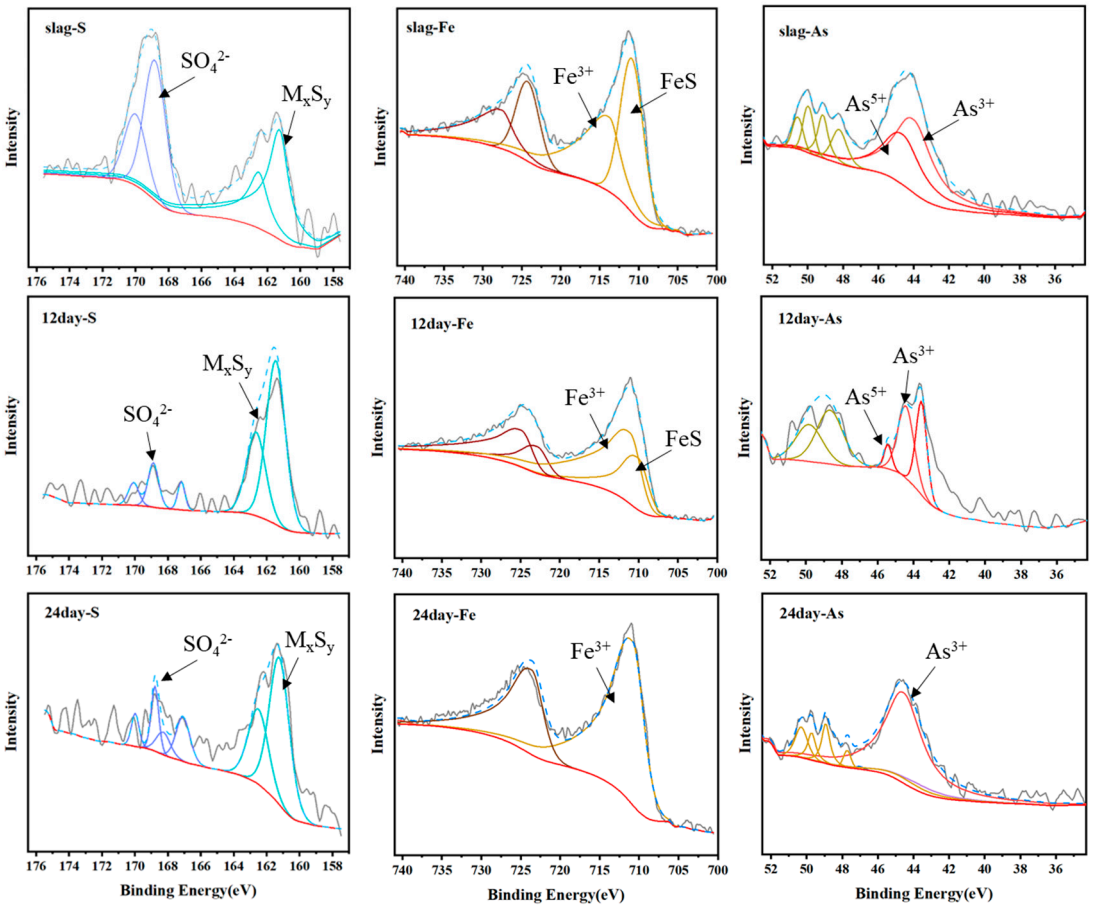


Figure S13 XPS profiles of lead smelting slag before and after rainfall leaching