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Enhancing Arsenic Solidification/Stabilisation Efficiency of Metallurgical Slag-Based Green Mining Fill and Its Structure Analysis

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Abstract: To dispose of arsenic-containing tailings with low carbon and high efficiency, sodium sulphate (Na_2SO_4), sodium hydroxide (NaOH), calcium nitrate $\text{Ca}(\text{NO}_3)_2$ and calcium hydroxide $\text{Ca}(\text{OH})_2$ were independently added to metallurgical slag-based binder (MSB) solidification/stabilisation (S/S)-treated tailings (MSTs) to enhance the MST arsenic S/S performance. Results showed that only $\text{Ca}(\text{OH})_2$ could increase the unconfined compressive strength of MST from 16.3 to 20.49 MPa and decrease the leachate As concentration from 31 $\mu\text{g/L}$ to below 10 $\mu\text{g/L}$. $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ and NaAsO_2 were used to prepare pure MSB paste for mechanism analysis. The results of microstructure analyses showed the high specific surface area and amorphous properties of calcium–sodium aluminosilicate hydrate facilitated the adsorption or solid-solution formation of As(V) and As(III). As(V) formed an inner-sphere complex in ettringite, whereas As(III) formed an outer-sphere complex, and the relatively larger size and charge of As(V) compared with SO_4^{2-} restrict substitution inside channels without affecting the ettringite structure under high loading of As(V). The added $\text{Ca}(\text{OH})_2$ promoted the hydration reaction of MSBs and facilitated the formation of a Ca–As(V) precipitate with low solubility, from $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($K_{sp} = 10^{-27.49}$) to $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ ($K_{sp} = 10^{-40.12}$). This work is beneficial for the application of cement-free MSB in the S/S process.

Keywords: metallurgical slag-based binders; solidification/stabilisation; As(III); As(V); calcium hydroxide

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1. Introduction

Arsenic (As) is a toxic and carcinogenic element, which can cause severe effects on human health, such as skin, lungs, kidney and liver cancers, even at a low concentration [1]. The mining, processing and smelting industry of nonferrous metals is the most widespread source of As emissions in China, accounting for 61.8% [2]. Mining wastewater, smelting slag, dust and tailings are piled up in tailings ponds, which have potential environmental risks and occupy a large percentage of soil [3]. Heavy metal pollution from a large number of tailings poses a major threat to the environment [4,5]. The treatment of heavy metal pollution has received increasing attention since the implementation of the Soil Pollution Prevention and Control Law of the People's Republic of China in 2019 [6]. It is imperative to develop effective and economically viable technologies to reduce pollution from the nonferrous metal industry.

Solidification/stabilisation (S/S) technology has been used to dispose of metal(loid)-containing waste by forming a less soluble, mobile or toxic product through adsorption, co-precipitation and physical encapsulation [7]. Ordinary Portland cement (OPC) is a

traditionally used binder in S/S processes, while the high carbon footprint of cement clinker manufacture is of concern [8,9]. To achieve an environment-friendly binder for the S/S of As-containing waste, many studies have been conducted to replace cement in part or whole using materials, such as red mud, blast furnace or metakaolin-assisted cement [1,10], cement-free clay-based binders [11], red mud-enhanced magnesium phosphate cement [12], pine sawdust biochar [13], coal fly ash [14], zero-valent iron or magnetic biochar [15]. However, there have been few reports on the use of cement-free metallurgical slag-based binders (MSB) [16,17], which consist of steel slag powder (SSP), ground-granulated blast furnace slag (GGBFS) and flue gas desulphurisation gypsum (FGDG). Steel slag is a by-product of a steel-making process, known as overburnt clinker because its mineral phase composition is similar to that of cement clinker [18]. In 2019, 149.45 million tonnes of it were produced in China; however, the usage rate is less than 40% [19]. A large accumulation of steel slag pressurises the environment [20]. GGBFS is a by-product of the steel-making industry and is used as a supplementary cementitious material. In the hydration process of MSB, the relatively high alkalinity of SSP facilitates the breakage of Si–O and Al–O bonds in the GGBFS vitreous structure to form SiO_4^{4-} and AlO_4^{5-} [21,22], which react with dissolved Ca^{2+} to form calcium silicoaluminate hydrate (C–A–S–H) gels [11,23]. The AlO_4^{5-} dissolved in solution transforms from four coordinated aluminium ions to six coordinated aluminium ions $[\text{Al}(\text{OH})_6]^{3-}$ in alkaline environments, which reacted with the Ca^{2+} and SO_4^{2-} dissolved from gypsum to form ettringite [24].

In this study, As-containing tailings were chosen as the S/S objects, as other hazardous elements' leaching risk is very low after S/S treatment (Table S1). In order to dispose of As-containing tailings with low carbon and high efficiency, the MSB (60 wt% GGBFS, 30 wt% SSP, and 10 wt% FGDG) was chosen as the binder for the As-containing tailings, based on a previous study [25]. SO_4^{2-} (Na_2SO_4), OH^- (NaOH), Ca^{2+} ($\text{Ca}(\text{NO}_3)_2$ or Ca^{2+} and OH^- ($\text{Ca}(\text{OH})_2$) was added to the MSB-S/S treated tailings (MST) to enhance the MST-As-S/S performance. Arsenic in tailing occurs in various states in the natural environment, and its main forms in regard to leaching and migration characteristics are soluble arsenite As(III) and arsenate As(V) compounds [26]. The As-S/S mechanism of MSB and the mechanism of efficiency improvement are both unclear; therefore, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ and NaAsO_2 were used to study the S/S mechanisms through X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscope-energy dispersive spectrometer (SEM-EDS) analysis. This study will improve the engineering application prospects of MSB and reusability of MST.

2. Materials and Methods

2.1. As-Containing Tailings and Metallurgical Slag-Based Binders

As-containing tailings were collected from a closed lead-zinc tailings pond in Hechi Nandan, Guangxi (China). The main components of the tailings were quartz, calcite and fluorite, of which the D_{50} and D_{90} particle sizes were 42 and 188 μm , respectively (Figure S1). The total concentration of As in the tailings was 2098 mg/kg, as determined using an Agilent 7500a ICP-MS (Agilent Technologies, Santa Clara, CA, USA) after aqua regia digestion (1/3 concentrated HNO_3 and HCl (v/v)) based on Chinese standard method HJ 803-2016. The leaching concentration of As in the tailings after horizontal oscillation-leaching tests was 0.57 mg/L, based on the Chinese standard method HJ 557-2010 (Table 1). The MSB consisted of GGBFS, SSP and FGDG. The chemical components of raw materials are shown in Table 1, and the XRD spectra of the binders are shown in Figure S2. The analytical reagents, Na_2SO_4 , NaOH , $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{OH})_2$, were used as added additive for the binders, respectively. A polycarboxylic acid water-reducer (WR) was used to achieve an acceptable flowability of mortar during S/S treatment. The analytical reagents, $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ and NaAsO_2 , were used to prepare the pure MSB paste to study the S/S mechanisms of As(III) and As(V).

Table 1. Raw material chemical components, blaine fineness, component concentrations and leaching concentration of As.

Inspected Item		Tailings	GGBFS	SSP	FGDG
Chemical composition Oxide (wt%)	SiO ₂	53.23	33.32	17.05	2.03
	TiO ₂	0.12	0.85	0.91	0.04
	Al ₂ O ₃	5.07	15.43	5.73	0.78
	Fe ₂ O ₃	1.65	1.01	22.33	0.48
	MnO	0.70	0.52	3.63	0.03
	MgO	1.17	10.78	9.01	1.04
	CaO	25.49	36.89	38.42	30.01
	Na ₂ O	-	0.49	0.16	0.06
	K ₂ O	1.38	0.38	0.09	0.15
	SO ₃	1.12	-	-	44.97
	As ₂ O ₃	0.18	-	-	-
	LOI	10.61	0.12	1.42	22.07
Blaine fineness (m ² /kg)	-	-	435	440	325
pH	-	7.64	11.78	11.96	7.68
Total As concentration (mg/kg)		2098	-	-	-
As leaching concentration (mg/L)		0.57	-	-	-

2.2. Cement-Free S/S Treatment

For the preparation of MST mortar samples, the different constituents of binders were mixed with tailings at specific ratios (Table 2). MSB with 60 wt% GGBFS, 30 wt% SSP and 10 wt% FGDG was chosen due to its high compressive strength, according to the findings of previous studies [25]. Four additives (Na₂SO₄, NaOH, Ca(NO₃)₂ and Ca(OH)₂) were incorporated into the MSB mass individually at 5 wt%, 10 wt% and 15 wt%. The binders-to-tailings (B/T), water-to-solids (W/S) and WR-to-solids (WR/S) mass ratios were maintained at 0.25, 0.2 and 0.008, respectively, in all MST samples. After the tailings and binders were mixed for 1 min using a standard cement mortar mixer, distilled water used to dissolve the WR was added, and the blended mortar was mixed for another 5 min, before being cast into steel moulds (40 mm × 40 mm × 160 mm) to prepare the MST samples. To prepare MSB paste samples, 5 wt% concentrations of the analytical reagent, Na₃AsO₄·12H₂O or NaAsO₂, was added (Table 2), which were then mixed with water until the mass ratio of water-to-binders (W/B) reached 0.35. The paste samples were stirred for 5 min and then cast into steel moulds (30 mm × 30 mm × 50 mm). All mortar and paste samples were cured in a moist cabinet at (40 ± 2) °C and (90 ± 1)% relative humidity (similar to the underground filling environment in Guangxi [27]) for 3 day, and then the samples were demoulded and placed under the same curing conditions until the appropriate degree of sample ageing was achieved.

2.3. S/S Performance and Spectroscopic/Microscopic Analysis

The S/S performance was evaluated in terms of the unconfined compressive strength (UCS) and As leachability of the MST samples. The UCS of the samples was assessed on the basis of the Chinese standard GB/T 17671-1999 method of testing cements. The determination of UCS on three replicates at each curing time, and the average value with standard deviations of less than 5% was reported. The leachability of MST was assessed using the Chinese standard method HJ 557-2010, wherein the ratio of leachant (deionised water) volume to solid specimen weight (crushed to size < 3mm) was maintained at 10:1 (L/kg). Leachate samples were oscillated horizontally at 110 ± 10 times/min for 8 h and then left to stand at room temperature for 16 h. The pH values were measured, and the leachate was filtered through a 0.45-µm polypropylene microfiltration membrane. Afterwards, the filtered leachate samples were acidified to below pH 2 using concentrated HNO₃ and then stored at 4 °C in the dark before As detection using a PerkinElmer Optima 8300 ICP-OES (Perkin Elmer, Cumberland, NJ, USA) or an Agilent 7500a ICP-MS (Agilent Technologies, Santa Clara, CA, USA), with all samples analysed in triplicate to ensure

accuracy. Mean results for triplicate sample analysis (with standard deviations of less than 5%) and error bars, are presented in this study. The As curing rate was evaluated using Equation (1):

$$\text{Curing Rate} = (1 - C_{S/S} / C_T) \times 100\% \quad (1)$$

where $C_{S/S}$ is the As leaching concentration of MST, and $\mu\text{g/L}$; C_T is the As leaching concentration of untreated tailings.

Table 2. Mixture formulations of MST and MSB samples (wt%).

Notation	GGBFS	SSP	FGDG	Na ₂ SO ₄	NaOH	Ca(NO ₃) ₂	Ca(OH) ₂	NaAsO ₂	Na ₃ AsO ₄ ·12H ₂ O	Tailing ¹
T	60	30	10	-	-	-	-	-	-	1:4
T-S1	57	28.5	9.5	5	-	-	-	-	-	1:4
T-S2	54	27	9	10	-	-	-	-	-	1:4
T-S3	51	25.5	8.5	15	-	-	-	-	-	1:4
T-H1	57	28.5	9.5	-	5	-	-	-	-	1:4
T-H2	54	27	9	-	10	-	-	-	-	1:4
T-H3	51	25.5	8.5	-	15	-	-	-	-	1:4
T-N1	57	28.5	9.5	-	-	5	-	-	-	1:4
T-N2	54	27	9	-	-	10	-	-	-	1:4
T-N3	51	25.5	8.5	-	-	15	-	-	-	1:4
T-C1	57	28.5	9.5	-	-	-	5	-	-	1:4
T-C2	54	27	9	-	-	-	10	-	-	1:4
T-C3	51	25.5	8.5	-	-	-	15	-	-	1:4
B	60	30	10	-	-	-	-	-	-	0
B(III)	57	28.5	9.5	-	-	-	-	5	-	0
B(V)	57	28.5	9.5	-	-	-	-	-	5	0
B-C3	51	25.5	8.5	-	-	-	15	-	-	0
B-C3(III)	48.45	24.225	8.075	-	-	-	14.25	5	-	0
B-C3(V)	48.45	24.225	8.075	-	-	-	14.25	-	5	0

¹ Binder-to-tailings mass ratio.

The hydration of pulverised and sieved paste samples was terminated using alcohol drenching at the specific testing age, with samples then dried at 50 °C under a vacuum for 24 h for further characterisation. Mineralogy was detected using a high-resolution powered Rigaku D/max-RB XRD with CuK α radiation, a voltage of 40 kV, current of 200 mA and 2 θ scanning, ranging between 10° and 70°. The morphology and elemental mapping of the samples were analysed using SEM-EDS (JSM-6701F). Structural and chemical bond analyses were performed using GX Perkin-Elmer FTIR (Perkin Elmer, Cumberland, NJ, USA) between wavelengths of 400–4000 cm^{−1} and at a resolution of 0.125 cm^{−1}.

3. Results

3.1. The S/S Performance of MST Samples

The UCS results for MST samples (Figure 1a) demonstrate that MST combined with various additives performed differently. The 3, 7 and 28 day UCS results for T were 11, 13.8 and 16.3 MPa, respectively. An increase in concentrations of Na₂SO₄, NaOH and Ca(NO₃)₂ reduced the USC of MST at every curing time, especially for the addition of NaOH, which inhibits hydration reactions and reduced the USC of MST (the lowest 28 day USC (T-H3 3.7 MPa) was only 22.7% of T). The addition of Ca(OH)₂ enhanced mechanical properties (the highest 28 d UCS (T-C3 20.49 MPa) was 125.7% of T). The USC of all samples could meet the filling requirements (5 MPa, the black line in Figure 1a), except for T-H3.

Figure 1. (a) UCS of MST samples at 3, 7 and 28 day; (b) As leachability of 28 day MST samples.

Figure 1b shows leachate As concentrations and the pH values of 28 day MST samples after the horizontal oscillation-leaching experiments. The leachate As concentration of T samples was 31 µg/L, which exceeded the prescribed As concentration limit value in the Chinese standard GB 5749-2006 for drinking water quality (10 µg/L, the black line in Figure 1b), indicating a relevant risk of environmental pollution. The addition of Na_2SO_4 , NaOH or $\text{Ca}(\text{NO}_3)_2$ enhanced leachate As concentration, particularly that of T-H3, which reached 530 µg/L. The addition of $\text{Ca}(\text{OH})_2$ reduced the leachate As concentration, particularly that of T-C2 and T-C3, which was less than 10 µg/L.

3.2. Spectroscopic/Microscopic Analysis

3.2.1. XRD Pattern Analysis

The XRD patterns of MSB paste hydrated for 3 and 28 day are presented in Figure 2a,b), respectively. The main mineral phases of the B sample, as shown in Figure 2a, are C-S-H gel, ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) and un-hydrated gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), C_2F ($2\text{CaO} \cdot \text{Fe}_2\text{O}_3$), RO phase ($(\text{MgO})_{0.239}(\text{FeO})_{0.761}$), akermanite ($\text{Ca}_2\text{MgSi}_2\text{O}_7$) and C_2S ($2\text{CaO} \cdot \text{SiO}_2$) (Figure S2). With the addition of As(III) (sample B(III)), the peaks of ettringite decreased. However, when As(V) was added (B(V)), the peaks of ettringite disappeared due to the formation of a new phase, $(\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 16\text{H}_2\text{O})$, and the peaks of Ca-As co-precipitation $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ appeared.

Figure 2. The XRD patterns of (a) B, B(III) and B(V) paste; (b) B-C3, B-C3(III) and B-C3(V) paste.

Compared with Figure 1a, the added $\text{Ca}(\text{OH})_2$ characteristic peaks appeared in the XRD patterns of B-C3 and B-C3(III); however, it did not appear in B-C3(V) (Figure 2b), and the peaks of Ca–As co-precipitation $\text{Ca}_5(\text{AsO}_4)_3\text{OH}\cdot x\text{H}_2\text{O}$ appeared.

3.2.2. FTIR Spectra Analysis

Figure 3a displays the FTIR spectra of the B, B(III) and B(V) samples. The spectra of the six samples are similar, presenting analogous adsorption bands. The pure B paste spectra (Figure 3a ① and ②) exhibit a small band at 3639 cm^{-1} associated with the O–H stretching vibration; bands at 3424 and 1646 cm^{-1} are related to the O–H stretching and bending modes of molecular interlayer water, respectively, and bands near 1450 (1478 , 1428) cm^{-1} and at 876 cm^{-1} are related to the anti-symmetric stretching (ν_3) and out-of-plane bending (ν_2) modes of CO_3^{2-} ions, respectively. The bands at 973 cm^{-1} and near 450 (462 , 422) cm^{-1} are associated with anti-symmetric Si–O(Al) stretching vibrations (ν_3) and in-plane Si–O bending vibrations (ν_2) in the SiO_4 tetrahedra of the C–(A)–S–H gel. The lack of a sharp band at 973 cm^{-1} indicates the wide distribution of $\text{SiQ}^n(\text{mAl})$ units. Moreover, the 3 day and 28 day infra-red spectra of B samples display large bands at 1114 cm^{-1} corresponding to the S–O₄ stretching mode (ν_3), with a shoulder at 537 cm^{-1} , potentially due to out-of-plane Si–O bending vibrations (ν_4).

Figure 3. FTIR spectra of (a) ① and ② B sample, ③ and ④ B(III) sample and ⑤ and ⑥ B(V) sample; (b) ① and ② B-C3 sample, ③ and ④ B-C3(III) sample and ⑤ and ⑥ B-C3(V) sample.

Nevertheless, some differences were observed in the infrared spectra of B(III) and B(V) samples. The weak band at 3639 cm^{-1} in the B sample (Figure 3a ① and ②) disappeared

in the B(V) (Figure 3a ⑤ and ⑥) samples, indicating that OH^- reacts with the added As(V), which is consistent with the result of XRD analysis (Figure 2a). The anti-symmetric Si–O(Al) stretching vibrations (ν_3) of the C–(A)–S–H gel (973 cm^{-1} for B) decreased to 968 cm^{-1} for B(III) and 964 cm^{-1} for B(V), indicating that the added As(III) and As(V) were combined in the microstructure network and changed the degree of polymerisation of the C–(A)–S–H gel. In addition, the O–H stretching band (3424 cm^{-1} for B) increased to 3448 cm^{-1} and became broader for B(V) due to the absence of ettringite, leading to the change of interchannel molecular water, which combined with the result of XRD pattern (Figure 2a). Moreover, some new bands were observed, with the appearance of broadband at 802 and 671 cm^{-1} for B(III), and at 866 cm^{-1} for B(V) (Figure 3a ③–⑥), which was due to the As–O stretching vibration of the As(III) and As(V) species [28,29].

Figure 3b display the FTIR spectra of the B-C3, B-C3(III) and B-C3(V) samples, respectively. These spectra are all similar to those presented in Figure 3a, except that the spectra of the B-C3 and B-C3(III) samples exhibited sharp adsorption bands at 3642 cm^{-1} due to the addition of $\text{Ca}(\text{OH})_2$. However, the sharp adsorption bands at 3642 cm^{-1} did not appear in B-C3(V), illustrating that $\text{Ca}(\text{OH})_2$ reacted with As(V). Bands around 1110 cm^{-1} , corresponding to the S–O₄ stretching mode (ν_3) in Figure 3b ①–⑥, were offset at 1114 cm^{-1} in B-C3 sample, 1111 cm^{-1} in B-C3(III) and 1117 cm^{-1} in B-C3(V), indicating that, after As(III) and As(V) were added, the hydration products associated with SO_4^{2-} were affected, as shown by the XRD pattern (Figure 2b).

3.2.3. SEM-EDS Analysis

Figure 4 show SEM-EDS images for B, B(V) and B(III) at hydration ages of 3 and 28 day. Dense structures with amorphous gels and needle-like mineral phases are visible in the cement-free B paste in Figure 4a,b, which are calcium-sodium aluminosilicate hydrate (C–(N)–A–S–H) gels and ettringite, combined with the component analysis results in Table S2 (b-1, b-2 and b-3). After As(V) was added, the needle-like ettringite structure was undetected (Figure 4c,d), and a small amount of As(V) was found in the short columnar crystals of sodium sulphate, combined with the component analysis results (Table S2 (d-1)). Moreover, according to the SEM-EDS mapping images (Figure S3) of the red box in Figure 4d, the distribution of As(V) was almost similar to that of Ca, Si and Al, and the distribution of Na was similar to that of S. Therefore, the majority of the added As(V) entered the C–A–S–H gels through isomorphism substitution or was adsorbed and encapsulated by the gels, whereas the tiny minority of that entered the sodium sulphate to form sodium arsenic alunite. After As(III) was added, combined with the component analysis results (Table S2 (e-1,f-3)), different amounts of As(III) were detected in the C–A–S–H, ettringite, Na_2SO_4 and $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ (Figure 4e,f).

Figure 5 show SEM-EDS images of B-C3, B-C3(V) and B-C3(III) at hydration ages of 3 and 28 day. In addition, amorphous C–A–S–H gels interwoven with needle-like ettringite structures were detected in the B-C3 paste. The images of B-C3(V) and B-C3(III) are similar to those for B(V) and B(III), except for the appearance of calcium hydroxide flakes in B-C3(V)-3d (Figure 5c) and calcium monosulfoaluminate hydrate (AFm) flakes in B-C3(III)-3d (Figure 5e), combined with the component analysis results in Table S3, which may be due to their content being lower than the detection limit of the XRD technique; both kinds of flakes disappeared as the hydration reaction proceeded.

Figure 4. SEM-EDS result for (a) B-3d; (b) B-28 d; (c) B(V)-3 d; (d) B(V)-28 d; (e) B(III)-3 d; (f) B(III)-28 d.

Figure 5. SEM-EDS result for (a) B-C3-3 d; (b) B-C3-28 d; (c) B-C3(V)-3 d; (d) B-C3(V)-28 d; (e) B-C3(III)-3 d; (f) B-C3(III)-28 d.

4. Discussion

This study demonstrates the different As S/S performance of MST samples after four additives (Na_2SO_4 , NaOH , $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{OH})_2$) were added, as shown in Table S4. The MSB is selective for additives and only $\text{Ca}(\text{OH})_2$ exerted a positive effect on the As S/S performance. The addition of Na_2SO_4 had little effect on the pH values, UCS and As curing rate, probably because gypsum in the MSB system (10 wt% FGDG in B) was sufficient to provide sulphate for the hydration reaction. The addition of NaOH resulted in a pH value above 13, which inhibited the dissolution of Ca^{2+} and hindered the hydration reaction, leading to a sharp decrease in UCS [30]. The amphoteric nature of arsenic in an alkaline environment and repulsion by OH^- during the adsorption process of the hydration products led to the sharp decrease of the As curing rate [31,32]. Neither NaOH

nor $\text{Ca}(\text{NO}_3)_2$ improved the As S/S performance, confirming that the individual addition of OH^- without Ca^{2+} would not improve As S/S efficiency and had a negative effect [33,34].

In addition, this study demonstrates that both the As(V) and As(III) S/S mechanism of MSB, and the effect of $\text{Ca}(\text{OH})_2$ addition on As(V) and As(III) S/S are different. The addition of $\text{Ca}(\text{OH})_2$ to MSB raised the pH of the reaction mixture (Figure 1), facilitated GGBFS dissolution and provided a source of Ca^{2+} , thus improving the As(V) and As(III) S/S related to the hydration products. Adsorption or solid solution formation of As(V) and As(III) occurred due to the high specific surface area and amorphous properties of C–A–S–H, based on the shift in anti-symmetric Si–O(Al) stretching vibrations (ν_3) in the discussion above (Figure 3) and SEM-EDS results (Figures 4 and 5).

Anion substitution in ettringite can occur via reaction with surface sites (ligand exchange), replacing Al/Ca coordinated surface OH^- or substituting for sulphate inside channels (isomorphic substitution) [35]. This occurs as the ettringite surfaces are negatively charged under alkaline pH range conditions and due to the column and channel-like structure of ettringite, which is composed of columns of $\text{Ca}_6[\text{Al}(\text{OH})_6]_2 \cdot 24\text{H}_2\text{O}^{6+}$ and channels of $[(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}]^{6-}$ [36]. The extent of channel substitution of ettringite may be inversely proportional to the difference in size and electronegativity of the oxyanion compared with SO_4^{2-} (0.29 Å), resulting in As(V) (0.47 Å) being likelier to be channel-substituted with sulphur than As(III) (0.69 Å) [37]. Thus, As(V) tended to form an inner-sphere complex in ettringite, whereas As(III) could form an outer-sphere complex [38], and the relatively larger size and charge of As(V) compared with SO_4^{2-} restricts the substitution inside channels without affecting the ettringite structure under high loading of As(V), which is consistent with the XRD, IR and SEM-EDS analysis results.

Previous studies [39–41] have verified the formation of Ca–As precipitates under alkaline conditions. In the present study, the distinct Ca–As(III) mineral phase characteristic peak was not found in the XRD patterns, maybe because of the content being below the detection limit of XRD analysis or mainly existing as an amorphous or more complex structure. When $\text{Ca}(\text{OH})_2$ was added, Ca–As(V) changed from $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($K_{sp} = 10^{-27.49}$) to $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ ($K_{sp} = 10^{-40.12}$) (Figure 2), which restricted As leaching [42].

Based on the findings of this study, alkaline solid waste with high calcium ion equilibrium concentrations and high alkalinity can be used to replace $\text{Ca}(\text{OH})_2$ added to MSB for the S/S of high As-containing solid wastes for low carbon and environmental protection.

5. Conclusions

In this study, the effects of four additives (Na_2SO_4 , NaOH , $\text{Ca}(\text{NO}_3)_2$ or $\text{Ca}(\text{OH})_2$) on the As S/S performance of MST to enhance the As S/S efficiency were investigated. As-containing analytical reagents were used to prepare pure MSB paste to study the S/S mechanisms of As(III) and As(V) and the mechanism of efficiency improvement using $\text{Ca}(\text{OH})_2$, based on XRD, IR and SEM-EDS analysis. Based on the results obtained from this study, the following conclusions can be drawn:

- An MSB is selective for the additives, and only $\text{Ca}(\text{OH})_2$ exerts a positive effect on the S/S performance of MST.
- As(V) can form an inner-sphere complex in ettringite, whereas As(III) can form an outer-sphere complex, and the relatively larger size and charge of As(V) compared with SO_4^{2-} restrict its substitution inside channels without affecting the ettringite structure under high loading of As(V).
- The added $\text{Ca}(\text{OH})_2$ facilitates the encapsulation and adsorption of As(V) and As(III) in MSB, and changes the Ca–As(V) from $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($K_{sp} = 10^{-27.49}$) to $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ ($K_{sp} = 10^{-40.12}$).
- Cement-free MSB with $\text{Ca}(\text{OH})_2$ added is feasible to dispose of high As-containing solid wastes with high efficiency and a low carbon footprint.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/met11091389/s1>, Figure S1: (a) XRD pattern and (b) grain size results of tailings, Figure S2: The XRD pattern of raw materials: (a) ground granulated blast furnace slag (GGBFS), C₂S: dicalcium silicate; (b) steel slag powder (SSP), C₃A: tricalcium aluminate, RO phase: (MgO)_{0.239}(FeO)_{0.761}, C₂S: dicalcium silicate, C₂F: dicalcium ferrite; (c) flue gas desulfurisation gypsum (FGDG), Figure S3: The SEM-EDS electron image and mapping images of Figure 4 (d), Table S1: Leached concentration of raw materials and T in Table 2, Table S2: Component analysis result of point in the Figure 4, Table S3: Component analysis result of point in the Figure 5, Table S4: Assessment summary of the S/S performance effects of Na₂SO₄, NaOH, Ca(NO₃)₂ and Ca(OH)₂ at different doses (wt%).

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