



Investigation into the semi-dynamic leaching characteristics of arsenic and antimony from solidified/stabilized tailings using metallurgical slag-based binders

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ABSTRACT

The leaching characteristics of metallurgical slag-based binders (MSB) solidified/stabilized tailings containing arsenic (As) and antimony (Sb), were investigated via a series of semi-dynamic leaching tests using three kinds of leachant, for the simulation of actual leaching conditions. The effectiveness of solidification/stabilization (S/S) treatment was evaluated by measuring the observed diffusion coefficients (D_{obs}). It was found that MSB efficiently prevented As and Sb leaching, providing D_{obs} values in the range of 10^{-15} to 10^{-13} cm²/s and 10^{-11} to 10^{-9} cm²/s, respectively, with the exception that the leaching mechanism of As was dissolution rather than diffusion under acetic acid leaching conditions. Physical encapsulation was found to be the dominant mechanism for Sb immobilization, while the dominant mechanism of As immobilization was precipitation in the monolithic MSB S/S treated tailings (MST). Results showed that the concentrations of leached As, Sb, Ca and Si, were affected by leachant pH and total acidity as well as the MSB constituent ratio. The effect of these parameters may be attributed to the stability of hydration products and their influence on the buffering capacity and structure of matrices, and the leachant pH and total acidity having the greatest influence on leaching characteristics.

1. Introduction

In 2017, China produced 1.616 billion tons of tailings, 451 million tons of metallurgical slag and 213 million tons of industrial by-products gypsum, accounting for 44.2%, 12.34% and 5.83% of the total production of bulk industrial solid waste in China, respectively (Ni, 2017). Pollution caused by heavy metals (e.g. Pb, Cu, Cd, Zn, Hg, Cr) and oxyanions (e.g. Se, As, Sb, Mo, V, W) related to tailings has also attracted extensive research attention worldwide (van der Sloot et al., 2006). The random stacking or disposal of metallurgical slag results in serious environmental pollution and secondary resources waste (Anon., 2019). Therefore, it is imperative to develop effective and economically viable technologies for the safe disposal and reuse of tailings and metallurgical slag.

Solidification/Stabilization (S/S) has been widely used along with a binder, to reduce contaminant leachability by both physical and chemical means and to convert hazardous waste into a less soluble, mobile or toxic form for land disposal or construction use (Shi and Spence, 2004). Portland cement is a traditionally used binder in S/S processes, and the production of Portland cement results in high levels of power consumption and abundant emissions of CO₂, dust and deleterious gases (SO₂, CO, NO_x). Furthermore, the use of non-renewable resources during the Portland cement production process is of concern (Wu et al., 2018). Thus, many researchers have studied on developing cement admixture or cement-free binders to reduce the usage of cement and improve the solidification/stabilization efficiency, such as, ground granulated blast furnace slag (GGBFS) (Wang et al., 2018a; Dinakar et al., 2013; Salihoglu, 2014) or waste biochar (Wang et al., 2019a) as

Abbreviations: AA, acetic acid; As, arsenic; CFL, cumulative fraction leached; C-S-H, calcium silicate hydrate; DW, distilled water; D_{obs} , observed diffusion coefficients; FGDG, flue gas desulfurization gypsum; GGBFS, ground granulated blast furnace slag; MSB, metallurgical slag-based binders; MST, the MSB S/S treated tailings; MT, mine tailings; OPC, Ordinary Portland Cement PO42.5; Sb, antimony; SN, dilute sulfuric/nitric acid; SSP, steel slag powder; S/S, solidification/stabilization; UCS, unconfined compressive strength

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cement admixture, alkali-activated clay binder (Wang et al., 2019b), fly ash Si-modified MgO style cement (Wang et al., 2019c), sodium hydroxide-stimulated the geopolymer mine tailings binder (Ahmari and Zhang, 2013), fly ashes and metakaolin composites-surface tailored geopolymer binder (Rasaki et al., 2019). However, there have been few reports to date on the application of steel slag powder (SSP) and cement without clinker (Criado et al., 2017; Yi et al., 2012). In the present study, metallurgical slag-based binders (MSB) with different constituent ratios of GGBFS-SSP-flue gas desulfurization gypsum (FGDG) were investigated as cementitious materials. In the hydration process, SSP and FGDG provide Ca^{2+} , OH^- , SO_4^{2-} and a small amount of silica tetrahedron (Wang and Yan, 2010; Li et al., 2018), facilitating the breakage of Si-O and Al-O bonds in GGBFS vitreous body (Zhang et al., 2019). This process promotes the formation of calcium silicate hydrate (C-S-H) and ettringite (Tsai et al., 2014; Park et al., 2016; Young and Cements, 2001), which would enhance the physical and mechanical properties of S/S treated matrix and reduce the leachability of contaminants in S/S treated waste containing As and Sb (van der Sloot et al., 2006; Salihoglu, 2014; Dutré and Vandecasteele, 1995). However, to the best of our knowledge, no relative studies have been performed on MSB immobilization of tailings containing high concentration of As and Sb, or the leaching characteristics of the MSB S/S treated tailings (MST).

Since the leaching characteristics of S/S materials under different environmental conditions are of high concern, numerous leaching test methods have been proposed. The system proposed by (Lewin et al. (1994)) classifies leaching tests based on whether the leachant is renewed or not, as either extraction tests such as TCLP, SPLP, DIN 38414-S4, BS EN 12457, HJ/T299-2007 (SEPA, 2007) and HJ557-2010 (SEPA, 2010), or dynamic tests such as the USEPA Multiple Extraction Procedure, ANSI/ANS-16.1-2003 (Institute and Society, 2004) and ASTM C1308-08 (ASTM, 2008). Extraction tests measure the chemical properties of the system and not the rate-limiting mechanisms, with tests conducted on granular material and therefore not accounting for reduction in leachability due to the production of monolithic material (Spence and Shi, 2004). Dynamic tests can provide more realistic simulations of the actual leaching conditions required for contaminants to be encapsulated in solidified matrices.

In the present study, tailings with high concentration of As and Sb were collected as the object. A series of semi-dynamic leaching tests were performed on MST as per ASTM C1308-08 (ASTM, 2008), using three types of leachant to simulate actual leaching conditions and investigate the effectiveness and environmental safety of the MSB S/S technique. The influence of MSB constituents and the leachant pH and total acidity on the leaching characteristics of MST were investigated. The findings of this study could facilitate the utilization of MSB in S/S processes and the reuse of MST as a secondary material.

2. Experimental

2.1. Materials and sample preparations

The materials used in this study included GGBFS, SSP, FGDG, high As- and Sb-containing mine tailings (MT) and Ordinary Portland Cement PO42.5 (OPC). MT samples were collected from a lead-zinc ore dressing plant in Hechi Nandan, Guangxi (China), which were fine-grained mill tailings with a grain size of $+74\ \mu\text{m} = 4.61\% < 20\%$ and $-19\ \mu\text{m} = 77.01\% > 50\%$ (Yilmaz et al., 2011), as shown in Table 1. GGBFS, SSP and FGDG were provided by Jintaicheng Environmental

Table 2

Raw material chemical components, physical properties, concentrations and leached concentration of As and Sb.

Materials		MT	GGBFS	SSP	FGDG
Chemical composition	MgO	0.91	10.78	6.36	1.04
Oxide (wt. %)	Al_2O_3	4.08	15.43	5.73	0.78
	SiO_2	36.92	33.32	18.16	2.03
	SO_3	15.84	0.83	0.29	44.97
	CaO	13.86	36.36	43.58	30.01
	Fe_2O_3	16.03	1.01	21.66	0.48
	Na_2O	—	0.49	0.21	0.06
	K_2O	0.89	0.48	0.12	0.15
	P_2O_5	0.32	0.08	1.92	0.06
	TiO_2	0.18	0.85	0.95	0.04
	Sb_2O_3	0.11	—	—	—
	As_2O_3	0.99	—	—	—
	LOI	8.35	0.12	1.42	21.07
Blaine fineness (m^2/kg)	—	—	440	380	350
pH	6.35	11.92	12.28	7.85	—
Total As/Sb concentration (mg/kg)	16440/1796	ND	ND	ND	ND
As/Sb leaching concentration (mg/L)	0.65/1.41	ND	ND	ND	ND

ND : not detected as the concentrations were below the method detection limit (0.004 mg/L).

Resources Co., Ltd. (Hebei, China). The total concentrations of As and Sb, were determined by an Agilent 7500a ICP-MS (Agilent Technologies, USA) after aqua regia digestion (1/3 concentrated HNO_3 and HCl (v/v)) according to the Chinese standard method HJ 803-2016, while the leaching concentration of As and Sb after horizontal oscillation leaching tests, were determined according to the Chinese standard method HJ557-2010 (Table 2). Fig.1 shows the results of XRD analysis of these materials, conducted on Rigaku D/max-RB X-ray diffract meter with $\text{CuK}\alpha$ radiation, voltage 40 kV, current 200 mA and 2θ scanning and ranging between 10° and 70° .

GGBFS, SSP and MT were dried in an oven at 105°C for 24 h, while FGDG was dried at 60°C for 48 h before tests. To prepare MST samples, the different constituents of MSB were mixed with MT at specific ratios as outlined in Table 3. OPC was used as cementitious material for the control group treatment. The binder-tailings (w/w) ratio was 1:4, with a solid concentration of 70%. Although sufficient FGDG must be present to stimulate GGBFS hydration, excessive FGDG may lead to matrix expansion in the later stage of the hydration reaction (Chen et al., 2012) and therefore, the proportion of FGDG was fixed at 10%.

The MT and MSB samples were first mixed for 1 min using a standard cement mortar mixer. Distilled water was added until the solid concentration reached 70% and the blended mortar was mixed for another 5 min, before being cast into steel molds ($40\ \text{mm} \times 40\ \text{mm} \times 160\ \text{mm}$) for assessment of the unconfined compressive strength (UCS) as per the Chinese Standard method GB/T 17671-1999 and cast into cylindrical PVC molds (diameter 50 mm, high 50 mm). Distilled water was added to MSB2 (70% GGBFS, 20% SSP and 10% FGDG (wt.%)) and OPC until water-binder ratio reached 0.35, and the blended paste was mixed for another 5 min, before being cast into steel molds ($40\ \text{mm} \times 40\ \text{mm} \times 160\ \text{mm}$). Only samples M2, M4, M6, M8 and P were chosen for semi-dynamic leaching tests. Triplicate samples were prepared for the UCS tests and semi-dynamic leaching tests respectively. All mortar and paste samples were cured in a moist cabinet with $40 \pm 2^\circ\text{C}$, $90 \pm 1\%$ relative humidity conditions (similar to the underground filling environment in Guangxi (Zhang et al., 2019)) for 3d, then samples were de-molded and placed in the same curing conditions until the appropriate degree of sample ageing was achieved.

Table 1

Particle size composition of tailings.

Grain Size/ μm	200	74	45	19	12	7	4.5	2.2	0.67	0.16	0.1
Differentiation/%	4.61	3.24	1.89	10.34	19.81	14.5	12.76	11.09	9.09	5.44	3.45
Accumulation/%	100	95.39	92.15	77.01	62	47.5	34.74	23.65	14.56	9.12	5.67

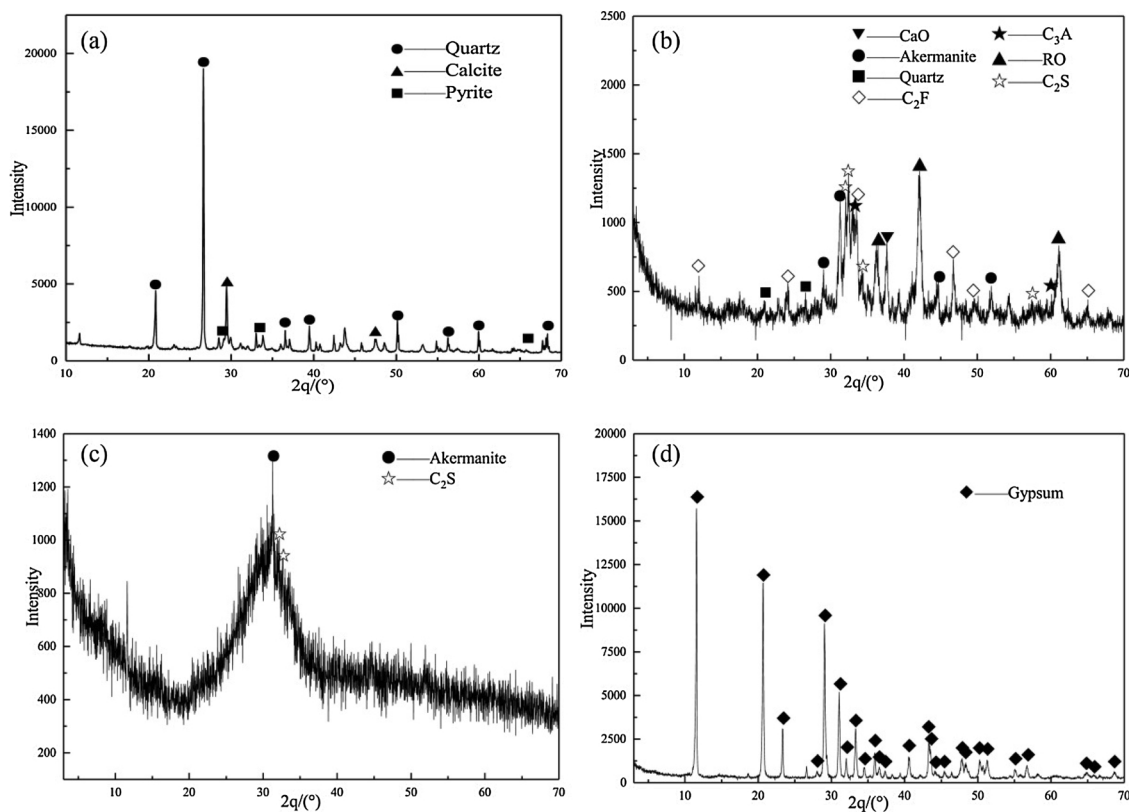


Fig. 1. XRD patterns of the raw materials: (a) MT; (b) SSP; (c) GGBFS; (d) FGDG.

Table 3

Different proportions of MSB components, with the equivalent binder-tailings ratio and solid concentration of MST samples.

Notation	MSB (mass fraction/ wt. %)			Binders/ tailings (w/w)	Solid concentration ^a (wt. %)
	GGBFS	SSP	FGDG		
M1	80	10	10	1/4	70
M2	70	20			
M3	60	30			
M4	50	40			
M5	40	50			
M6	30	60			
M7	20	70			
M8	10	80			
P ^b	100(OPC)				

^a Solid concentration = (binders + tailings) / (binders + tailings + water).

^b OPC used as a cementitious material for the control group.

2.2. Methods

The debris formed during the UCS test was collected to perform extraction leaching tests, according to the Chinese standard method HJ557-2010. The ratio of leachant (deionized water) volume to specimen weight was maintained at 10:1(L/Kg), with a specimen particle size of < 3 mm. Samples were oscillated horizontally for 8 h and then allowed to stand at room temperature for 16 h. After filtration using a 0.45 μ m polypropylene microfiltration membrane, the leachate was investigated using ICP-MS.

The semi-dynamic leaching tests were conducted as per the ASTM standard method C1308. Before tests, loose particles on the specimen surface were removed by thorough rinsing for 30 s using distilled water. In order to suspend each S/S sample near the centroid of the leachant, a nylon mesh harness was used to support the cylindrical MST in a high

density polyethylene container. The ratio of volume of leachant (1177.5 mL) to the external geometric surface area of cylindrical MST (117.5 cm²), was maintained at 10 ± 0.2 (cm). In the present study, three types of leachant were chosen to simulate the actual leaching conditions: (1) distilled water (DW) for the simulation of groundwater or surface water environments (according to the Chinese standard method HJ557-2010); (2) dilute sulfuric/nitric acid (SN) for the simulation of acidic precipitation exposure environments (according to Chinese standard HJ/T 299-2007, pH 3.20); (3) acetic acid (0.17 mol/L) (AA) for simulation of a pH 2.64 sanitary landfill leachate environment (according to the Chinese standard method HJ/T 300-2007). Leaching tests were conducted at a constant temperature of $40 \pm 2^\circ\text{C}$, with the leachate collected and replaced at designated time intervals of 2 h, 5 h, 17 h, 1d, 2d, 3d, 4d, 5d, 6d, 7d, 8d, 9d, 11d and 13d. The pH values were measured when the leachate temperature decrease to $25 \pm 2^\circ\text{C}$ and then the leachate was filtered through a 0.45 μ m polypropylene microfiltration membrane. Afterwards, the leachate samples were acidified to below pH 2 using concentrated HNO₃ and then stored at 4°C in the dark prior to As and Sb detection by ICP-MS. The concentration of soluble calcium and silica was analyzed using a PerkinElmer Optima 8300 ICP-OES. The concentrations of As, Sb, Ca, and Si were analyzed in triplicate using the acidified sample leachate to ensure accuracy. Mean results for triplicate samples (with standard deviations less than 5%) and error bar are presented in this study. The cumulative fraction leached (CFL) of As, Sb, Ca and Si in semi-dynamic leaching tests was calculated using Eq. (1), and its plot against time square root ($t^{1/2}$) enabled the computation of observed effective diffusion coefficients (D_{obs}) using Eq. (2) (ASTM, 2008). If diffusion is the dominant mechanism, this theory suggests the following relationship, as described by Eq. (3) (de Groot and van der Sloot, 1992). The relationship between observed, effective, and molecular diffusivity (Spence and Shi, 2004) is shown in Eq. (4) (See attachment for detailed description):

$$CFL = \frac{A_t}{A_0} = \frac{1}{A_0} \sum_i (C_i \times V_i) \quad (1)$$

$$D_{obs} = \frac{\pi}{4} \times \left(\frac{V}{S} \right)^2 \times \frac{CFL^2}{t} \quad (2)$$

$$\log(B_t) = \frac{1}{2} \log(t) + \log(U_{max} d \sqrt{\frac{D_{obs}}{\pi}}) \quad (3)$$

$$D_{obs} = \frac{D_{eff}}{R} = \frac{D_{mol}}{\tau \times R} \quad (4)$$

Where A_t = the cumulative mass of the contaminant leached from the medium surface (mg); A_0 = the total mass of substance contained in the soil prior to analysis (mg); c_i = the measured concentration of the leached contaminant in the leachate at the i^{th} test interval (mg/L); V_i = the volume of the leachate at the i^{th} test interval (L); V = the specimen volume (cm^3); S = the surface of the sample used in the semi-dynamic leaching test (cm^2); t = leaching time(s); B_t = the cumulative maximum release of the compound (mg/cm^2); U_{max} = the maximum leachable quantity (mg/kg); d = the bulk density of the S/S product (kg/m^3); D_{obs} = diffusivity in chemically reactive systems (cm^2/s); D_{mol} = the term denoting the rate of change in the concentration gradient for a species diffusing in an aqueous media; τ = tortuosity; R = chemical retardation; D_{eff} = the term to describe the mass transport when physical retardation is present.

3. Results

3.1. UCS test results and XRD spectra of MSB paste

Fig. 2 shows the results of UCS tests, where with an increase in MSB SSP content, the USC at 28 days decreased, in all samples except for M1. All samples could be satisfied strength requirement (1Mpa) of fill materials (Wang et al., 2019a, 2019b; EPD, 2011). The highest 28-day USC of 5.65 MPa was obtained by M2 samples, containing 70% GGBFS, 20% SSP and 10% FGDG. Fig. 3 shows the XRD spectra of MSB2 and OPC paste. The main hydrates of MSB2 are ettringite and C-S-H gel, and the main hydrates of OPC are ettringite, C-S-H gel and portlandite. The UCS of M1 and M8 at 3 days were zero, indicating that an excess of GGBFS or SSP in MSB will result in slow hydration reactions and reduced strength in the early phase. The UCS of M2 and M3 at 3, 7 and 28 days were higher than the OPC of S/S treated samples, indicating that MSB with an appropriate constituent ratio has both good mechanical performance and broad application prospects.

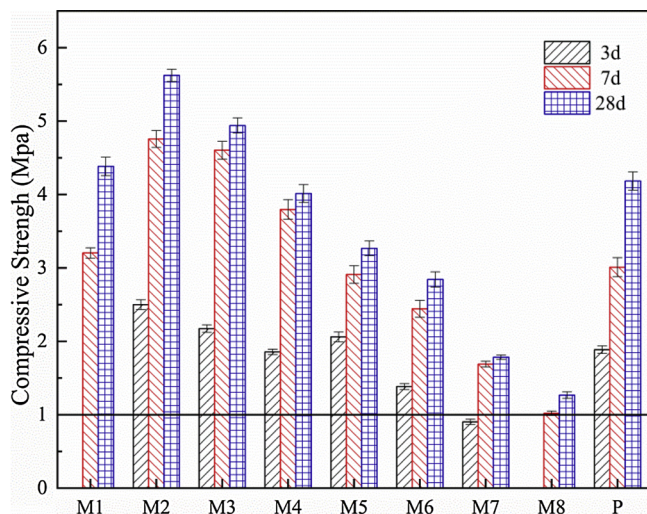


Fig. 2. Compressive strength of MST samples (black line at 1Mpa: required strength for fill materials.).

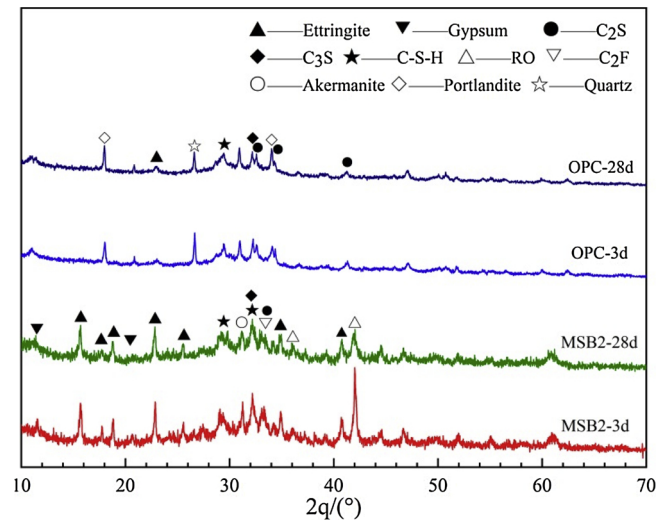


Fig. 3. XRD spectra of MSB2 and OPC paste.

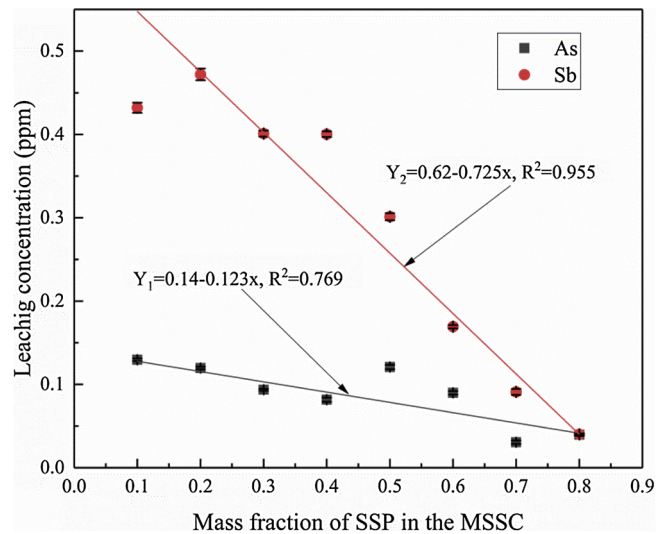


Fig. 4. Variation in leached concentrations of As and Sb, according to the mass fraction of SSP in MSB.

3.2. Extraction test results

Fig. 4 shows the variation in leached concentration of As and Sb, according to differing mass fractions of SSP in MSB. In all leachate samples, the As and Sb concentrations mainly ranged from 0.03 to 0.13 mg/L and from 0.04 to 0.472 mg/L respectively, with mean concentrations of 0.088 and 0.287 mg/L, respectively. It is of note, that the leachate concentrations of As and Sb far exceeded the stipulated drinking water quality limits according to the Chinese standard GB 5749-2006, even though the extraction test is an equilibrium leaching test and does not well simulate the actual monolithic material leaching condition, the possible risk of contamination deserves more research attention. Investigation into the effect of varying mass fractions of SSP in MSB on the leached concentrations of As and Sb, found that relatively strong negative linear relationships were observed, with R^2 values of 0.769 and 0.955, respectively.

3.3. The semi-dynamic leaching test results

Fig. 5 shows the variation in leachate pH according to leaching time, under semi-dynamic leaching test conditions with different leachants. The pH of the leachate increased with higher SSP contents in MSB,

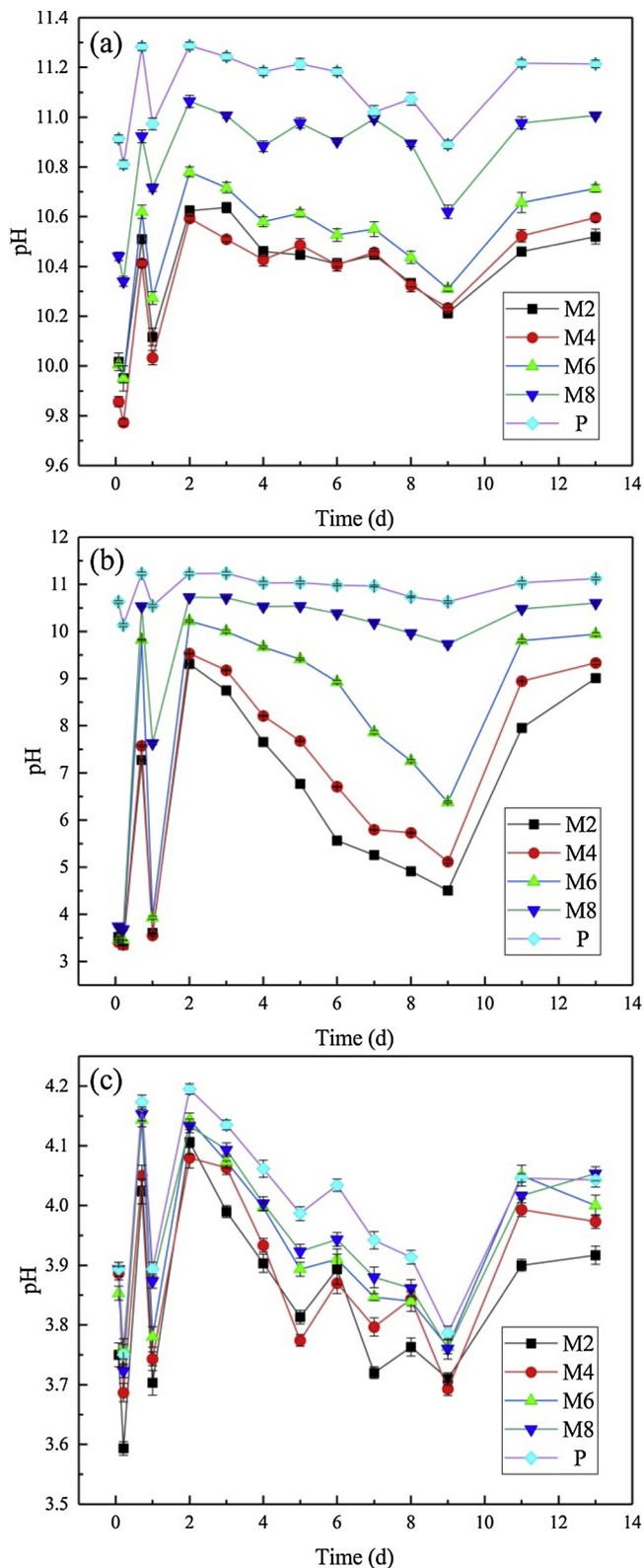


Fig. 5. Variation in leachate pH with leaching time. Leachant: (a) Distilled water, (b) Dilute sulfuric/nitric acid, (c) Acetic acid.

irrespective of the type of leachate, due to SSP dissolution and hydration (Li et al., 2019). The pH values of OPC-treated samples were higher than all MST samples, as higher amounts of $\text{Ca}(\text{OH})_2$ were produced during the cement clinker hydration. Leachate pH values range from 9.79 to 11.29, 3.41 to 11.22 and 3.6 to 4.2, for the DW, SN and AA

leaching conditions, respectively. These pH variations can be attributed to a greater amount of H^+ than OH^- being leached from the sample and the higher buffering capacity of AA. Conversely, for DW and SN the opposite was observed and Fig. 5(b) highlights that the increasing SSP content improved the ability of MST to resist acid corrosion.

Fig. 6 shows the variation in leachate As and Sb concentrations with leaching time. For the AA leachant, the leached As concentration was an order of magnitude greater than that of DW and SN leachants, while the concentration of Sb did not increase significantly. However, the As and Sb concentrations differed marginally between DW and SN leaching conditions. The leachate As concentration showed a consistent downward trend with increasing SSP content in MSB, under all leaching conditions, with the exception of M6 under AA leaching conditions. In contrast, the leachate Sb concentrations showed a consistent upward trend with increasing SSP content in MSB, presenting an opposite trend to As. The control group of OPC-treated samples showed excellent results for immobilization of As, while did not effectively immobilize Sb. This phenomenon may indicate the existence of different dominant immobilization mechanisms for As and Sb.

3.4. Observed diffusion coefficient

Table 4 shows the slope of $\log(B_t) - \log(t)$, established from semi-dynamic tests and the leaching mechanisms of As and Sb under different leaching conditions, according to Eq. (3). This study shows that under DW and SN leaching conditions, the As and Sb $\log(B_t) - \log(t)$ slope for all MST samples were in the range of 0.47 to 0.6, indicating that the controlling mechanism is diffusion. Under AA leaching conditions the Sb leaching mechanism is also diffusion, although As leachability is dissolution controlled as the As $\log(B_t) - \log(t)$ slopes were in the range of 0.91 to 0.99.

Fig. 7 presents the variation in CFL of As and Sb, with the square root of leaching time. In all leachant types assessed in this study, with the exception of As under AA leaching conditions, the plot of $\text{CFL} \cdot t^{-1/2}$ for As and Sb is well represented by a linear line of fit throughout the entire leaching duration, irrespective of varying MST samples.

Table S3 in Supplementary information lists the calculated D_{obs} values for As and Sb, which were established according to Eq. (2). The D_{obs} for As and Sb were in the range of 10^{-15} – 10^{-13} and 10^{-11} – 10^{-9} , respectively. According to Malviya and Chaudhary (2006), when $D_{\text{obs}} < 3 \times 10^{-9} \text{ cm}^2/\text{s}$, the mobility of contaminants is low, and the S/S waste can be applied for “controlled utilization” in scenarios such as road bases, lagoon closure and quarry rehabilitation, and the risk of environmental pollution is within an acceptable range (Fuller, 2018). Under the sanitary landfill leaching environment simulated by AA leaching conditions at 40°C , the D_{obs} values for Sb were lower than $3 \times 10^{-9} \text{ cm}^2/\text{s}$, although the As leaching mechanism is dissolution, so the disposal of high As-containing MST in sanitary landfill environments is improper.

3.5. Leachate concentrations of Ca and Si

The leachate Ca and Si concentrations were also monitored in the present study. Leachate Ca concentrations ranged from 12.07 to 64.34 mg/L, 19.46 to 77.31 mg/L and 196.16 to 599.54 mg/L, under DW, SN and AA leachant conditions, respectively, while the leachate Si concentrations ranged from 0.02 to 2.01 mg/L, 0.06 to 1.98 mg/L and 6.00 to 23.48 mg/L, respectively. The concentrations of Ca and Si were much higher than those of As and Sb. With the increase in SSP content of MSB, the leachate Ca concentrations showed an upward trend and the leachate Si concentrations showed a downward trend (Fig. 8). Ca exists in cement-like base materials in three forms, including free form (dissolved in the pore water), absorbed form (absorbed with matrix particles) and hydrated form (in the hydrated products), with the mobility of the hydrated form being less than the other two types (Du et al., 2012). The variation in Ca concentration with increasing SSP

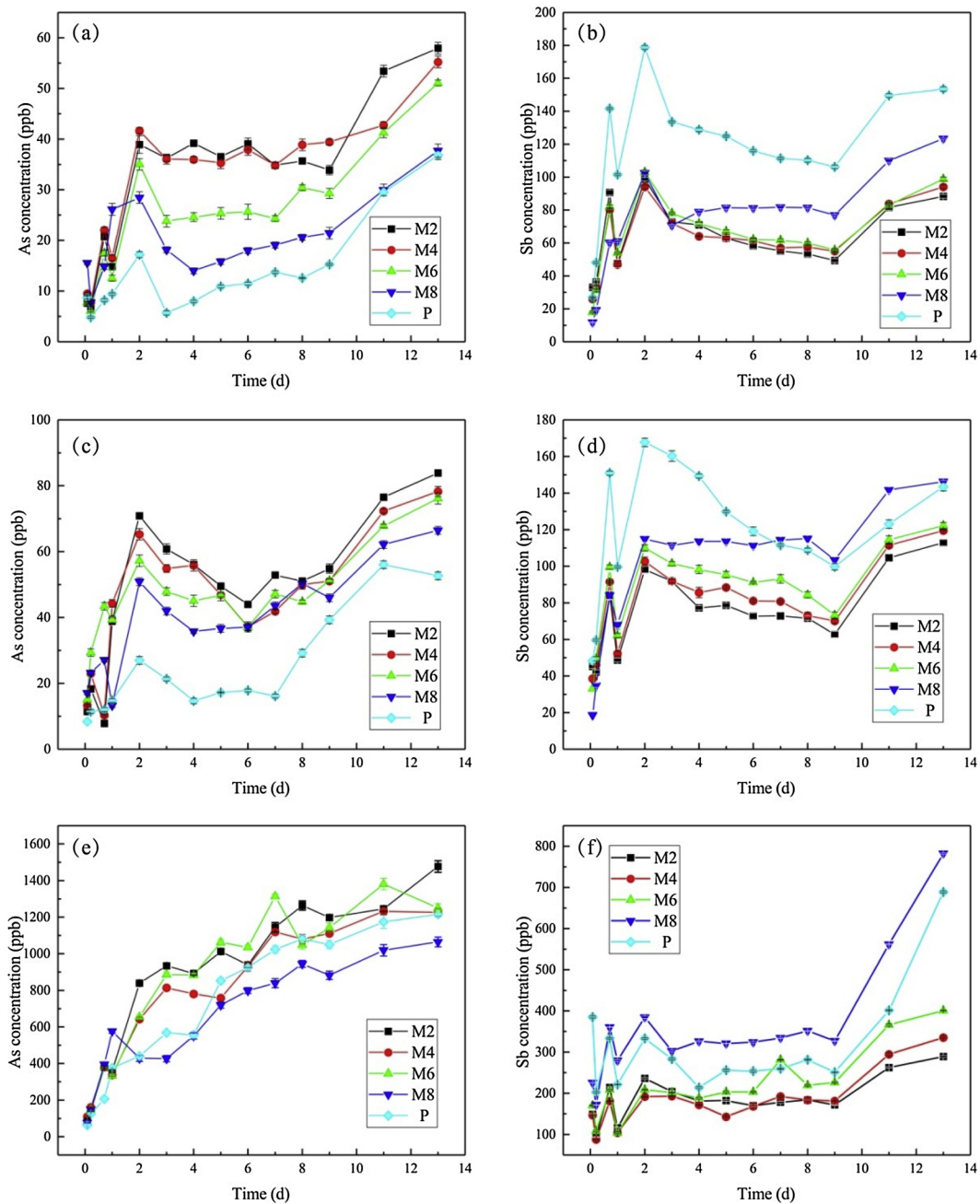


Fig. 6. Variation in leachate As and Sb concentrations with leaching time. Leachant: (a) (b) Deionized water, (c) (d) Dilute sulfuric/nitric acid, (e) (f) Acetic acid.

Table 4

The slope of $\log(B_t) - \log(t)$ established from semi-dynamic tests and leaching mechanisms of As and Sb under different leaching conditions.

Leachant		Deionized water			Dilute sulfuric/nitric acid			Acetic acid		
	Sample	Slope	R ²	Mechanism	Slope	R ²	Mechanism	Slope	R ²	Mechanism
As	M2	0.53	0.9976	Diffusion	0.56	0.9667	Diffusion	0.96	0.9976	Dissolution
	M4	0.58	0.9971	Diffusion	0.57	0.978	Diffusion	0.91	0.9958	Dissolution
	M6	0.57	0.9971	Diffusion	0.58	0.9983	Diffusion	0.99	0.9969	Dissolution
	M8	0.58	0.9899	Diffusion	0.59	0.9941	Diffusion	0.91	0.9914	Dissolution
	P	0.55	0.976	Diffusion	0.6	0.9831	Diffusion	0.99	0.9906	Dissolution
Sb	M2	0.53	0.9957	Diffusion	0.51	0.9988	Diffusion	0.57	0.9973	Diffusion
	M4	0.51	0.9953	Diffusion	0.55	0.9978	Diffusion	0.56	0.9908	Diffusion
	M6	0.54	0.9892	Diffusion	0.53	0.9952	Diffusion	0.56	0.9846	Diffusion
	M8	0.47	0.9948	Diffusion	0.59	0.9958	Diffusion	0.6	0.9916	Diffusion
	P	0.48	0.9881	Diffusion	0.59	0.9957	Diffusion	0.46	0.9889	Diffusion

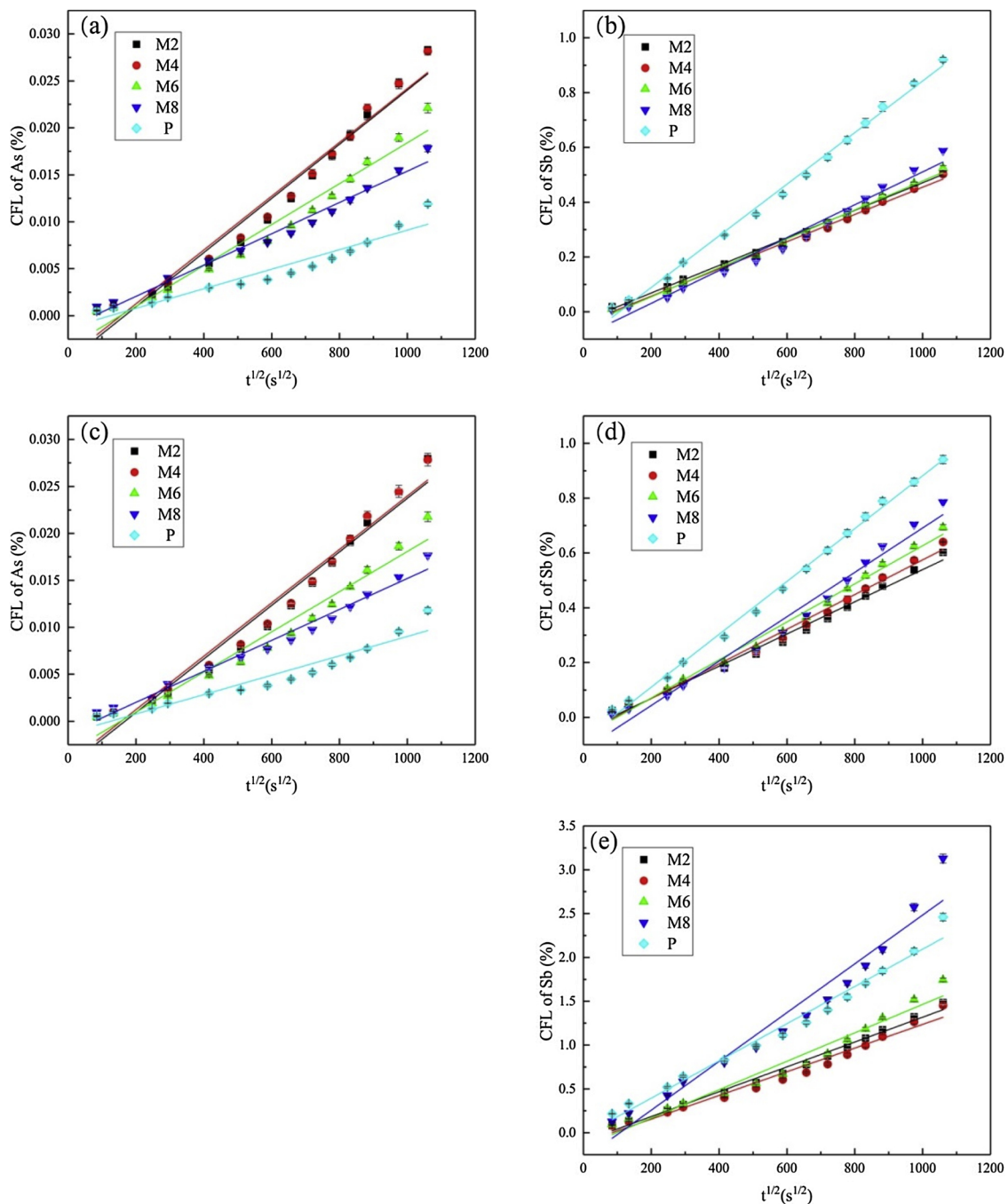


Fig. 7. Variation in CFL of As and Sb with square root of leaching time. Leachant: (a) (b) Deionized water, (c) (d) Dilute sulfuric/nitric acid, (e) Acetic acid.

content in MSB (Fig. 8 (a) (c) (e)), can be attributed to less hydration products being formed, which is supported by the UCS test results (Fig. 2). The variation in Si concentration with increasing SSP content was attributed to the different content of Si in GGBFS and SSP (Table 2), as well as the mineral phase of GGBFS mainly being vitreous body leading to a higher release of Si in the GGBFS hydration process, compared with SSP (Fig. 1).

4. Discussion

This study demonstrates that variation of the constituents of MSB affects the leaching characteristics of MST samples. This finding can be attributed to the effect of different MSB constituents on the dominant immobilization mechanisms of As and Sb in MST. Immobilization of As

and Sb by cement-like materials includes the following three mechanisms, affecting the leaching behavior of As and Sb in MST simultaneously. Firstly, precipitation during which low solubility Ca-As and Ca-Sb precipitation occurs. Previous research (Li et al., 2016; Lei et al., 2017; Hiraga and Shigemoto, 2012; Lei et al., 2018; Zhu et al., 2006; Bothe and Brown, 1999; Raposo et al., 2004; Stronach et al., 1997; Johnson et al., 2005; Cornelis et al., 2008) has proven the formation of CaHAsO_3 , $\text{Ca}_3(\text{AsO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{CaNaAsO}_4 \cdot 7.5\text{H}_2\text{O}$, $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ca}_5(\text{AsO}_4)_3(\text{OH})$ precipitates as shown in Table S4. And (Cornelis et al. (2012)) reported the precipitation of Roméite ($(\text{Ca}, \text{Na})_2\text{Sb}_2\text{O}_6(\text{O}, \text{OH}, \text{F})$) in cement matrix. It has also been well recognized that the formation of amorphous Fe arsenate and/or insoluble secondary oxidation minerals occurs as shown in Table S5 (Kumpiene et al., 2008; Fujita et al., 2009, 2012). Secondly, adsorption and solid

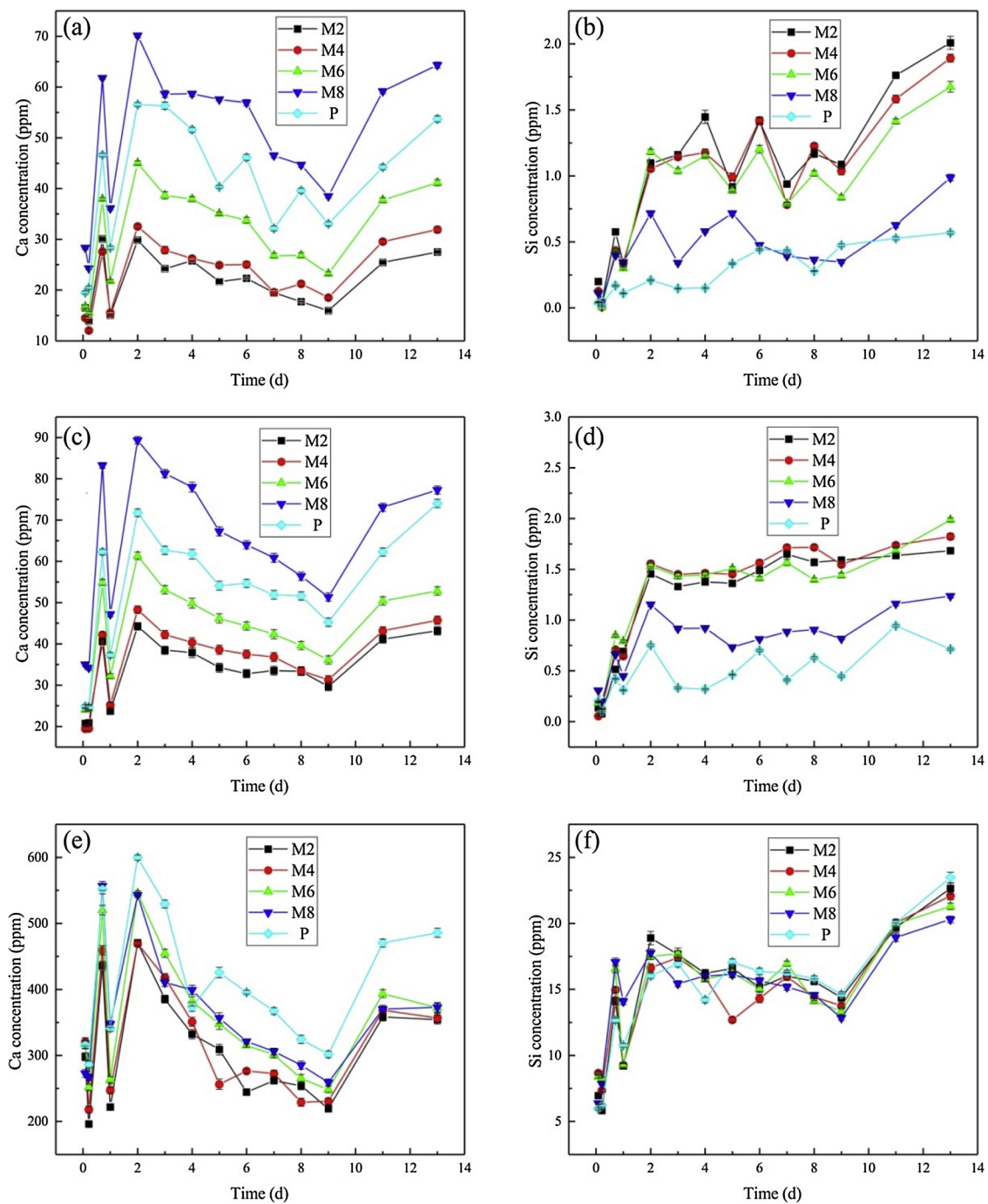


Fig. 8. Variation in leachate Ca and Si concentration with leaching time. Leachant: (a) (b) Deionized water, (c) (d) Dilute sulfuric/nitric acid, (e) (f) Acetic acid.

solution formation occurs due to its high surface area and amorphous properties, several studies have reported that C-S-H is a principle mineral phase for the adsorption of As (Min et al., 2019) and Sb (Hale et al., 2012). Solid solution formation with ettringite is likely for As and Sb oxyanions because it is a common mineral and it has been shown that partial or full replacement of SO_4^{2-} is possible in the case of AsO_4^{3-} (Tolonen et al., 2016) and $\text{Sb}(\text{OH})_6^-$ (Cornelis et al., 2012). Thirdly, physical encapsulation occurs, where for low permeability materials ($< 10^{-9}$ m/s) infiltration of water is negligible and the rate of constituent release is limited by the diffusion of species to the surface (Wang et al., 2018b). According to the Eq. (4), the tortuosity τ and chemical retardation R of MSTs determine the value of As and Sb D_{obs} . With the increase in SSP content of MSB, the UCS test values decreased (Fig. 2), indicating less hydration products, weaker relevant absorption

and physical encapsulation effects and smaller tortuosity τ values; However, extraction tests showed more effective immobilization of both As and Sb (Fig. 4), ignoring the different influence of physical encapsulation and tortuosity τ by crushing matrices into debris, indicating more active chemical retardation and larger R values; For the semi-dynamic tests, the As D_{obs} values decreased and Sb D_{obs} values increased respectively with the increase in SSP content of MSB (Table S3), indicating the increasing effect of chemical retardation for As canceled out the decreasing effect of MSTs' tortuosity, while the opposite was true for Sb. Therefore, precipitation is the dominant immobilization mechanism for As affecting the leaching characteristics of As, while the dominant mechanism of Sb immobilization is physical encapsulation.

This study demonstrates that the leachant pH and total acidity have

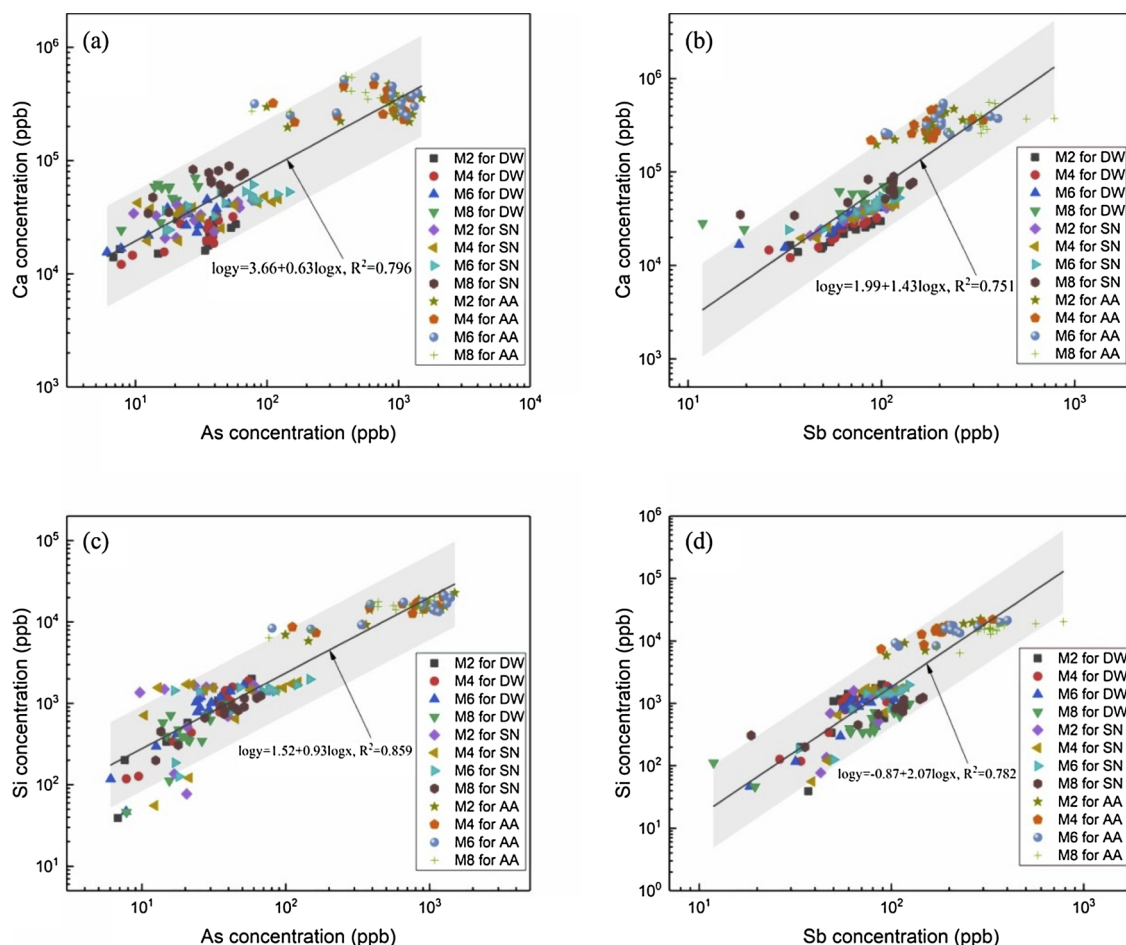


Fig. 9. Variation in the leached concentration of (a) Ca with As; (b) Ca with Sb; (c) Si with As; (d) Si with Sb.

a considerable effect on the leaching characteristics of MST, which can be attributed to the effects of pH and total acidity on the stability of hydration products, such as C-S-H, ettringite and Ca(OH)_2 . With increased leachant total acidity, samples gradually lost their acidity buffering capacity (Fig. 5) displaying increased leaching parameter values including leached concentration, CFL and D_{obs} for As, Sb, Ca and Si. Compared to DW and SN leachant conditions, AA leachants lead to the release of numerous components. The effects of leachant pH and total acidity and MSB constituents on the stability of hydration products are reflected by the linear log-log relationship, as shown in Fig. 9. Overall, the effect of leachant pH and total acidity on leaching characteristics is much more influential than the MSB constituents.

In this study, it is not clear which precipitation is the dominant immobilization mechanism and further studies are needed to effectively optimize the design of MSB constituents. Compared with actual leaching condition, the laboratory simulated conditions were simplified and idealized, with further studies required on the effectiveness of MSB immobilization of As and Sb in tailings and the leaching characteristics of MST, under actual leaching conditions.

5. Conclusions

This study investigates the effect of three types leachant on the leaching characteristics of MST via a series of semi-dynamic leaching tests. The effects of the leachant pH and total acidity and MSB constituents on the leachate pH, leached As, Sb, Ca and Si concentrations, As and Sb leaching mechanisms, as well as the D_{obs} values for As and Sb, were investigated. Based on the results obtained from this study, the following conclusions can be drawn:

(1) AA leachant conditions (0.17 mol/L, pH 2.64) resulted in a substantially lower leachant pH, with increased leached As, Sb, Ca and Si concentrations compared to under DW and SN leachant conditions.

(2) The dominant leaching mechanism of As under DW and SN leaching conditions is diffusion, while under AA leaching condition, mineral dissolution was found to be the dominant mechanism. The dominant leaching mechanism for Sb under DW, SN and AA leaching conditions was diffusion.

(3) Physical encapsulation was the dominant mechanism for Sb immobilization in monolithic MST, while the dominant mechanism for As immobilization was precipitation.

(4) The effects of leachant pH and MSB constituents on the leached As, Sb, Ca and Si concentrations, can be attributed to the stability of hydration products and their influence on the matrices buffering capacity and structure. Leachant pH and total acidity had the greatest influence on the leaching characteristics of MST.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jhazmat.2019.120992>.

References

- Ahmari, S., Zhang, L., 2013. Durability and leaching behavior of mine tailings-based geopolymer bricks. *Constr. Build. Mater.* 44, 743–750.
- Anon, 2019. The Disposal of Millions of Tons of Steel Slag by the Yangtze River Threatens the Ecological Environment of the Yangtze River. Available from: http://www.mee.gov.cn/gkml/sthjbgw/qt/201806/t20180628_445704.htm.
- ASTM, 2008. Standard Test Method for Accelerated Leach Test for Diffusive Releases From Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching From Cylindrical Waste Forms.
- Bothe, J.V., Brown, P.W., 1999. The stabilities of calcium arsenates at $23 \pm 1^\circ\text{C}$. *J. Hazard. Mater.* 69 (2), 197–207.
- Chen, I.A., Hargis, C.W., Juenger, M.C., 2012. Understanding expansion in calcium sulfoaluminate–belite cements. *Cem. Concr. Res.* 42 (1), 51–60.
- Cornelis, G., et al., 2008. Leaching mechanisms of oxyanionic metalloid and metal species in alkaline solid wastes: a review. *Appl. Geochem.* 23 (5), 955–976.
- Cornelis, G., et al., 2012. Mechanisms and modelling of antimonate leaching in hydrated cement paste suspensions. *Cem. Concr. Res.* 42 (10), 1307–1316.
- Criado, M., et al., 2017. Alternative inorganic binders based on alkali-activated metallurgical slags. Sustainable and Nonconventional Construction Materials Using Inorganic Bonded Fiber Composites. Elsevier, pp. 185–220.
- de Groot, G.J., van der Sloot, H.A., 1992. Determination of leaching characteristics of waste materials leading to environmental product certification. Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes: 2nd Volume. ASTM International.
- Dinakar, P., Sethy, K.P., Sahoo, U.C., 2013. Design of self-compacting concrete with ground granulated blast furnace slag. *Mater. Des.* 43, 161–169.
- Du, Y.-J., et al., 2012. Experimental investigation of influence of acid rain on leaching and hydraulic characteristics of cement-based solidified/stabilized lead contaminated clay. *J. Hazard. Mater.* 225, 195–201.
- Dutr  , V., Vandecasteele, C., 1995. Solidification/stabilisation of arsenic-containing waste: leach tests and behaviour of arsenic in the leachate. *Waste Manag.* 15 (1), 55–62.
- EPD, H., 2011. Practice Guide for Investigation and Remediation of Contaminated Land. Environmental Protection Department. Hong Kong SAR Government.
- Fujita, T., et al., 2009. Immobilization of arsenic from novel synthesized scorodite—Analysis on solubility and stability. *Mater. Trans.* 50 (2), 321–331.
- Fujita, T., et al., 2012. Environmental leaching characteristics of scorodite synthesized with Fe(II) ions. *Hydrometallurgy* 111–112, 87–102.
- Fuller, W.H., 2018. Soils in waste treatment and utilization. Pollutant Containment, Monitoring, and Closure Vol. II CRC Press.
- Hale, B., Evans, L., Lambert, R., 2012. Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils. *J. Hazard. Mater.* 199, 119–127.
- Hiraga, Y., Shigemoto, N., 2012. Removal of As and Se oxoanions from solution using calcination products of Ca (OH) 2–Al (OH) 3 and CaCO3–Al (OH) 3 mixtures. *J. Chem. Eng. Jpn.* 45 (7), 554–562.
- Institute, A.N.S., Society, A.N., 2004. American National Standard Measurement of the Leachability of Solidified Low-level Radioactive Wastes by a Short-term Test Procedure. American Nuclear Society.
- Johnson, C.A., et al., 2005. Solubility of Antimony and other elements in samples taken from shooting ranges. *J. Environ. Qual.* 34, 248–254.
- Kumpiene, J., Lagerkvist, A., Maurice, C., 2008. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments—a review. *Waste Manag.* 28 (1), 215–225.
- Lei, J., et al., 2017. Modeling and optimization of lime-based stabilization in high alkaline arsenic-bearing sludges with a central composite design. *J. Environ. Sci. Health Part A* 52 (5), 449–458.
- Lei, J., et al., 2018. Effects of anions on calcium arsenate crystalline structure and arsenic stability. *Hydrometallurgy* 177, 123–131.
- Lewin, K., Bradshaw, K., Blakey, N., 1994. Leaching Tests for Assessment of Contaminated Land: Interim NRA Guidance. National Rivers Authority.
- Li, Y., et al., 2018. Corrosion evaluation of steel slag based on a leaching solution test. *Energy Sources Part A Recovery Util. Environ. Eff.* 41 (7), 790–801.
- Li, Y., et al., 2019. Corrosion evaluation of steel slag based on a leaching solution test. *Energy Sources Part A Recovery Util. Environ. Eff.* 41 (7), 790–801.
- Li, Y.-C., et al., 2016. Co-treatment of gypsum sludge and Pb/Zn smelting slag for the solidification of sludge containing arsenic and heavy metals. *J. Environ. Manage.* 181, 756–761.
- Malviya, R., Chaudhary, R., 2006. Leaching behavior and immobilization of heavy metals in solidified/stabilized products. *J. Hazard. Mater.* 137 (1), 207–217.
- Min, X.B., et al., 2019. Comparison of arsenic immobilization properties among calcium silicate hydrate, ettringite, and Friedel's salt in a slag-based binder. *Environ. Prog. Sustain. Energy* 38 (s1), S422–S428.
- Ni, W., 2017. China Bulk Industrial Solid Waste Comprehensive Utilization Industry Development Report. 2018. Industrial Solid Waste Network, Beijing, pp. 20–21.
- Park, H., et al., 2016. Strength enhancement and pore-size refinement in clinker-free CaO-activated GGBFS systems through substitution with gypsum. *Cem. Concr. Compos.* 68, 57–65.
- Raposo, J.C., et al., 2004. Study of the precipitation equilibria of arsenate anion with calcium and magnesium in sodium perchlorate at 25°C . *Appl. Geochem.* 19 (6), 855–862.
- Rasaki, S.A., et al., 2019. Geopolymer for use in heavy metals adsorption, and advanced oxidative processes: a critical review. *J. Clean. Prod.* 213, 42–58.
- Salihoglu, G., 2014. Immobilization of antimony waste slag by applying geopolymerization and stabilization/solidification technologies. *J. Air Waste Manage. Assoc.* 64 (11), 1288–1298.
- SEPA, 2007. Solid Waste-extraction Procedure for Leaching Toxicity-sulphuric Acid & Nitric Acid Method. SEPA, China.
- SEPA, C., 2010. Solid Waste-extraction Procedure for Leaching Toxicity-horizontal Vibration Method. China SEPA, China.
- Shi, C., Spence, R., 2004. Designing of cement-based formula for solidification/stabilization of hazardous, radioactive, and mixed wastes. *Crit. Rev. Environ. Sci. Technol.* 34 (4), 391–417.
- Spence, R.D., Shi, C., 2004. Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes. CRC press.
- Stronach, S.A., et al., 1997. Reactions between cement and As(III) oxide: The system CaO–SiO2–As2O3–H2O at 25°C . *Waste Manag.* 17 (1), 9–13.
- Tolonen, E.-T., et al., 2016. The removal of sulphate from mine water by precipitation as ettringite and the utilisation of the precipitate as a sorbent for arsenate removal. *J. Environ. Manage.* 181, 856–862.
- Tsai, C.-J., et al., 2014. Mechanical and cementitious characteristics of ground granulated blast furnace slag and basic oxygen furnace slag blended mortar. *Mater. Des.* 60, 267–273.
- van der Sloot, H.A., et al., 2006. Developments in the characterisation of waste materials for environmental impact assessment purposes. *J. Geochem. Explor.* 88 (1–3), 72–76.
- Wang, Q., Yan, P., 2010. Hydration properties of basic oxygen furnace steel slag. *Constr. Build. Mater.* 24 (7), 1134–1140.
- Wang, L., et al., 2018a. Low-carbon and low-alkalinity stabilization/solidification of high-Pb contaminated soil. *Chem. Eng. J.* 351, 418–427.
- Wang, L., et al., 2019a. The roles of biochar as green admixture for sediment-based construction products. *Cem. Concr. Compos.* 104.
- Wang, L., et al., 2019b. Green remediation of As and Pb contaminated soil using cement-free clay-based stabilization/solidification. *Environ. Int.* 126, 336–345.
- Wang, Y.-S., et al., 2018b. Influence of lead on stabilization/solidification by ordinary Portland cement and magnesium phosphate cement. *Chemosphere* 190, 90–96.
- Wang, L., et al., 2019c. Novel synergy of Si-rich minerals and reactive MgO for stabilization/solidification of contaminated sediment. *J. Hazard. Mater.* 365, 695–706.
- Wu, H.-L., et al., 2018. Leaching and microstructural properties of lead contaminated kaolin stabilized by GGBS–MgO in semi-dynamic leaching tests. *Constr. Build. Mater.* 172, 626–634.
- Yi, H., et al., 2012. An overview of utilization of steel slag. *Procedia Environ. Sci.* 16, 791–801.
- Yilmaz, E., et al., 2011. Use of high-density paste backfill for safe disposal of copper/zinc mine tailings. *Gospod. Surowcami Miner.* 27, 81–94.
- Young, J.F., Cements, Portland, et al., 2001. In: Buschow, K.H.J. (Ed.), *Encyclopedia of Materials: Science and Technology*. Elsevier, Oxford, pp. 7768–7773.
- Zhang, Y., et al., 2019. Immobilisation of high-arsenic containing tailings by using metallurgical slag-cementing materials. *Chemosphere* 223, 117–123.
- Zhu, Y.N., et al., 2006. Solubility and stability of calcium arsenates at 25°C . *Water Air Soil Pollut.* 169 (1–4), 221–238.