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Original Research

Release Mechanism and Stabilization Effect of Sb and As: A Case Study of the Antimony Mine in Karst Area, Southwestern China

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Abstract

To investigate the heavy metal enrichment mechanisms and release characteristics of typical deposits in karst areas, the Sb tailing pond of Dachang, Qinglong, Guizhou Province, China, one of the three largest Sb mines in the word, was selected as the study area. In this study, samples were collected from tailings (0~120 cm) and analyzed for changes in Sb and As content at different pH values by simulated acid rain static release experiments, and solid waste materials (fly ash, quicklime, and zeolite powder) were selected to design an orthogonal test to explore the optimal stabilization effect of Sb and As. The results showed that the average contents of Sb and As exceeded background values of Guizhou soil to different degrees. The content of As leaching revealed slight differences in the leachate. Sb was sensitive to more acidic conditions, and its release content can pose an ecological risk. Further, the best stabilization effect of Sb and As was observed after adding different ratios of fly ash, quicklime, and zeolite powder for a period of maintenance, which can be used as promising stabilizing materials for mine tailings remediation. This study provides comprehensive theoretical support for enhancing source control and risk management of heavy metals.

Keywords: antimony mine tailings, antimony, arsenic, release characteristics, stabilization

Introduction

China is the world's richest country in antimony (Sb) resources. Relevant studies have shown that China's Sb accounts for 56% of the world's basic reserves, and the Sb resources in southwest China account for 63% of the country's total reserves [1].

The massive exploitation of Sb mineral resources has significantly contributed to the rapid development of the local economy; however, it has also caused a series of environmental problems [2]. During mineral extraction and smelting, heavy metals can be transported to the surrounding environment through atmospheric deposition, surface water, groundwater seepage, etc. Liu et al. [3] used high-performance liquid chromatography/inductively-coupled plasma mass spectrometry (HPLC/ICP-MS) to study the water bodies around the Hunan tin mine and found that the total Sb concentration (mg·L^{-1})

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in the water was 2~3 orders of magnitude higher than the dissolved Sb concentration (<1μg·L^{-1}) in unpolluted rivers. Li et al. [4] studied the tin polymetallic ore in Nandan, Guangxi, and found that the Sb concentration in its water system was as high as 5,475 μg·L^{-1} and that of Arsenic (As) reached 1,877 μg·L^{-1}; Sb and As were also homologous in the region.

Moreover, the accumulation of most heavy metals in the environment is irreversible. They can even enter the human body through the food chain, posing a risk to human health. For example, Sb and As are toxic and carcinogenic metalloids that cause cardiovascular and respiratory disease, cell carcinogenesis, and other serious health effects [5, 6]. As has been recognized as a human carcinogen (Group I) by the International Agency for Research on Cancer. Sb was also included in the Basel Convention Hazardous Waste List, which is related to the transboundary movement of hazardous wastes [7]. It can be seen that the pollution of Sb, As, and other heavy metals brought on by the development of mineral resources has been an urgent environmental problem.

The Guizhou Province has the largest distribution of karst areas in China and is one of the provinces most affected by acid rain. The famous Qinglong Dachang Sb mine located in this province has been in operation for more than 100 years [8]. The mine is situated in an area with a wide distribution of carbonate rocks on a plateau in mountainous terrain. The tailing pond is close to the smelter and is surrounded by mountains. This geological environment is unique and complex, with significantly strong karstification. Since the mine closed in 2008, its tailing pond has become a natural stockpile; it is of a large size and contains various types of mining waste material [9]. Under the effect of long-term rainwater leaching and surface runoff, tailings leachate containing a variety of toxic and harmful elements will most likely be released vertically into the groundwater environment, resulting in different degrees of threat to the surrounding ecological environment. Therefore, the special karst landscape and fragile ecosystems of the region determine the complexity and necessity of heavy metal pollution management in the Dachang tailing pond.

The Dachang Sb mine in Qinglong, Guizhou Province, was selected as the study area. This study aimed to (1) conduct an analysis of the distribution characteristics of the common heavy metals Sb and As from the tailing pond profiles, (2) study the release characteristics of Sb and As under simulated acid rain conditions, and (3) determine the best combination of stabilizing materials (fly ash, quicklime, and zeolite powder) for maximum stabilization efficiency using an orthogonal test. In order to provide basic support for pollution prevention, control, and management of tailing ponds of the same type in karst areas.

Materials and Methods

Study Area

The study area (25°40′30″N~25°40′30.1″N, 105º08′00″E~105º08′03″E) is located in Dachang town, Qinglong County, Guizhou Province, China (Fig. 1). The elevation is 1,200~1,800 m, and the site is located in the sloping zone between the Yunnan-Guizhou Plateau and the Guangxi hilly basin. The terrain is high in the northwest and low in the southeast and characterized by a typical karst landform with high relief, several cliffs, and a highland subtropical monsoon climate (average annual temperature and rainfall of

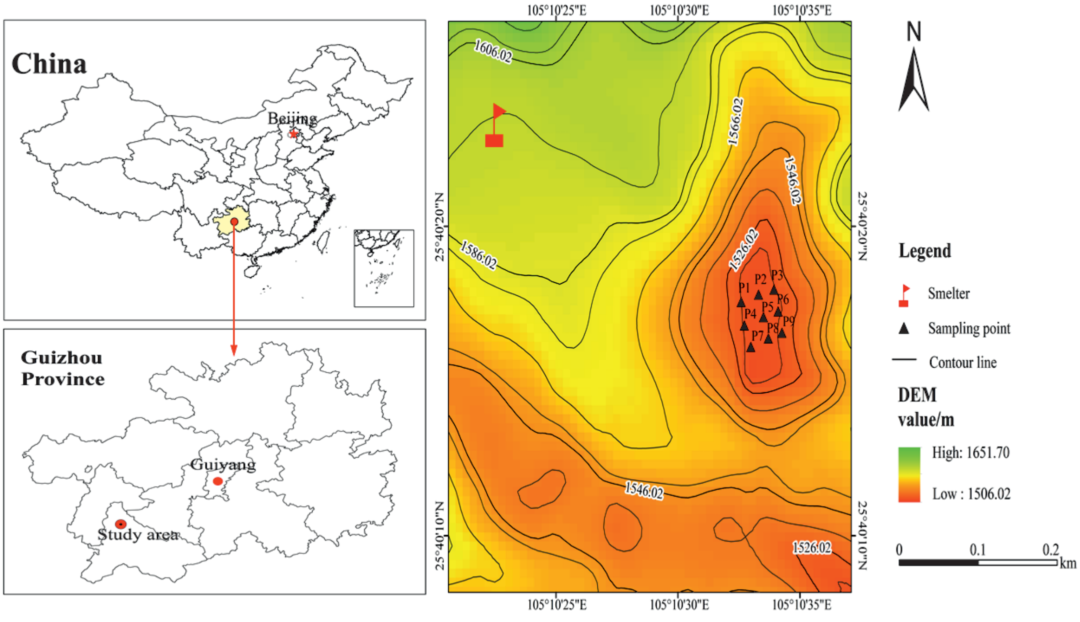

Fig. 1. Geographical location of the study area and layout of the sampling points.

14ºC and 1,500 mm, respectively). The arable land in the vicinity is mainly dry, with corn being the primary food crop grown.

The tailing pond is adjacent to the smelter and is situated in a typical karst depression formed by the surrounding mountains, with underground dissolution fissures and karst pipes crisscrossing the area on a large scale. Waste rock containing ores such as stibnite and pyrite produced by mining was placed in the tailing pond. Its beneficiation methods include crushing, hand screening, flotation, and re-election; the smelting process relies on (1) herringbone furnace smelting for roasting and desulfurization and (2) flat furnace smelting for selenium removal. The mine is one of the most significant Sb mines in southwest China. The Sb reserves accumulate to a total of 199,600 tons. The accumulated tailings (slag) stockpile is 2,883,700 tons, including 2,770,600 tons of hand-selected tailings, 154,600 tons of smelting slag, and 28,500 tons of flotation slag [10].

Sample Collection

A total of nine sampling points – that were selected according to the age of tailing sand accumulation and distribution distance, and considering the topography, wind direction, and other factors – were laid out (P1~P9) (Fig. 1). First, three tailing sand levels were selected within 1 m^2 of each sampling site, and the samples were collected every 10 cm from top to bottom using a splitter with a sampling depth of 120 cm. Second, three tailing sand samples of the same depth were mixed into one sample of approximately 1 kg; a total of 108 tailing sand samples were prepared. Finally, each sample was stored in a sterile self-sealing bag, and the location of each sampling site was recorded using the global positioning system (GPS).

Experimental Methods

Physical and Chemical Indexing of Tailings

A part of the collected tailing sand sample was air-dried naturally, ground, and filtered using a 10-mesh and 200-mesh sieve to remove debris such as stones and plant roots. Subsequently, a part of the filtered tailing sand sample from the 10-mesh sieve was separated, and its pH value was determined by the glass electrode method (the water-soil ratio maintained at 2.5:1 $L·kg^{-1}$). A pHS-3c pH meter (Yoke, Shanghai, China) was used to measure the pH of the supernatant of the tailing sand three times continuously, and the average value was recorded. A total of 10.0000 g of fresh tailing sand was weighed and placed in crucibles before being oven-dried at 105ºC for 4 h and cooled in a desiccator. This was repeated until a constant weight was achieved, in that when the difference between the two weights did not exceed 0.0006 g. The moisture content of the tailing sand was calculated using the gravimetric method. A 0.5 g sample of naturally air-dried tailing sand was weighed separately and combined with approximately 25 mL of ultrapure water. After ultrasonic vibration dispersion for 15min, the particle size was measured using a Bettersize 2000 laser particle size analyzer (Dandong Baxter, China). At the same time, water was selected as the medium, with a refractive index of 1.33 and a measurement range of 0.02~2000 μm. The samples were processed with reference to the standard (HJ 680-2013) for the determination of soil Sb and As and measured with an AFS-8510 atomic fluorescence spectrophotometer (the detection limit of Sb and As was 0.01 $ng·mL^{-1}$).

Static Leaching Experiment

In order to study the release characteristics of Sb and As in the Sb mine tailing profiles with time under different initial pH leaching agents, simulated rainwater was prepared using H_2SO_4, HNO_3, and deionized water; the mass ratio of SO_4^{2-} and NO_3^- was controlled at 3:1. The pH value was adjusted with NaOH solution to prepare leaching agents with pH values of 2.98, 5.10, 7.00, and 9.77. First, the 10-mesh-sieve-filtered tailing sand samples were thoroughly mixed, divided into several 50 g portions, and placed in 500 mL beakers successively. Second, 200 mL of the prepared leaching agent was added to these beakers, and the water-soil ratio was maintained at 4:1 ($L·kg^{-1}$); three replicates were set for each treatment. Finally, after standing and soaking for 2d, 4d, 6d, 8d, 10d, 12d, and 14d, the supernatants were filtered through a 0.45 μm microporous membrane, and their pH, electrical conductivity (EC), and redox potential (Eh) were measured immediately. The determination method of Sb and As content was the same as described above.

Stabilization Experiment

Three kinds of stabilizers – fly ash, quicklime, and zeolite powder – were selected for testing. All stabilizers used commercially available products, and their chemical composition by percentage is given in Table 1. A four-factor four-level orthogonal test was conducted with a total of 16 treatment groups. The dosing ratios and maintenance days are shown in Table 2. First, 300 g of well-mixed tailing sand was prepared for each treatment group, and stabilizers were added and mixed evenly. Second, the moisture content was maintained at approximately 40% by the gravimetric method after the addition of ultrapure water. The samples were stirred evenly again and placed in a room for sealing and curing under natural conditions. Finally, after the maintenance period, the stabilized samples were spread out, air-dried, and passed through a 100-mesh sieve. The samples were weighed at 150 g using the quadratic method, and the toxicity leaching experiment was carried out as per the solid waste leaching toxicity

Table 1. Main components and proportions of stabilizer raw materials.

Stabilizer	Chemical composition (%)			
Fly ash	SiO_2	Al_2O_3	CaO	Fe_2O_3
	54.94	34.86	2.63	2.52
Quicklime	CaO	MgO	SiO_2	Al_2O_3
	92.71	2.24	4.09	1.52
Zeolite powder	SiO_2	Al_2O_3	K_2O	MgO
	62.55	13.65	3.26	1.22

Table 2. Orthogonal test factor levels.

Level	(A) Quicklime (%)	(B) Fly ash (%)	(C) Zeolite powder (%)	(D) Maintenance days (d)
1	0	0	0	1
2	5	5	5	7
3	10	10	10	14
4	15	15	15	28

leaching method-horizontal shaking method (HJ/T 299-2007) to measure the leaching concentration and stabilization efficiency.

The following formula was applied in this study to describe the stabilization effect of stabilizers on heavy metals in tailings:

$$\eta\% = \frac{C_0 - C_s}{C_0} \times 100 \tag{1}$$

where η is the stabilization efficiency (%); C_0 is the leaching concentration of heavy metals from the tail sand before stabilization (μg·L $^{-1}$); and C_S is the leaching concentration of heavy metals from the tailing sand after stabilization (μg·L $^{-1}$) [11].

Quality Control and Statistical Analysis

Reagent blank, parallel, and national standard soil samples (GSS-4) were used for quality control during the experiments. The calibration curves of the standard solutions were determined with coefficients greater than 0.999. The experimental water was ultrapure, and all reagents used were of superior purity. The experimental vessels were soaked in 10% HNO_3 solution for more than 24 h, then washed with ultrapure water and dried for later use.

Microsoft Excel 2019 (Microsoft; Redmond, WA, USA) was used for data processing. ArcGIS 10.7 (Esri; Redlands, CA, USA) was used for the associated sampling mapping. Origin 2018 (Origin Lab, Northampton, MA, USA) was used to map heavy metal distribution and release characteristics. SPSS 25.0 (IBM, Armonk, NY, USA) was used for correlation analysis.

Results and Discussion

Physical and Chemical Characteristics of Tailings

Tailings pH, Particle Size, and Moisture Content

The pH of the tailings samples from the study area varied from 6.10 to 7.72, with a mean value of 6.96, indicating a neutral environment. The pH values of P1, P7, and P8 fluctuated widely, while P3 and P5 showed the least variation (Fig. 2a). Related studies have shown that the tailing sand in this area contained a large amount of calcite – the main component of which is $CaCO_3$ – which dissolves extremely easily in an oxidizing environment [12]. Thus, the area was alkaline in the early stages of tailing sand stockpiling. The primary product of the Qinglong Dachang Sb mine is stibnite (Sb_2S_3), and its associated minerals are mainly iron sulfides [12]. Under the joint action of water and oxygen, the sulfide minerals react readily to produce acid mine drainage. Moreover, as the area is subject to acid rain, the pH of the tailings has been decreasing under the influence of drenching by strongly acidic rainwater and various other factors, causing a gradual shift from the previously alkaline environment to a neutral one.

The size of tailing sand particles is inversely correlated with their specific surface areas; smaller particles with larger specific surface areas have a faster reaction rate with the water interface. Therefore, the determination of tailing sand particle size is important to explore the release of heavy metals from tailing sand. The tailing sand profiles in the study area varied in particle size from 180.39 to 1,083.90 nm, with an average grain size of 505.02 nm (Fig. 2b). The difference in tailing sand particle size between sampling sites in the mine area was not significant. The tailing sand particle size was irregularly distributed on each profile, with small-sized tailing sand alternating with larger-sized particles, consistent with the results of Luo et al. [8].

The complexity of the particle size distribution of the tailings and the variability of the climate can, to some extent, affect their moisture content. This further influences the release migration process of heavy metal elements and can potentially alter the availability of heavy metals and the risk they pose to the environment [13]. The moisture content of tailing sand in the study area varied from 0.34% to 28.46%, with large fluctuations between the levels; however, no obvious pattern of change was found in its distribution (Fig. 2c). Meanwhile, the moisture content of the surface tailing sand in the study area was low due to factors such as sunlight, wind, and vegetation root uptake. Moreover, due to the good permeability of the tailing sand, its

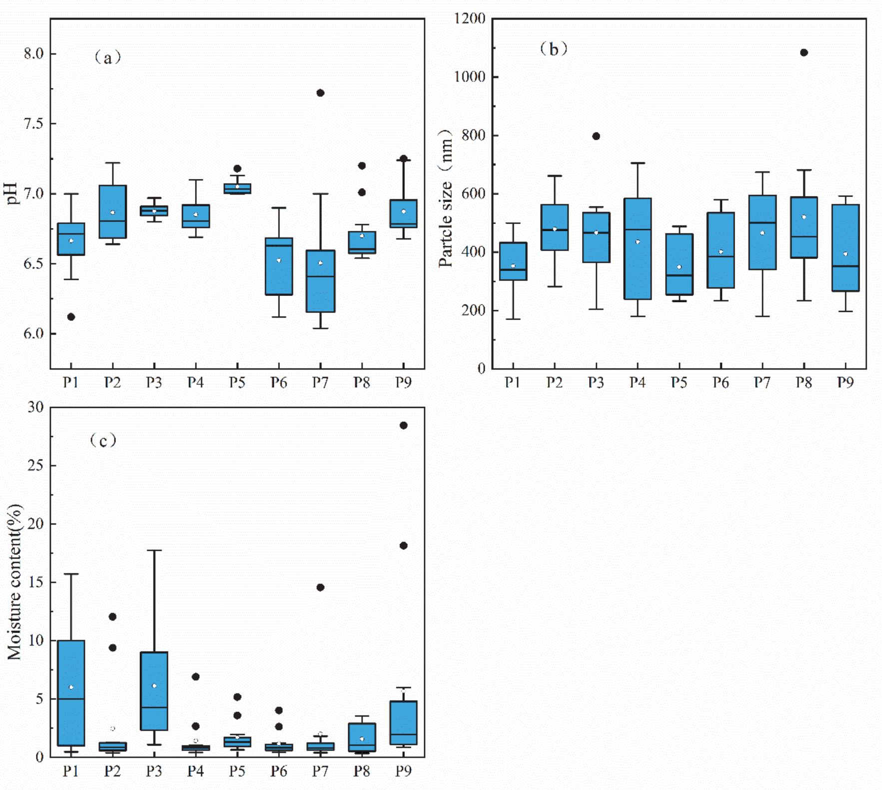

Fig. 2. Characteristics of pH, particle size, and moisture content variation in tailing sand profile.

moisture content showed an obvious vertical increasing trend with increasing depth of the profile.

Distribution Characteristics of Sb and As in Tailings

The storage environment of tailings in different levels and the weathering rate of various minerals were different, resulting in certain differences in the migration ability of heavy metal elements. Characteristics of the distribution of heavy metal content in each layer of the tailing sand profile of the tailing pond were studied, and the trend of heavy metal variation in the mine was effectively analyzed to provide basic support for tailings pond management.

The variation in Sb and As content in different layers of each sampling profile was analyzed and presented as trend graphs. Evidently, Sb varied more significantly between the nine tailing sand profiles than did As, and its vertical distribution fluctuated more as well (Fig. 3). The highest and lowest As contents were

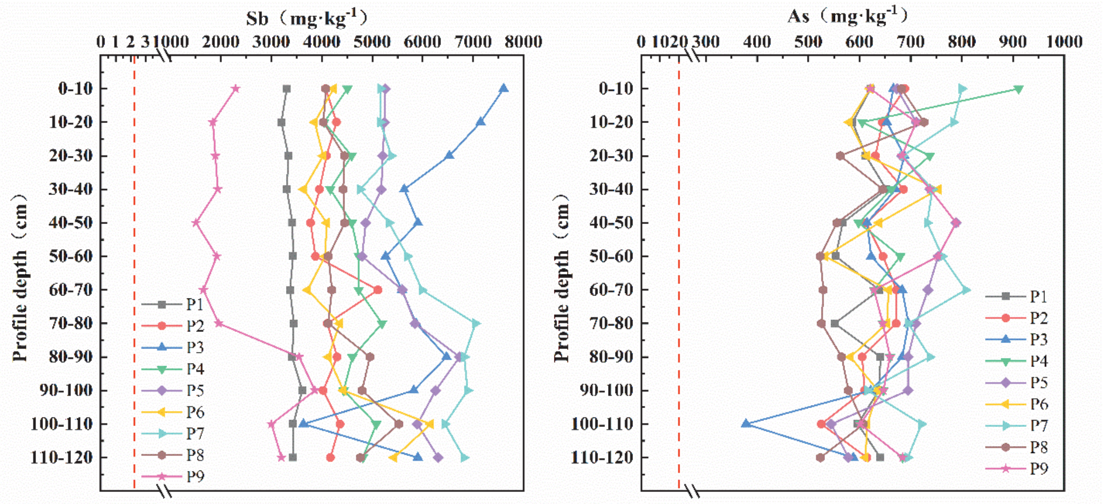

Fig. 3. Characteristics of the total variation of Sb and As in the tailing sand profile. (Reference line Guizhou Province soil background values)

observed in the surface layer of P4 and in the sub-bottom layer of P3, respectively; however, the overall distribution of As was relatively uniform. The Sb content in P3, P5, and P7 was higher than in the other profiles, with P9 being the lowest. Bottom enrichment of Sb was observed in all tailing sand profiles, which is likely because the bottom of most tailing sand profiles was mainly clay-grade tailing sand, which has a strong water storage capacity; the heavy metals released in the upper leaching level are not pass through it, leading to the enrichment of heavy metal elements mainly at the bottom. Additionally, the heavy metal content in the tailing sand of different levels was closely related to the heavy metal content in the original tailing sand at that particular layer [14]. Therefore, in the presence of a consistent external environment, heavy metals were enriched at different levels due to different release migration capacities and an uneven distribution of tailing sand particle size. Concurrently, the Sb and As content in all levels exceeded the standards, as per the background values of soil in the Guizhou province (Sb: 2.24 mg·kg^{-1}; As: 20 mg·kg^{-1}) [15]. Of which, the average concentration (4,547.82 mg·kg^{-1}) of Sb was 2,030 times higher than the soil environmental background value in the Guizhou Province, and the average concentration (650.85 mg·kg^{-1}) of As was 33 times higher than the background value. Thus, the environment surrounding the mine may be threatened by Sb and As in the tailings if it is exposed to natural conditions for a long period of time.

To characterize the relationship between Sb, As, and the tailings indicators, a correlation coefficient matrix was calculated by correlation analysis (Table 3). There was some variability in the effect of different tailing sand indicators on the distribution of Sb and As. A significant positive correlation was shown between them, possibly because Sb and As had the same S^2P^3 outer orbital electron configuration and exhibited the same oxidation state range (from -3 to +5) in the environment, indicating a companion relationship between them. This also suggests that Sb and As may have similar geochemical behaviors during atmospheric transport and deposition [9]. Sb and pH had a significant positive correlation, whereas no significant correlation was shown between As and pH, which indicates that the acidity and alkalinity of the mine tailings environment had a greater influence on the distribution of Sb. This further verified that Sb fluctuated more in the tailing sand profile, while the overall distribution of As was more uniform. In addition, there was a significant correlation between the pH and moisture content of the tailing sand samples, which suggested that they influenced each other.

Table 3. Tailing indicators with Sb and As Pearson correlation coefficients (n = 108).

Item	Sb	As	pH	Moisture content
Sb	1			
As	0.303*	1		
pH	0.291*	0.232	1	
Moisture content	0.156	-0.020	-0.283*	1

* $p<0.05$; ** $p<0.01$.

Variation Characteristics of Tailings Leaching Solution

Variation Characteristics of pH, EC, and Eh

pH is a key factor affecting the release and migration of heavy metals [16-18]. Changes in pH can change the characteristics of the ion surface charge, thus affecting the adsorption-desorption process of heavy metal ions. Under different pH initial solutions, the pH of the leaching solution of the samples in the study area changed in an "M" shape with increasing leaching time (Fig. 4a). In the early stage (0~6d) of leaching, when the pH of the initial solution was 2.98 and 9.77, the pH value of the leaching solution first increased and then decreased, respectively. When the pH of the initial solution was 5.10 and 7.00, the pH value of the leachate gradually reduced. In the middle and late stages (6~14d) of leaching, the leachate pH showed an overall increasing trend. When the pH of the initial solution was 5.10 and 9.77, the maximum pH values of the leaching solution were 7.05 and 6.97, respectively, and both occurred on the 8th day. When the pH of the initial solution was 2.98 and 7.00, the maximum pH values of the leaching solution were 6.93 and 7.19, respectively, and both occurred on the 12th day. In addition, under different initial pH leaching conditions, the overall pH value of the leaching solution changed from 6.36 to 7.20 and eventually tended to a weakly acidic or neutral environment, which was similar to the results of previous studies [19].

Related studies found that the tailing sand of the mine mainly comprised three minerals, quartz (SiO_2), pyroxene (Sb_2S_3), and calcite ($CaCO_3$) [12]. With the change in environmental conditions, the dissolution of sulfur- and oxygen-containing Sb minerals is promoted, forming acidic mine wastewater containing Sb with high sulfate levels. Compared with the original tailing sand in the study area, the pH value of the tailing sand did not change significantly after liquid leaching with different initial pH values. It is possible that the soaking process of sulfide minerals releases H^+, while CO_3^{2-} on the surface of the tailing sand reacts with water to produce OH^-, and the mineral surface adsorbs Na^+, Ca^{2+}, etc., creating a buffering effect on acidic and alkali substances [20]. Another reason could be the smaller the particle size of the tailing sand, the faster the reaction rate with the water interface, thus possibly releasing more buffer ions and neutralizing the acidic or alkaline background solution.

The various salts in the soil leachate are generally present in the form of ions. The change in EC may reflect the concentration change of the total mass of ionic components in the solution. When the ratio between several salts is relatively fixed, the total salt mass concentration indicated by the EC value is more accurate. Overall, the EC values of the tailing sand leachate in the study area showed a trend of first increasing and then decreasing. The variation range was 550~804 μS·cm^{-1}, and all of them reached their maximum values on the 4th or 6th day (Fig. 4b). When the pH of the initial solution was 2.98, the EC of the leaching solution was significantly higher than that of other initial solutions, at this point, the maximum EC of the leachate in this study is 804 μS·cm^{-1}. The release of ions may be more favored under a strongly acidic background solution. During the leaching process of tailing sand at different pH values, some sulfide mineral components and soluble salts were dissolved into the solution; when their release reached a certain level, the disintegration of certain mineral components with adsorption in the tailing sand in turn prompted the solidification of some ions in the leachate, thus leading to continuous changes in the leachate's EC [21].

Eh is an indicator of the redox state of the soil and a key factor affecting the activity of heavy metals [22]. The tailings leachate Eh in this mine was negative during the leaching process, with solutions having a different initial pH and an overall variation range of -49 ~ -17 mV, indicating a reductive environment (Fig. 4c). Overall, the reducibility of the tailing sand leachate was continuously enhanced in the early stage (2d~8d). After this time, its reducibility continued to diminish.

Sb and As Release Characteristics

The variation characteristics of Sb and As concentrations in the tailing sand leachate were similar, and both showed an overall trend of increasing with time, although the Sb release was much higher than that of As (Fig. 5). In the initial four pH solutions, the leaching content of As and Sb was 2.12~2.61 μg·L^{-1} and 12.98~41.86 μg·L^{-1}, respectively. The bioavailability of heavy metals (weak acid extractable, reducible and oxidizable states) are readily activated and released into the environment under certain conditions, and the mass fraction of each form of Sb in the tailings of the mine has been previously characterized as: residue state (83.06%)>reducible state (9.83%)>weak acid extractable state (3.97%)>oxidizable state (3.14%), and the magnitude of each form of As was: residue state (69.66%)>reducible state (18.13%)>oxidizable state (10.92%)>weak acid extract (1.29%) [12]. The reducible forms of Sb and As were the main bioavailable elements, and the reducible states mainly refer to the forms of elements that are held by absorption, such as Fe-Mn oxides. This indicates that the tailing sand in the study area had a high content of Fe-Mn oxides and adsorbed a large amount of heavy metal ions. The oxidizable state of As was higher than that of Sb; the oxidizable

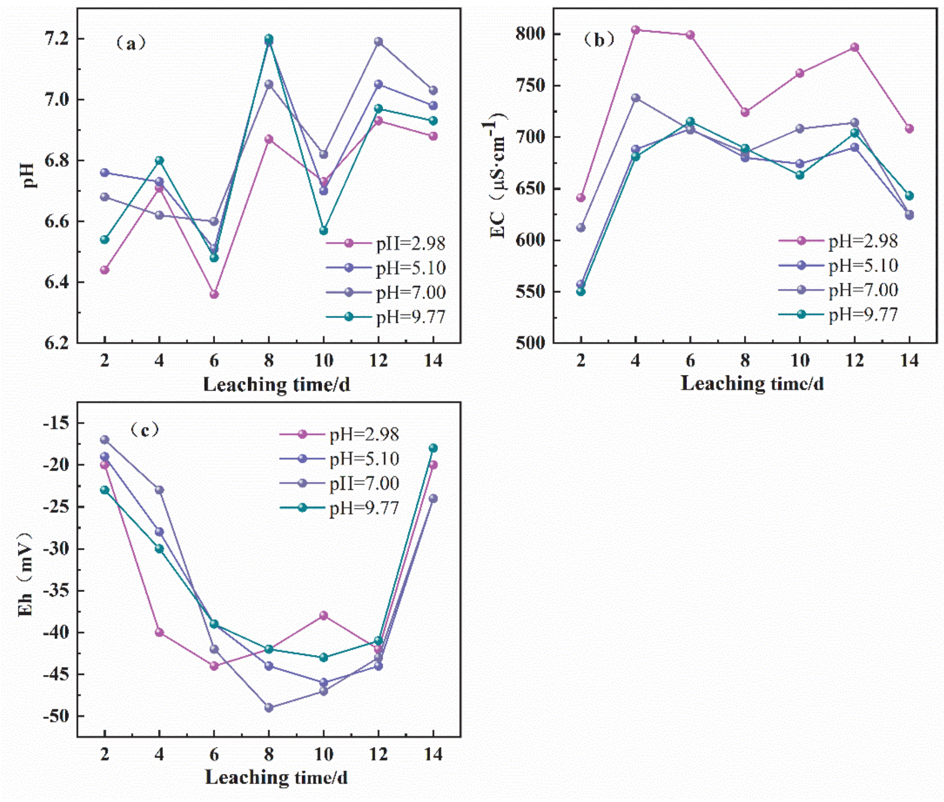

Fig. 4. Characteristics of changes in pH, EC, and Eh of tailing sand in leaching solutions with different initial pH.

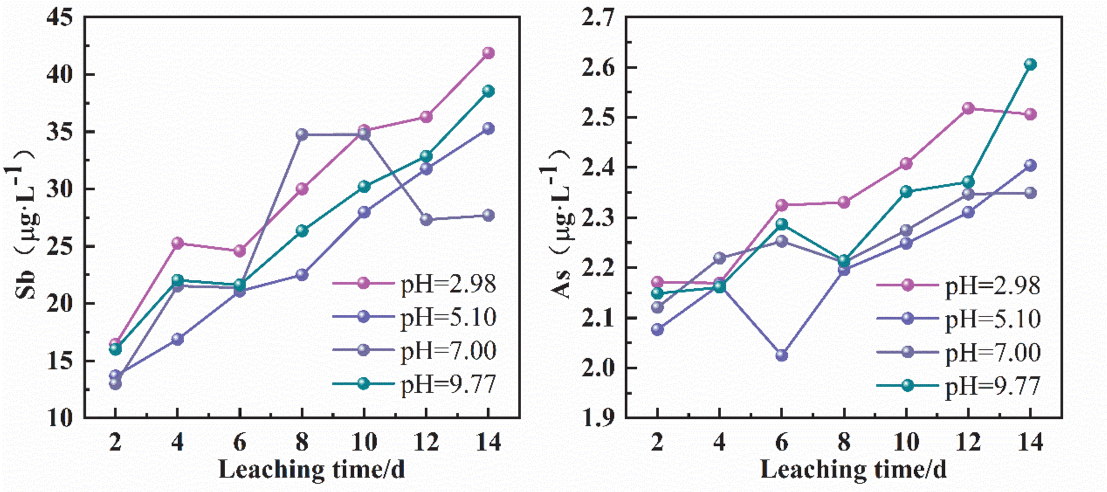

Fig. 5. Characteristics of Sb and As release from tailing sand under different initial pH leaching solution.

states that occurred was mainly the oxidation of sulfide to soluble sulfate, indicating that the tailing sand may contain sulfides of As and its oxidation rate was less than that of Sb. Meanwhile, the percentage of weak acid extractable state of Sb was higher than that of As, which indicates that the Sb migration was stronger in the study area [23, 24]. In summary, As was relatively more stable in the tailing sands of the study area. In summary, Sb that was adsorbed electrostatically on the surface of the tailing sand particles was more easily released into the solution, resulting in it having a higher release than that of As. To some extent, this also explains the variability in the profile variation characteristics of Sb and As content. Meanwhile, combined with the fact that the Sb content in the tailing sand above was much higher than the As content, it further indicated that the Sb release in the study area was closely related to the total Sb content in the tailing sand. This result was consistent with the results of Hu et al. [25] who reported on the leaching characteristics of Sb-bearing ores.

The Sb in the tailings leachate of the mine exceeded the standard for Class III water (Sb:5 μg·L^{-1}; As:10 μg·L^{-1}) by 2.60~8.37 times, according to the Chinese Groundwater Quality Standard (GB/T 14848-2017). This indicates that under the action of rainwater, especially acid rain, the open-air stacking of tailings in mining areas may cause some degree of pollution in the groundwater environment. Although As in the leachate did not exceed the standard, it may pose some degree of threat under the action of rainwater leaching and surface runoff over a long period, especially to groundwater. The average leaching concentrations of Sb in the leaching solutions of pH 2.98, 5.10, 7.00, and 9.77 were 29.93, 24.16, 25.78, 26.80 μg·L^{-1}, respectively. These results indicated that the release of Sb was more sensitive to strongly acidic conditions, possibly because calcite ($CaCO_3$) in the tailing sand reacts more readily to release free Ca^{2+} under lower pH conditions, and it exchanges ions with Sb. This was consistent with the findings of Cai et al. [26] who simulated acid rain at full submersion conditions.

The average leaching concentrations of As in the in the leaching solutions of pH 2.98, 5.10, 7.00, and 9.77 were 2.35, 2.20, 2.25, and 2.31 μg·L^{-1}, respectively. The average leaching content of As was lower and not significantly different at different pH values of the initial solution, indicating that As was less likely to be leached under simulated acid rain conditions, which was consistent with the results of previous studies [27]. The leaching of As reached its minimum value (2.02 μg·L^{-1}) at the initial solution pH of 5.10, indicating that the release of As at this time mainly occurred via adsorption complexation and co-precipitation. Under the initial solution pH of 9.77, the leaching amount increased rapidly from 2.37 to 2.61 μg·L^{-1} during the 12~14d period, possibly because the anaerobic environment caused by long-term flooding promoted the reductive release of As-containing minerals [26].

Stabilization Effect of Sb and As in Tailings

The commonly used inorganic stabilizing materials include lime, clay minerals, metal oxides, and phosphorus-containing substances. The effect of various stabilizing materials on the remediation of heavy metal contaminated soil varies based on the type of soil and the amount of material applied [28]. According to the orthogonal test scheme described in this paper, the stabilization effect of quicklime, fly ash, and zeolite powder on Sb and As in the tailing samples was calculated using equation (1) and the range analysis method was used to further analyze them [29]. The average value of the test results of each factor at its specific level was represented by k_1, k_2, k_3, and k_4. R was utilized to denote the extreme difference. When the R value was larger, it indicated that the value of this column of factors had a greater impact if the value of the column changed within the designed test range.

Table 4. Tailing stabilization treatment conditions and efficiency of Sb and As

No.	Experimental factors				SE (%)	
	Q/S (m/m)	FA/S (m/m)	ZP/S (m/m)	MD (d)	Sb	As
1	0	0	0	1	0.19	1.92
2	0	5	5	7	46.24	62.00
3	0	10	10	14	68.16	79.77
4	0	15	15	28	87.62	83.65
5	5	0	5	14	34.73	57.37
6	5	5	0	28	73.23	83.69
7	5	10	15	1	73.76	84.25
8	5	15	10	7	85.26	84.35
9	10	0	10	28	68.02	85.06
10	10	5	15	14	84.42	84.94
11	10	10	0	7	80.17	84.43
12	10	15	5	1	86.84	84.39
13	15	0	15	7	83.41	74.60
14	15	5	10	1	87.70	80.85
15	15	10	5	28	86.07	82.31
16	15	15	0	14	87.10	85.91

Therefore, the column with the largest R value was the most important influencing factor in the test.

Among the 15 treatment groups that applied a stabilizer (except group No.1), the highest stabilization efficiency for Sb was in group No.14 and the lowest was in No.5. The stabilization efficiency of these treatments ranged from 34.73% to 87.70% (Table 4). Evidently, the test factor of Sb had the largest value of k_4 in quicklime (Table 5), and the optimal dosage of this factor was 15%. Similarly, the optimal dosage of fly ash and zeolite powder was 15%, with an optimal maintenance time of 28 days. The R values of the dosage of quicklime, fly ash, and zeolite powder, and the maintenance time were 35.52%, 47.62%, 22.13%, and 16.61%, respectively. Therefore, the order of factors affecting the stabilization effect on Sb from highest to lowest was fly ash>quicklime>zeolite powder>maintenance time. The best ratio was determined by the orthogonal test as $A_4B_4C_4D_4$. Group No.16 had the best stabilization effect on As with a stabilization efficiency of 85.91%, whereas Group No.5 had the worst stabilization effect with a stabilization efficiency of 57.37%. The optimal stabilization parameters for As were 10% quicklime, 15% fly ash, and 15% zeolite powder, with a maintenance time of 28 days. The order of decreasing effect of various test factors on As stabilization was quicklime>fly ash>maintenance time>zeolite powder. The optimal stable ratio was $A_3B_4C_4D_4$ (Table 6).

Related studies have found that the degradation of soil insoluble materials, such as carbonates and metal hydroxides, were directly controlled by pH – irrespective of the type of stabilizing material treatment

Table 5. The Range analysis of Sb (%).

Range analysis	Experimental factors			
	Q/S (m/m)	FA/S (m/m)	ZP/S (m/m)	MD (d)
k_1	50.55	39.09	60.17	62.12
k_2	66.74	72.90	63.47	73.77
k_3	79.86	77.04	77.28	68.60
k_4	86.07	86.71	82.30	78.73
R	35.52	47.62	22.13	16.61

Table 6. The Range analysis of As (%).

Range analysis	Experimental factors			
	Q/S (m/m)	FA/S (m/m)	ZP/S (m/m)	MD (d)
k_1	49.13	54.74	63.99	62.85
k_2	74.84	77.87	71.52	73.77
k_3	84.70	82.69	79.74	76.99
k_4	80.92	84.57	81.86	83.67
R	31.79	29.83	17.87	20.82

– and that it also influenced the nature of the soil surface charge [30]. Thus, soil pH is the key to controlling the stability of heavy metals. Since the alkaline passivation material neutralizes the active acid in the tailing sand, the pH value of the tailing sand sample was raised, strengthening the bond between the iron and manganese oxides and the organic matter in the tailing sand [31].

The OH^- and CO_3^{2-} produced by the hydrolysis of lime materials form strong hydroxide precipitation and metal-carbonate co-precipitation with metal ions at the adsorption point of the tailing sand [32]. Fly ash has a large specific surface area, providing more active adsorption sites. Additionally, fly ash has a rich pore structure, where the cations in the pore channels inside its lattice can exchange ions with Sb and As in the tailing sand, thus effectively reducing the mobility of Sb and As [33]. Moreover, the higher content of SiO_2 and Al_2O_3 surface hydroxyl radicals in fly ash ionizes to generate variable electric charges, which is conducive to the electrostatic adsorption of heavy metal ions of Sb and As [34]. Related studies have shown that Ca^{2+} reacts with arsenate to form $CaHAsO_4$ and $Ca_3(AsO_4)_2$ precipitates under strong oxidizing and appropriate pH conditions to form As [35, 36]. Therefore, the addition of fly ash can induce some As to change from the effective state to the insoluble state. In addition, a large number of aluminum-silicon-oxygen tetrahedra (AlO^-, SiO^-) inside the clay mineral skeleton have a large static electricity attraction force, which continuously attracts heavy metal cations for coordination reactions [37]. The above experimental results proved the effectiveness of using fly ash, quicklime, and zeolite powder in combination to reduce the activity of Sb and As in tailing sand. Considering the stabilization efficiency and the range analysis results of Sb and As, it is reasonable to consider the optimal conditions as: 10%~15% of quicklime, 15% of fly ash, and 15% of zeolite powder with a 28-day maintenance time; however, other influencing factors should also be considered in the actual application process.

Conclusions

In this study, we presented the distribution of Sb and As in different levels of the tailings of the Qinglong Dachang Sb mine in the karst region of China. The release characteristics of Sb and As in the tailings over time were also studied by simulating acid rain conditions. Furthermore, we selected solid waste materials (fly ash, quicklime, zeolite powder) for an orthogonal test and determined the best combination to achieve maximum stabilization efficiency. The following main conclusions were drawn.

(1) The tailing sand in the study area exhibited a neutral environment. Compared with the soil background values in Guizhou Province, the Sb and As content in the vertical levels of the tailing sand of the mine area exceeded the standards. The average concentration of Sb (4,547.82 $mg·kg^{-1}$) was 2,030 times higher than that of the background value of the soil environment of Guizhou Province, with a trend of bottom enrichment. The average concentration of As (650.85 $mg·kg^{-1}$) was 33 times higher than that of the background value, although its overall distribution was more uniform.

(2) During static leaching of the initial solution at different pH values, the pH of the tailing sand leachate tended to be weakly acidic and neutral, the EC of the leachate was higher under strongly acidic conditions, and the leachate behaved as a reducing environment throughout the process. The release of both Sb and As from the tailing sand in the study area increased as the leaching time increased, and both showed an overall increasing trend. In the solutions, As leaching did not differ significantly at four different initial pH levels, whereas Sb was sensitive to more acidic conditions (pH = 2.98). The quantity of Sb released was significantly higher than that of As. Sb concentrations in the leachate exceeded the Class III of the Groundwater Quality Standard in China (GB/T 14848-2017).

(3) According to the results of the orthogonal test, under the three types of stabilizing materials and maintenance time, the best solution for Sb ($A_4B_4C_4D_4$) was 15% of quicklime, fly ash, and zeolite powder, with a maintenance time of 28 days, and that for As ($A_3B_4C_4D_4$) was a quicklime content of 10%, and 15% for both fly ash and zeolite powder, with a maintenance time of 28 days.

These results provide effective practical guidance on the composition of stabilizing materials to maximize the stabilization efficiency for Sb and As contamination at the Qinglong Dachang Sb mine. These results may also be effective at other sites with similar contamination profiles and geological influences.

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Conflict of Interest

The authors declare no conflict of interest.

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