sustainability

Review

Present Situation and Research Progress of Comprehensive Utilization of Antimony Tailings and Smelting Slag

Zeen Yu [1,2,3,4], Lei Wang [1,2,3,4,*], Qi Zheng [1,2,3,4,*], Xiaokui Che [1,2,3,4], Xinglan Cui [1,2,3,4], Shenyu Wei [1,2,3,4], Hongxia Li [1,2,3,4] and Xinyue Shi [1,2,3,4]

[1] GRINM Resources and Environment Tech. Co., Ltd., Beijing 100088, China; yuzeen99@163.com (Z.Y.); xkche@grinm.com (X.C.); cuixinglan@grinm.com (X.C.); weishenyu1129@163.com (S.W.); lihongxia@grinm.com (H.L.); shixinyue@grinm.com (X.S.)
[2] General Research Institute for Nonferrous Metals, Beijing 100088, China
[3] Beijing Engineering Research Center of Strategic Nonferrous Metals Green Manufacturing Technology, Beijing 100088, China
[4] National Engineering Research Center for Environment-Friendly Metallurgy in Producing Premium Non-Ferrous Metals, GRINM Group Corporation Limited, Beijing 100088, China
[*] Correspondence: wanglei@grinm.com (L.W.); mr1311@grinm.com (Q.Z.); Tel.: +86-10-13910161083 (Q.Z.)

Abstract: The production process of antimony produces a large amount of solid waste, such as waste rock in mining, tailings in the beneficiation, metallurgical slag in the smelting, and so on. At present, most of these solid wastes are currently in storage, and the storage of a large amount of solid wastes is not only harmful to the local ecological environment but also a waste of resources. In view of this situation, this paper will take antimony tailings and metallurgical slag as examples and summarize them according to their different treatment methods. The comprehensive utilization of antimony tailings is mainly recovering metals by beneficiation and metallurgy and using antimony tailings as building materials and underground filling materials, while the comprehensive utilization method of antimony metallurgical slag is mainly the recovery of valuable metals by pyrometallurgy or hydrometallurgy or the stabilization technology. This paper summarizes the advantages and disadvantages of different treatment methods and puts forward the prospect of future research directions for the treatment of different metallurgical slags and tailings.

Keywords: antimony tailings; antimony metallurgical slag; resource recovery; sorting; comprehensive utilization

check for updates

Citation: Yu, Z.; Wang, L.; Zheng, Q.; Che, X.; Cui, X.; Wei, S.; Li, H.; Shi, X. Present Situation and Research Progress of Comprehensive Utilization of Antimony Tailings and Smelting Slag. *Sustainability* **2023**, *15*, 13947. https://doi.org/10.3390/su151813947

Academic Editor: Rajesh Kumar Jyothi

Received: 1 July 2023
Revised: 10 August 2023
Accepted: 11 August 2023
Published: 20 September 2023

1. Introduction

Antimony is a common metal. Based on its excellent properties, antimony is widely used in many fields such as national defense, people's livelihood, and economy, which include solar panels, semiconductors, refractories, and so on [1]. Therefore, the world's demand for antimony is increasing, and stibnite is also listed by the EU as a key raw material list in 2020 [2]. Although antimony is not very abundant in the Earth's crust, at about 0.2 g/t, it is widely distributed in more than 100 minerals [3]. China is the country with the richest antimony resources in the world. According to the results of the United States Geological Survey in 2021, China's antimony reserves account for about 25.6% of the world's total reserves [4], which is the country with the largest antimony reserves in the world. The distribution of antimony resources in the world is shown in Figure 1. In recent years, with the increasing demand for antimony resources, the mining activities of antimony ore are also increasing year by year. The large-scale mining and smelting activities of antimony have seriously affected the regional ecological environment. According to statistics, about 3.8×10^4 t of antimony is released into the environment every year through mining, beneficiation, smelting, and other activities [5]. Due to the large amount of antimony-containing waste discharged, the ecological environment in many areas has been seriously polluted [6]. Among them, the most polluted solid wastes are antimony tailings and antimony metallurgical slag. Although a lot of research has been done on the resource utilization of these two solid wastes, most of the antimony tailings and antimony metallurgical slag are still in storage. Toxic elements such as antimony and arsenic will migrate due to long-term storage. Antimony and its compounds will have a long-term effect on human health [7]. This has aroused extensive attention and further research on the treatment of antimony tailings and antimony metallurgical slag [8].

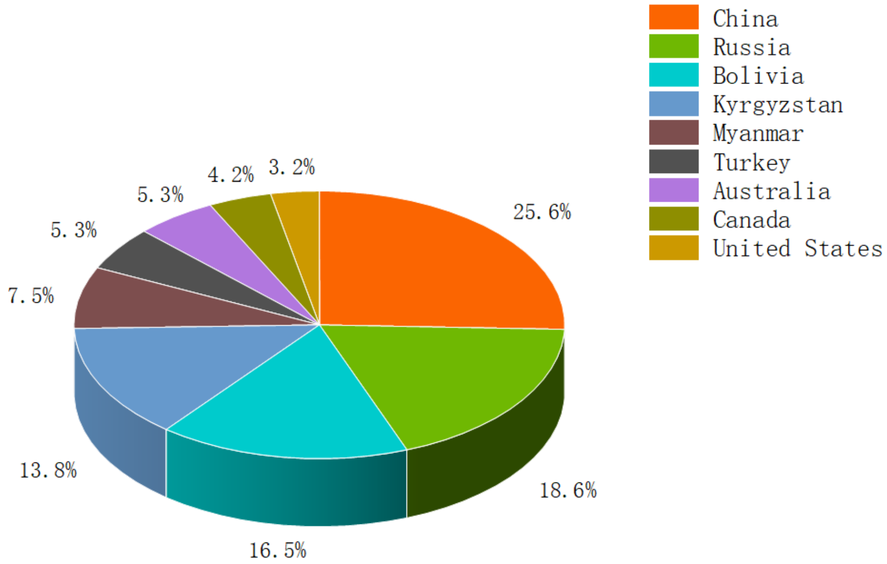

Figure 1. Distribution of antimony resources in the world.

2. Pollution Status and Problems

At present, antimony resources mainly exist in the form of antimony sulfide ore, and the enrichment of the ore is mainly carried out by flotation [2], but a large amount of antimony tailings is produced in the beneficiation process, which is characterized by low content of target minerals or difficult to extract and utilize valuable metals, and most of the tailings are very fine. Due to the particularity of its properties, there is no suitable treatment method for most antimony tailings at present. The production factor of antimony tailings in the antimony beneficiation process (the number of tailings produced per ton of antimony ore after beneficiation) is generally 0.96 to 0.97 t/t raw ore [9]. According to the data analysis results of OCED, more than 60% of antimony in the waste needs to be recycled to alleviate the shortage of antimony resources [10]. However, taking China as an example, there are 34 antimony tailings ponds in 2019, with a total inventory of more than 9.62 million cubic meters [9]. Nevertheless, the comprehensive utilization rate of tailings is only 34.05% [11], which is far less than the target utilization rate. In addition, at present, 20% of China's current tailings ponds have no management, 60% of them have no design plan for safe utilization, and 50% of them are diseased (dangerous) ponds, which have a serious impact on the safety of the local ecological environment [12]. For example, the leakage of Xihe antimony tailings pond in China in 2015 caused serious pollution of the surrounding environment and a series of problems such as excessive heavy metal content in the local soil [13]. In 2003, the Abaróa antimony tailings pond in southern Bolivia leaked due to rainfall. About 5500 cubic meters of tailings were leaked in this accident, resulting in concentrations of lead, antimony, and zinc in the lower reaches of Rio Tupiza exceeding the local agricultural standards [14]. After a long period of weathering and rainwater erosion, the stored antimony tailings have become the main source of heavy metal pollution [15]. If not treated properly, they can do great harm to the local environment. With the gradual depletion of high-quality antimony ore resources, more and more refractory antimony resources have gradually become a difficult problem that the beneficiation must face. Although the separation of antimony from vein minerals can be solved to a certain extent by increasing the liberation of antimony through fine grinding, the fine tailings increase the difficulty of subsequent solid waste reuse and cause more serious potential environmental hazards.

The metallurgy of antimony is mainly divided into two methods, namely pyrometallurgy and hydrometallurgy. Pyrometallurgy refers to the method that is used to separate metals and impurities such as gangue at high temperature, which causes a series physical and chemical reactions. Different from pyrometallurgy, hydrometallurgy is a process of separating and enriching useful metals in solution by reaction, while leaving the impurities in the solid phase. Pyrometallurgy accounts for more than 95% [16]. The main method of pyrometallurgy is the volatilization smelting in blast furnace of antimony concentrate. During the smelting process of antimony concentrate, a large amount of smelting slag is produced, including smelting slag, arsenic alkali slag, lead removal slag, and so on. Disordered stockpiling of smelting antimony slag is one of the main sources of antimony pollution [17]. Taking arsenic alkali slag as an example, since the sodium arsenate and soluble sodium carbonate cannot be well treated, they often fail to meet the landfill requirements and can only be stored [18]. At present, the stockpiling of arsenic slag in China has exceeded 200,000 tons and is still growing at the rate of 5000 tons per year [19]. However, an environment contaminated by metallurgical slag is difficult to restore; for example, some antimony contamination has been found at medieval metallurgical sites in southern France [20]. Due to the high content of toxic elements such as antimony and arsenic in this kind of slag, the separation is not complete, and it is difficult to reuse and can only be stored. However, long-term storage causes a large number of toxic elements in the slag to infiltrate into the surface, resulting in greater pollution with the migration of groundwater [21].

Over time, how to properly solve the problem of solid waste stockpiles and reuse them as resources has become a key challenge. The byproducts of the antimony production process represented by antimony tailings and antimony metallurgical slag seriously endanger the ecological environment around the selection plant and smelter, and also waste a lot of resources. Currently, recycling has become the key method to cope with the shortage of resources. Many scholars have carried out a lot of research on how to make rational use of such solid wastes to meet the pollution-free target and recover the valuable metals to alleviate the current situation of resource shortage.

3. Comprehensive Utilization Status of Antimony Tailings

Antimony resources are dominated by antimony sulfide ore, accounting for 85% of the total antimony resources. The main minerals of antimony sulfide ore are stibnite (Sb_2S_3) and lead antimony sulfide ore ($Pb_4FeSb_6S_{16}$). Antimony oxide ores are mainly senarmontite and valentinite (Sb_2O_3) [22]. In the process of beneficiation, to achieve the monomer dissociation of antimony-containing minerals and obtain a better grade and recovery rate, antimony ore is generally ground to a finer grain size, which brings some difficulties to the follow-up treatment of antimony tailings. According to the content of antimony in the antimony tailings, different technical means will be used for treatment. It can be seen from Table 1 that the content of precious metals such as gold and silver in antimony tailings is high and can be recycled. As can be seen from Table 2, the content of valuable metals is low, which can be recycled, and the tailings can also meet the needs for mining backfill or building materials.

Table 1. Compositions of typically recoverable antimony tailings [23] (%).

Groups	**Au**	**Ag**	**Sb**	**S**	**Zn**	**Pb**	**As**	**TiO_2**	**SiO_2**	**Al_2O_3**	**CaO**	**MgO**	**C**
content	2.92	0.50	1.21	0.76	0.01	0.10	0.38	0.59	64.42	14.50	1.54	1.81	1.62

The unit of Au and Ag is g/t.

Table 2. Composition analysis of typical unrecoverable metal antimony tailings [24] (%).

Groups	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**K_2O**	**TiO_2**	**MnO**	**Pb_2O_5**	**Na_2O**	**FeO**	**LOI**
content	88.78	3.86	0.98	0.61	0.11	0.42	0.17	0.03	0.04	0.02	0.27	2.98

3.1. Recovery of Antimony Tailings Resources

For the antimony tailings with high grade of valuable metals, the main treatment method is to recover the high-grade metals. In this process, not only antimony can be recovered, but also the associated metals such as gold, silver, and mercury can be recovered.

In view of the different properties of antimony tailings, different technical means are often used for treatment. In the treatment of antimony oxide tailings, the gravity separation and shaking table are often used to recover the fine antimony oxide. The principle is to use the difference in relative density between fine antimony oxide and other components to separate. However, the use of shakers has the problem of low recovery. In view of this difficulty, Chu et al. [25] used an agitated reflux classifier to pretreat the antimony tailings; the degritting rate of this process was as high as 73.13%, and the final recovery could be increased from 35.68% to 39.82% and the grade from 9.01% to 10.54% by pretreatment.

Some scholars have tried many methods to recover antimony oxide tailings. Liu et al. [26] pretreated antimony oxide tailings by the countercurrent separator. By optimizing the parameters of feed size, bottom flow, and rising water flow, and constructing the second-order response function, the advantages of the counter-current sorter for the separation of fine-grained antimony oxide ore were verified. Under the condition that the raw material grade is only 0.8%, it finally increases the concentrate grade to 2.31%. The recovery rate is 83.17%, which provides a strong support for the separation of fine antimony oxide.

For the mixed tailings of sulfide ore and oxide ore, a variety of separation methods are usually selected to achieve effective recovery. Kangwofei [27] re-selected this type of antimony tailing. Antimony sulfide was mainly beneficiated by flotation. Antimony oxide was first classified by hydrocyclone, and then fine antimony oxide was recovered by a suspended cone concentrator. The concentrate grade and recovery of fine-grained oxidized ore are improved by adjusting the vibration frequency of the suspension vibration cone concentrator and the disc rotation speed. The experimental results show that the concentrate grade can reach 13.54% and the recovery rate is 45.08% when the vibration frequency is 15 Hz.

Some scholars have studied the recovery of gold, silver, and mercury associated with antimony tailings. Ming Tianping [22] conducted an experimental study on the flotation of antimony tailings from a processing plant in Qinghai to recover gold. The main problem with the tailings treatment was pelletization, which led to a low gold recovery rate. In view of this characteristic, the carbon-in-leach method is used to leach gold. By adjusting the leaching concentration and the fineness of the tailings during leaching, the final gold recovery rate can reach 65.10%. Antimony tailings not only contain precious metals but also contain other valuable elements. Ren Linzhu et al. [28] carried out comprehensive flotation recovery of mercury and antimony from antimony tailings containing mercury. By optimizing the regulation of the agent in flotation, grinding fineness and other conditions, the process flow was finally determined (Figure 2). The closed-circuit experiment was carried out under the condition of using this process. When the mercury grade of the raw ore was 0.084% and the antimony grade was 0.21%, the final antimony concentrate grade was 15.01%, and the recovery rate could reach 41.17%. The grade of mercury concentrate is 46.89%, and the recovery rate is 50.24%. The mercury and antimony in the antimony tailings are effectively recovered, and the tailings are recycled, which solves the difficulty of the tailings reuse.

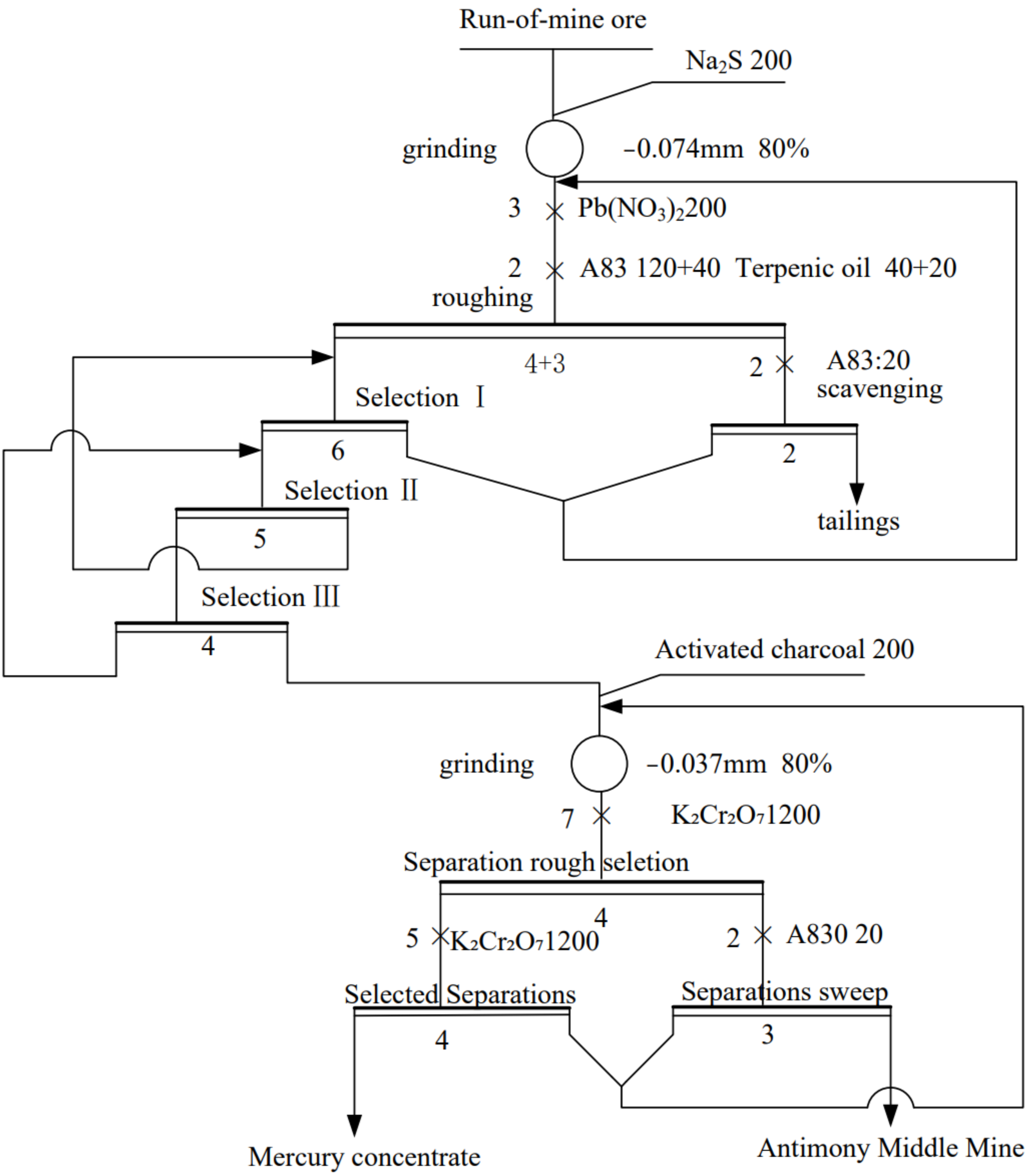

Figure 2. Process flow chart of mixed flotation recovery of mercury-containing antimony tailings [28].

The secondary resourceization of antimony tailings is mainly through flotation, re-election, leaching, and multiple other methods to recover the valuable metals in the tailings and make full use of the tailings. It can not only create certain economic value, but also effectively alleviate the problem of resource shortage.

3.2. Using Antimony Tailings to Prepare Building Materials and Underground Filling Materials

Antimony tailings are used as underground filling and building materials. The principle is to use the solidification/stabilization technology to solidify the toxic elements that may be leached from the tailings and adjust the compressive strength, fluidity, and other conditions for use. The method technique has been used to some extent [29].

3.2.1. Using Antimony Tailings to Prepare Raw Materials for Building Materials

The main use of tailings as building materials is to replace the aggregate in traditional concrete or to prepare cementitious materials instead of cement in combination with other solid wastes. Many scholars have dug down deep into this field. For example, Li et al. [30] and Wang et al. [24] used antimony tailings as coarse aggregate instead of lifting coarse aggregate in conventional concrete and explored its indices in terms of strength, stability, and toxic leaching aspects. When antimony tailings were used as coarse aggregate, the specimens had better tensile strength and compressive modulus of elasticity than the concrete using a natural rock as coarse aggregate; the cubic compressive strength, splitting tensile strength, and prismatic compressive elastic modulus are 1.31, 2.22, and 1.40 times that of natural rock, respectively, but their alkali activity and cracking sensitivity were less compared to conventional concrete. Wu et al. [31] used Portland cement, S95 slag powder, fly ash, phosphogypsum, water-based aluminum powder paste, foaming agent, and antimony tailings to prepare test blocks and put them into molds. After curing for 3 d, 7 d, 14 d, and 28 d, the compressive strength, flexural strength, and toxicity leaching were measured. The flexural strength of the final test block can reach 2.5 MPa and the compressive strength is 15 MPa at 28 d, which has good mechanical properties. In addition, the water absorption of the curing body is about 27%, the softening coefficient is about 0.7, the dry density is 900 kg/m^3, and the wet density is 1100 kg/m^3, which meets the requirements of waterproof and lightweight. In this experiment, antimony tailings were solidified by synergistic utilization of various solid wastes. The optimum ratio of raw materials was determined by strength tests, toxicity leaching, and other test methods. The leaching concentration of Zn in the toxicity leaching results of the test block was the highest, which was 1.2 mg/L. The leaching concentrations of other elements under the two curing conditions were lower than 1 mg/L, and As was not detected in the two solidified bodies, which was relatively safe.

3.2.2. Using Antimony Tailings as Underground Filling Materials

In addition to the preparation of building materials, some scholars have proposed to use a variety of solid wastes to prepare cementing materials as the cementing agent for antimony tailings and prepare underground filling materials for the disposal of antimony tailings. Li et al. [32] used high-content antimony tailings, blast furnace slag, steel slag, and flue gas desulfurization gypsum to prepare green mine filling materials. According to the test results, its compressive strength is greater than 1 Mpa, which meets the needs of mine filling. In addition, the solidification rate of the filling material for Sb in the tailings can reach 99%, and the result of toxic leaching meets the requirements of green mining filling samples. Li Yunyun [10] used antimony tailings as aggregate, steel slag, slag, and desulfurization gypsum as cementitious materials to prepare full tailings sand paste filling material. Figure 3 shows the preparation process of this all-tailed sand paste charging material. According to the experimental results, the compressive strength is greater than 3 Mpa, and the fluidity of the filling material is 225 mm greater than the cement fluidity under the same conditions. Both of them meet the fluidity required for pumping and meet the requirements of underground filling.

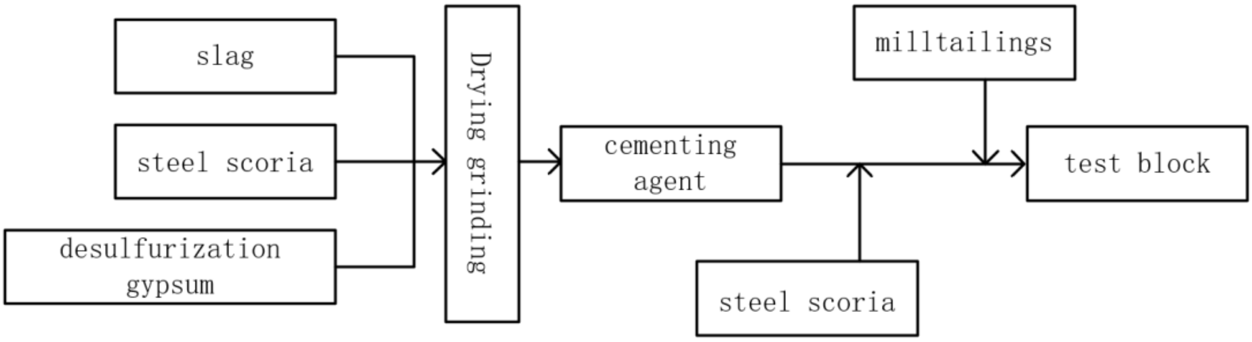

Figure 3. The preparation process of all-tailed sand paste filling material [10].

In addition, scholars have analyzed the mechanism of curing/stabilization technology. Gao et al. [29] used semi-dynamic leaching experiments to study the diffusion mechanism and solidification mechanism of As and Sb in antimony tailings in metallurgical slag-based binder (MSB). In this experiment, three different leaching agents were used for the experiments separately. According to the experimental results, the variation curves of As and Sb leaching concentration with the mass fraction of calcium superphosphate in MSB were drawn. The slopes of the three curves of Sb were between 0.47 and 0.60, indicating that Sb was diffusion leaching. While the slope of the curve of As does not fall within the interval, it is mainly diffusive leaching and to a lesser extent, dissolved leaching. In addition, this scholar explored the curing mechanism of Sb by adjusting the content of steel slag powder in MSB. According to the experimental results, it can be seen that with the increase of steel slag powder, the effective diffusion coefficient of As is decreasing, and the effective diffusion coefficient of Sb is increasing. Therefore, the mechanism of solidification of As is mainly chemical precipitation, and the mechanism of solidification of Sb is physical encapsulation.

In summary, the stabilization/solidification treatment technology of solid waste such as antimony tailings is mainly based on physical packaging. By using cementitious materials or binders, the toxic elements are solidified, reducing mobility and meeting the basic needs of underground fill and building materials.

4. Comprehensive Utilization Status of Smelting Slag

The flow chart of the blast furnace volatilization smelting method is shown in Figure 4. The metallurgical slag of antimony produced by the blast furnace volatile smelting method mainly includes smelting slag, lead removal slag, arsenic alkali slag, etc.

Smelting slag is a byproduct produced in the smelting process of the blast furnace in the blast furnace volatilization smelting method. Crude antimony and antimony matte are mainly obtained by this process. Table 3 shows the composition of typical melting slag. It can be concluded from the table that the main components of the smelting slag are FeO, SiO_2, and CaO, and the content of antimony in smelting slag No.2 and No.3 is higher than that in smelting slag No. 1.

Table 3. Typical composition of melting slag (%) [32,33].

	Pb	**Zn**	**Sb**	**In ***	**FeO**	**SiO_2**	**CaO**
1	3.01	5.04	0.76	103	13.54	25.52	16.73
2	0.91	6.56	3.21	110	16.97	20.44	14.82
3	0.10	--	1.22	--	26.64	42.03	16.11

Note: No. 1 and No. 2 are blast furnace smelting slag of brittle sulfur lead antimony ore; No. 3 is the smelting slag of a stibnite blast furnace; * represents the unit is g/t; '--' indicates that the element has not been detected.

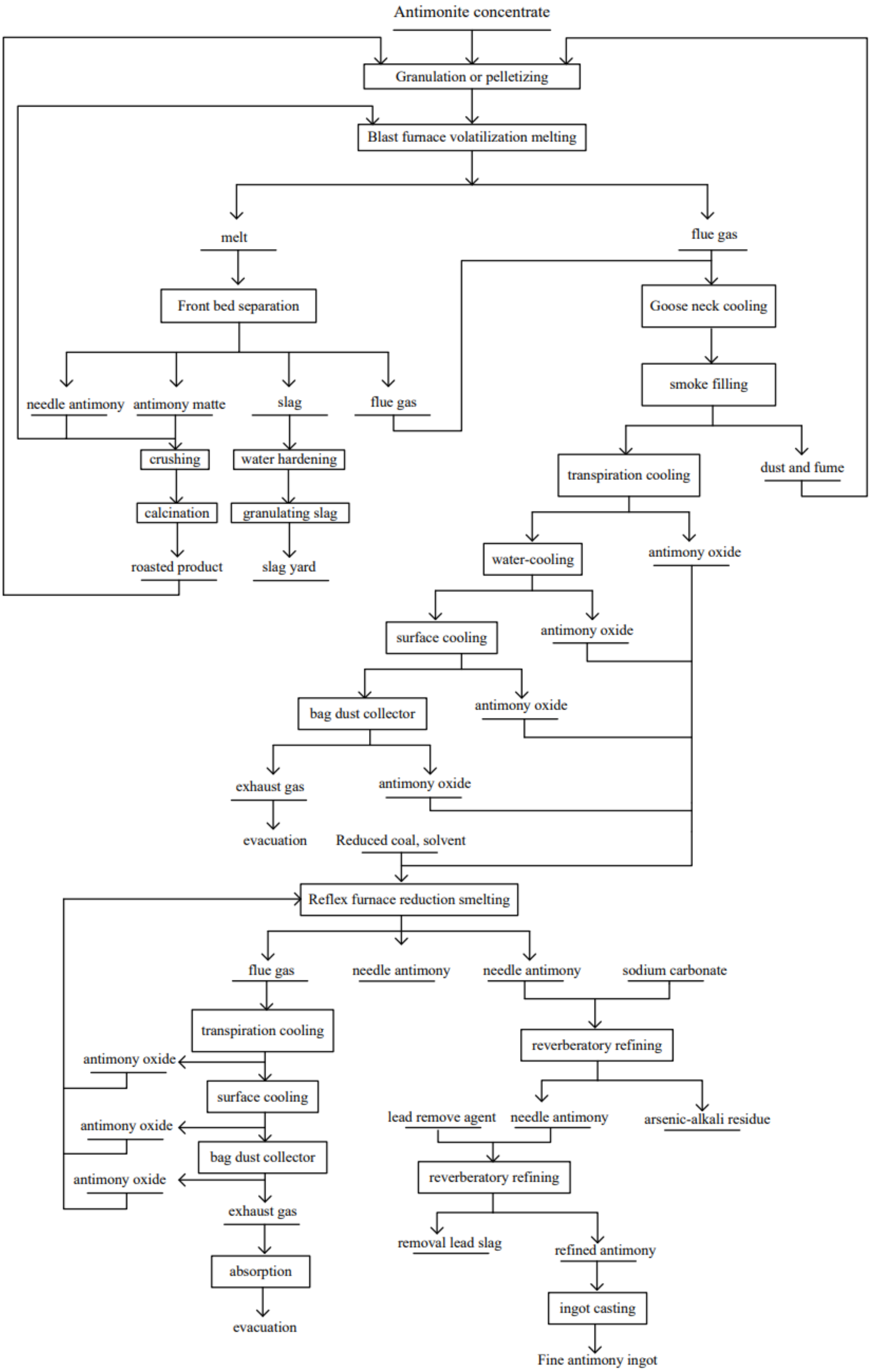

Figure 4. Flow chart of blast furnace volatile smelting method [33].

Arsenic alkali slag is a byproduct produced by the refining of the reverberatory furnace in the process of antimony smelting. This process is mainly to remove arsenic from crude antimony. Table 4 is the main chemical composition of arsenic alkali residue.

Table 4. The main chemical composition of arsenic alkali residue [34] (unit: %).

Component	**As**	**Sb**	**Se**	**Na_2CO_3**	**$NaHCO_3$**
Content	3.8	1.0	0.18	34.0	8.2

Lead removal slag is a byproduct obtained by adding lead removal agent in the blast furnace reaction after removing arsenic from crude antimony, and the main process is lead removal. The composition of lead removal slag is unstable, with antimony content ranging from 5 to 45%, and lead content from 5 to 15% [35]. The main problems with these slags are that the metal is difficult to dissociate and the arsenic content is high. The high arsenic content is the main factor hindering its effective utilization [36].

The comprehensive utilization of metallurgical slag is mainly to recover valuable elements and stabilize or solidify them. The recovery of valuable elements is mainly through the separation and recovery of antimony, lead, arsenic, zinc, and other elements in metallurgical slag by wet and fire methods. The stabilization/solidification method is to use a variety of materials to encapsulate and adsorb the toxic elements that can be leached from the metallurgical slag to achieve harmless treatment.

4.1. Recovery of Valuable Elements from Metallurgical Slag

As there are more valuable metals in smelting slag, the content of antimony in the smelting slag is high, which can be recycled for secondary utilization. For example, Qiu et al. [37] prepared nano-Sb_2O_3 by vacuum evaporation, which can absorb the smelting slag without secondary pollution. However, this method has the problem of high energy consumption and little demand for the prepared products. Mo Wei [38] used the fuming volatilization method to treat the stored smelting slag. The principle of this method is to mix the pulverized coal and air into the molten slag and use the fly ash as the fuel and reducing agent to provide the reducing atmosphere and the heat required for deducing metal, so that the metals such as lead, antimony, and zinc in the slag are volatilized and enriched in the form of oxides and recovered in the soot. Figure 5 shows the process flow diagram of the fuming volatilization method.

The method is to start feeding when the temperature in the furnace is 1200–1300 °C. The secondary recovery of the melting slag is carried out by controlling the furnace temperature, air coefficient, and reduction time, and finally the metal is collected by cloth bag dust collector. Under these conditions, the recovery rate of Pb and Zn can reach more than 80%, and the recovery rate of Sb can reach more than 85%. He Qixian et al. [39] used the fuming volatilization method, at the condition temperature of 1250 °C, the feeding and slagging time was 1.5–2.5 h, the reduction blowing time was 2 h, and the recovery rates of lead, antimony, zinc, and indium were 86.9%, 83.4%, 62.5%, and 57.7%, respectively. The feasibility of the method is proven again. This method is currently the most commonly used method for treating smelting slag. The advantage is that the metal in the smelting slag can be enriched, but the metal cannot be completely separated. Only a mixture of metals can be obtained and needs to be reprocessed, which increases the cost and reduces the economic benefits.

The iron in the smelting slag is a big problem in the traditional pyrometallurgical methods. Some scholars have optimized the traditional pyrometallurgical method to solve the problem of iron pollution. Luo et al. [40] conducted experimental purification experiments on oxygen-rich bottom-blown high antimony smelting slag using the reduction method and determined the optimal process conditions for this technique by examining the effects of CaO and coal addition, and slag type on the reduction process. In the slag system with SiO_2:FeO:CaO mass ratio 45:27:18, the grade of Au in the remaining slag after reduction is <1 g/t, and the grade of Sb is <1%. In the metal phase, the recovery rate of gold is as high as 98%, the recovery rate of antimony can reach 80%, and the content of iron is less than 7%, which effectively controls the influence of iron. From the reaction, it can be concluded that the larger the amount of coal, the higher the content of iron in the metal phase, and the smaller the amount of coal, the higher the content of antimony in the residue. According to this law, the ratio of raw materials is adjusted to reduce the content of impurities in the product to realize the recovery of antimony, so as to achieve greater economic effects.

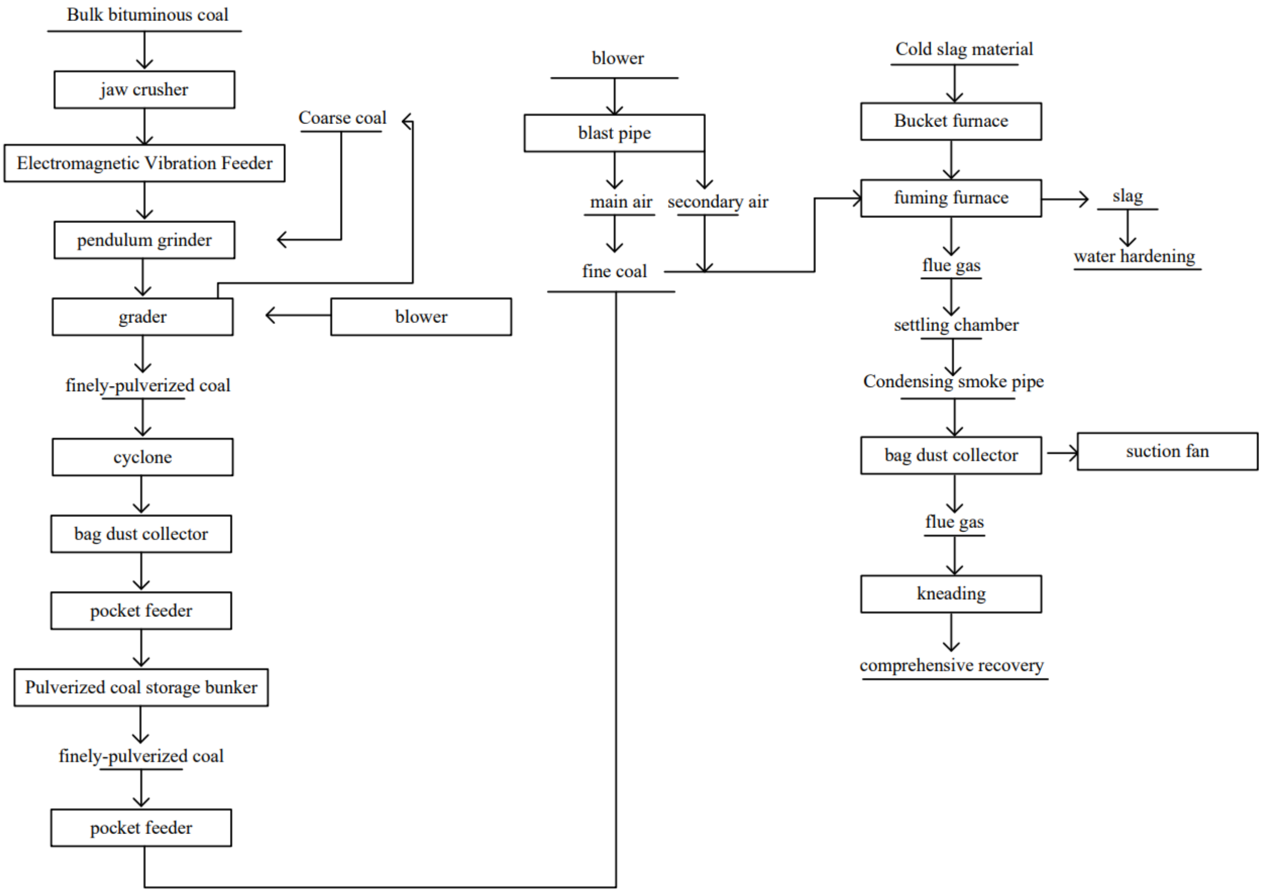

Figure 5. Process flow chart of fuming volatilization method [38].

The recoverable metals in the lead removal slag are mainly lead and antimony. Its traditional recovery method is similar to that of smelting slag, and it is also pyrometallurgy. However, there are some problems such as low recovery rate of lead and antimony and secondary pollution, which lead to a large amount of lead removal slag still in storage [41]. Shan Taoyun [36] has made some adjustments to the method of pyrometallurgical treatment of lead slag removal. In this method, alkali, lead removal slag, and iron chips are mixed according to the corresponding proportion. The mixed material is heated to 1035–1050 °C and kept for 30–90 min. During this period, the material will undergo the following four states: melting, reaction, clarification, and cooling. Finally, antimony–lead alloy and scum are obtained. The experimental results show that the recovery rate of lead and antimony in this method can reach more than 90%, which effectively solves the problem of partial lead slag storage, and there is no secondary pollution. This method mainly uses the principle of replacement, using active metal iron to replace the lead and antimony crystals in the lead removal slag to achieve the effect of recovering lead and antimony in the lead removal slag. Equations (1)–(4) are the main reaction chemical equations of this method.

$$2SbPO_4 + 3Fe \xrightarrow{Hyperthermy} Fe_3(PO_4)_2 + 2Sb \downarrow \tag{1}$$

$$Sb_2(HPO_4)_2 + 3Fe \xrightarrow{Hyperthermy} 3FeHPO_4 + 2Sb \downarrow \tag{2}$$

$$Pb_3(PO_4)_2 + 3Fe \xrightarrow{Hyperthermy} Fe_3(PO_4)_2 + 3Pb \downarrow \tag{3}$$

$$PbHPO_4 + Fe \xrightarrow{Hyperthermy} FeHPO_4 + Pb \downarrow \tag{4}$$

Compared with the traditional hydrometallurgical treatment, this method has the advantage of no potential secondary pollution in the treatment of lead slag. In addition, compared with the reduction reflector treatment of deleaded slag, the method is more advantageous in controlling temperature, and the recovery rate of lead antimony can be improved by uniform temperature. However, this method has the problem of incomplete separation of lead and antimony, and the lead and antimony obtained by replacement is a mixed metal, which needs further separation.

In response to this problem, some scholars proposed using wet leaching to treat the lead removal slag to achieve effective separation of lead and antimony. Wei Yansong et al. [42] used nitric acid as the leaching agent and sulfuric acid as the precipitant. By adjusting the experimental conditions such as liquid–solid ratio and acid concentration, the liquid–solid ratio was finally determined to be 4, the temperature was 80 °C, the leaching time was 50 min, and the nitric acid concentration was 7.0 mol/L. The final leaching rate of lead can reach 94%. This method effectively achieves the separation of lead–antimony, but its reaction waste acid still has a certain risk of pollution, and a large amount of acid used will increase the cost and thus reduce the economic efficiency.

Arsenic alkali residue is a kind of hazardous waste, and its environmental pollution is very serious. Arsenic alkali residue is the biggest problem in the current disposal of solid waste. Due to the incomplete separation of arsenic and alkali in the treatment process, arsenic–alkali mixed salt is easily formed, resulting in secondary pollution [43]. This problem has not been well treated, leading to no mature process to recover valuable metals in arsenic–alkali residue. Some scholars have put forward some solutions, such as Deng Weihua, Chai Liyuan, et al. [44]. A new process of hydrothermal leaching–antimony salt oxidization–concentration crystallization for recovering antimony, arsenic, and alkali from the arsenic alkali residue of antimony smelting has been put forward. The method is to separate antimony and arsenic from arsenic–alkali slag by hydrothermal leaching, antimony salt oxidation, and crystallization. The feasibility of the method was further verified by industrial experiments based in the laboratory. This method uses secondary arsenic alkali residue containing 9.86% antimony and 4.51% arsenic as raw materials. The recovery rates of antimony and arsenic can reach 95.27% and 95.21%, respectively, and the arsenic content in the crystal is only 0.6%, which greatly meets the purpose of antimony and arsenic separation.

In addition, Long et al. [45] proposed a new process for the treatment of arsenic–alkali residue by water leaching, CO_2 secondary alkali recovery, acidified selenium recovery, SO_2 reduction evaporation, and arsenic recovery. This method uses the difference in solubility at different temperatures to obtain the product. Figure 6 is the flow chart of recovering arsenic, antimony, and selenium from arsenic–alkali residue. In this process, the arsenic–alkali residue is first immersed in water, and antimony is enriched in the residue. Then, CO_2 is used to recover the alkali in the leaching solution to achieve the effect of arsenic–alkali separation. The acidification treatment of the solution after alkali removal can not only achieve the effect of deep alkali removal but also extract selenium. Finally, arsenic is recovered from the solution. The experimental results showed that the recoveries of antimony, arsenic, and selenium could reach 98.2%, 79.4%, and 80.6%, respectively.

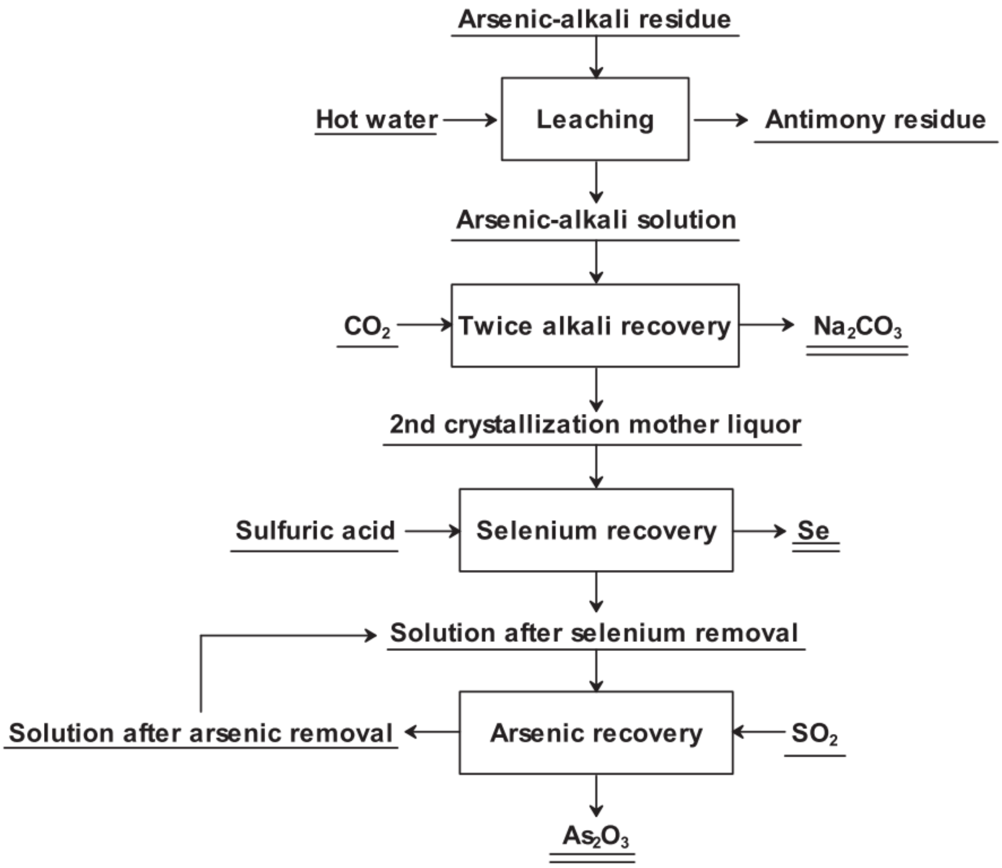

Figure 6. Flow chart of arsenic, antimony, and selenium recovery from arsenic–alkali residue [45].

The most important feature of this technology is that the complex metals in the arsenical slag can be effectively separated and the valuable metals in them can be recovered separately. It has a potential application prospect in the future, but the process is more complicated and the production cost is higher. In addition, the problem of steam with arsenic is generated in the production process. All these problems limit the application of this method.

Tian et al. [46] proposed the use of an integrated chemical precipitation and distribution crystallization method to treat arsenic–alkali slag, which is a novel and safe process. The method has three main components, which are arsenic–alkali slag leaching, selective detachment of arsenic, and evaporative crystallization of the alkali solution. Figure 7 shows the flow chart of the comprehensive disposal of arsenic–alkali slag.

The products obtained by this process are leaching residue containing 0.83% arsenic, arsenic residue containing 24.93% arsenic, and sodium carbonate containing 0.18% arsenic. In the first stage, the process is mainly grinding and stirring leaching. The innovation of this process is the addition of NH_4HCO_3 during the leaching process, which provides a reactant for the subsequent arsenic separation. In the second stage, $MgSO_4$ and NH_4HCO_3 react with the leaching solution to form magnesium ammonium arsenate precipitation to separate arsenic. In the third stage, Na_2CO_3 is obtained in alkali solution by evaporation crystallization, which can effectively separate arsenic and alkali, but the leaching process is complicated.

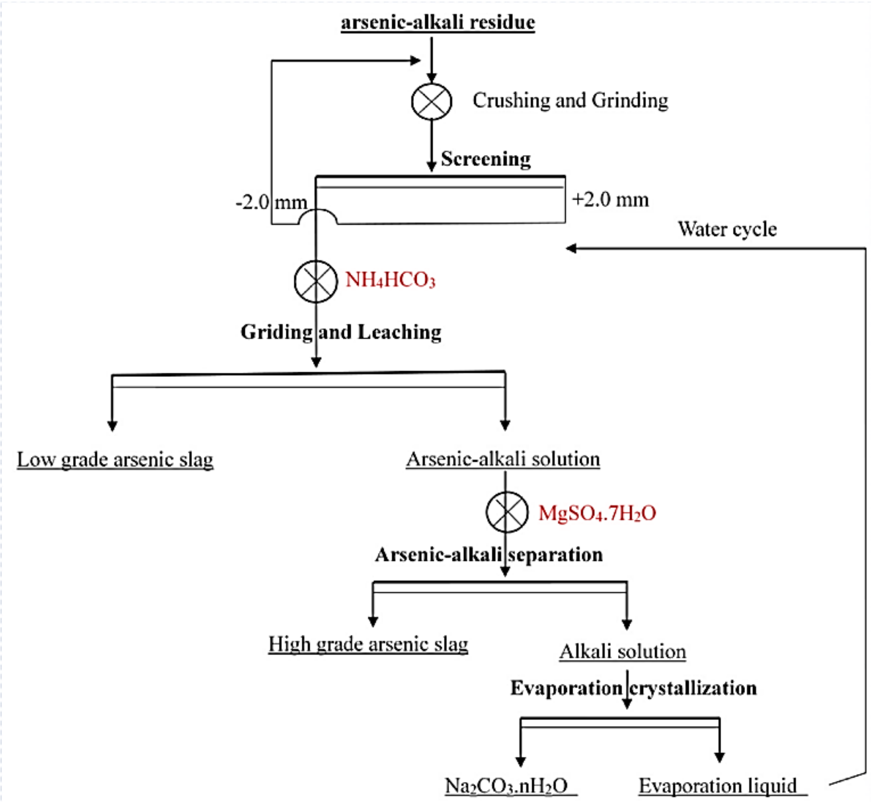

Figure 7. Arsenic alkali slag comprehensive disposal flow chart [46].

In summary, the difficulty of recovering valuable components from metallurgical slag mainly lies in how to separate metals, reduce energy consumption, and avoid secondary pollution. Methods that can effectively separate metals often have problems such as high energy consumption and complicated processes. However, simple processes cannot effectively treat metallurgical slag currently. There are some problems in both the fire method and the wet method, which make them unable to be widely used.

4.2. Stabilization/Solidification Method for Metallurgical Slag Treatment

At present, recovering metals from metallurgical slag is only applicable to the slag produced by some smelters. The most common methods for treating metallurgical slag are still stabilization/solidification and stockpiling. The stabilization/solidification method uses microorganisms or minerals to encapsulate and adsorb toxic metals dissolved in metallurgical slag to eliminate their environmental hazards.

For example, Jia et al. [47] studied the adsorption of antimony in smelting slag by *Shewanella oryzicola*. The scholar studied the dissolution behavior of smelting slag and bacteria under reduction conditions. The experiment showed that *Shewanella oryzicola* had an adsorption effect on Sb and preferentially adsorbed Sb^{3+}. Under the combined action of Fe^{3+} and *Shewanella australis*, Sb and Fe were co-precipitated to form Sb^{5+}-O-Fe^{3+} secondary minerals to achieve the effect of solidifying Sb. This experiment provides certain theoretical support for solidifying antimony.

Wang et al. [48] used ferrous sulfate and lime to solidify arsenic alkali residue. Sun et al. [49] prepared geopolymers with fly ash to cure arsenical slag, and according to the test results, the leaching toxicity was reduced from the original 2343.73 mg/L to 0.18 mg/L at 28 d after curing with geopolymers. Figure 8 shows the schematic diagram for curing arsenic from arsenical slag using geopolymer at different pH conditions.

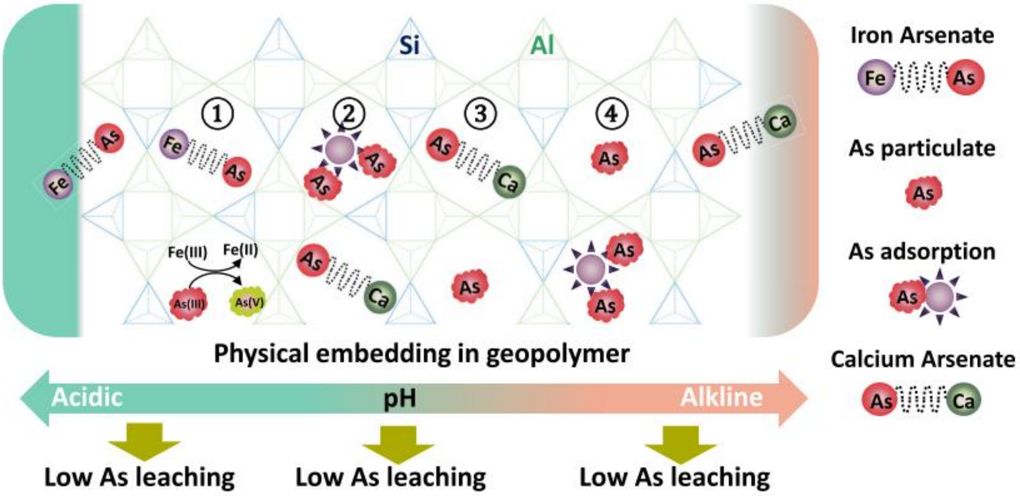

Figure 8. Principle of arsenic solidification by geopolymer [49].

The principle of curing arsenical slag with geopolymer varies under different pH conditions. In a strong acid environment, the iron element in the geopolymer will form iron arsenate with arsenic, which hinders the leaching of arsenic. In a weakly acidic environment, the physical adsorption is mainly carried out by iron hydroxide and magnetite. In a weakly alkaline environment, it is mainly solidified by forming calcium arsenate. In a strongly alkaline environment, As-containing particles are mainly encapsulated. The method has a more pronounced curing effect on As at wider pH conditions, allowing the product to be used in a wider range of conditions. The stability of the As–Fe system as well as the As–Ca system is confirmed, and the formation of iron arsenate, as well as calcium arsenate, can greatly stabilize the solidification of As therein. In addition, partially active metallurgical slag can also be used as building materials; for example, some of the active smelting slag can be used as cement raw materials [35].

The stabilization/solidification techniques can effectively solidify metallurgical slag and prevent it from polluting the environment. However, this technology lacks long-term observation to determine whether the cured product is unstable for a long run. In addition, in the secondary resourceization, because of the use of highly toxic metallurgical slag as raw materials, the sales of its products are not optimistic.

5. Conclusions and Prospect

Currently, due to the fine particle size and the low metal content of antimony tailings, the treatment technology of antimony tailings is mainly to fill and prepare building materials, and the resource technology is less. In terms of metal recovery, antimony, gold, mercury, and other valuable elements often associated with sulfide ore are still dominantly recovered by flotation. Oxidized ore mainly depends on gravity, such as shaking table to separate or make new equipment. The main problem is that the value elements in the stored tailings are not high, and many symbiotic and associated metals are not easy to recycle. A variety of treatment methods should be combined to achieve comprehensive recovery of multi-minerals and improve economic value. Antimony tailings that are difficult to recover can be used as building materials or underground filling materials to solidify antimony and arsenic by adsorption and encapsulation between minerals, but there is no long-term safety guarantee for toxic leaching. The uncertainty of leaching should be solved as far as possible to avoid secondary pollution during use.

In terms of metallurgical slag, due to the various properties of the metallurgical slag, some mature technologies are only suitable for specific slag, and most of the process of mental separation is not complete and cannot make full use of the metal. The method of partially separable metals has some problems, such as high cost of separating metals, secondary pollution, and high arsenic content in the products obtained after treatment. For the metallurgical slag produced by antimony smelting, the development of new technology to recover valuable elements should follow the principles of green environmental protection in order to reduce secondary pollution. The separation effect of metals should be improved to create higher economic value. For metallurgical slag with low content of valuable metals, the solidification/stabilization method can be used to solve a large number of stockpiling problems. However, the metal content in metallurgical slag is much higher than that in tailings, which has certain activity. Therefore, it is necessary to establish a long-term leaching risk assessment to determine whether the products produced by this method can be used safely in the long time.

Author Contributions: Methodology, Q.Z.; validation, L.W.; formal analysis and investigation, Z.Y.; resources, H.L.; writing—original draft preparation, Z.Y.; writing—review and editing, Q.Z.; visualization, S.W. and X.S.; supervision, X.C. (Xinglan Cui); project administration and funding acquisition, X.C. (Xiaokui Che). All authors have read and agreed to the published version of the manuscript.

Funding: The National Key Research and Development Project (No. 2020YFC1807702); The National Natural Science Foundation of China (Grants No. 52274272); The Guangxi Scientic Research and Technology Development Plan (Grant Nos. Guike AB22080078 and Guike AB23026043).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Anderson, C.G. *Antimony Production and Commodities*; Society for Mining, Metallurgy and Exploration: Englewood, CO, USA, 2019.
2. Ozer, M. Flotation of Antimony Ores with High Arsenic Content. *Physicochem. Probl. Miner. Process* **2022**, *58*, 152865. [CrossRef]
3. Schulz, K.J. (Ed.) *Critical Mineral Resources of the United States: Economic and Environmental Geology and Prospects for Future Supply*; Geological Survey: Reston, VA, USA, 2017.
4. Summaries, M.C. *Mineral Commodity Summaries 2022*; Geological Survey: Reston, VA, USA, 2022; p. 206.
5. Deng, R.-J.; Jin, C.-S.; Ren, B.-Z.; Hou, B.-L.; Hursthouse, A. The Potential for the Treatment of Antimony-Containing Wastewater by Iron-Based Adsorbents. *Water* **2017**, *9*, 794. [CrossRef]
6. Hiller, E.; Lalinská, B.; Chovan, M.; Jurkovič, L'.; Klimko, T.; Jankulár, M.; Hovorič, R.; Šottník, P.; Fl'aková, R.; Ženišová, Z.; et al. Arsenic and Antimony Contamination of Waters, Stream Sediments and Soils in the Vicinity of Abandoned Antimony Mines in the Western Carpathians, Slovakia. *Appl. Geochem.* **2012**, *27*, 598–614. [CrossRef]
7. Guo, X.; Wang, K.; He, M.; Liu, Z.; Yang, H.; Li, S. Antimony Smelting Process Generating Solid Wastes and Dust: Characterization and Leaching Behaviors. *J. Environ. Sci.* **2014**, *26*, 1549–1556. [CrossRef]
8. Guo, Z.; Yao, J.; Yuan, Z.; Zhu, M. Spatial Distribution and Potential Ecological Risk Assessment of Heavy Metals in Tailing, Guangxi Autonomous Region. *Guangzhou Chem. Ind.* **2015**, *43*, 156–158+178.
9. Zhang, J.; Qiu, X.; Li, N. Analysis on characteristics of heavy metal pollution of antimony mine tailings pond. *Non-Ferr. Met. (Min. Part)* **2022**, *74*, 126–130.
10. Brink, S.V.D.; Kleijn, R.; Sprecher, B.; Mancheri, N.; Tukker, A. Resilience in the Antimony Supply Chain. *Resour. Conserv. Recycl.* **2022**, *186*, 106586. [CrossRef]
11. Li, Y. Study on the Solidification Mechanism of Antimony-Containingtailings by Using BFS-SS-FGDG Based Cementitious Materials. Ph.D. Thesis, University of Science and Technology Beijing, Beijing, China, 2022.
12. Song, S. Environmental Effects of Mining and Strategies for Integration of Mine Resources and Environment. Ph.D. Thesis, Zhongshan University, Guangzhou, China, 2004.
13. Wang, K.; Xu, Z.; Cao, G.; Zang, N.; Zhou, X.; Yu, F. Construct a collaborative disposal mechanism for cross-regional sudden water pollution incidents. *Environ. Econ.* **2021**, *18*, 64–69.
14. Villarroel, L.F.; Miller, J.R.; Lechler, P.J.; Germanoski, D. Lead, Zinc, and Antimony Contamination of the Rio Chilco-Rio Tupiza Drainage System, Southern Bolivia. *Environ. Geol.* **2006**, *51*, 283–299. [CrossRef]
15. Punia, A. Role of Temperature, Wind, and Precipitation in Heavy Metal Contamination at Copper Mines: A Review. *Environ. Sci. Pollut. Res.* **2021**, *28*, 4056–4072. [CrossRef]
16. Deng, W. State of art of antimony metallurgy in China. *Min. Metall.* **2017**, *26*, 50–54.

17. Liu, F.; Le, X.C.; McKnight-Whitford, A.; Xia, Y.; Wu, F.; Elswick, E.; Johnson, C.C.; Zhu, C. Antimony Speciation and Contamination of Waters in the Xikuangshan Antimony Mining and Smelting Area, China. *Environ. Geochem. Health* **2010**, *32*, 401–413. [CrossRef]
18. Tian, J.; Sun, W.; Zhang, X.; Han, H.; Yu, Z.; Yue, T.; Wang, L.; Yang, Y.; Tang, H.; Li, E. Comprehensive Utilization and Safe Disposal of Hazardous Arsenic-Alkali Slag by the Combination of Beneficiation and Metallurgy. *J. Clean. Prod.* **2021**, *295*, 126381. [CrossRef]
19. Zhang, W.; Gao, G.; Miao, Y.; Zhou, L. *Harmless Disposal and Resource Utilization Technology of Arsenic Alkali Slag in Antimony Smelting Industry*; Chinese Society of Environmental Sciences: Beijing, China, 2013; pp. 2319–2322.
20. Baron, S.; Carignan, J.; Ploquin, A. Dispersion of Heavy Metals (Metalloids) in Soils from 800-Year-Old Pollution (Mont-Lozère, France). *Environ. Sci. Technol.* **2006**, *40*, 5319–5326. [CrossRef] [PubMed]
21. Liu, M.; Hao, C.; Jia, Y.; Zhang, W. Space-temporal evolution and hydrochemistry analysis of Qingfeng river in Tin mine. *J. North China Inst. Sci. Technol.* **2021**, *18*, 25–31.
22. Wang, J.; Chen, J.; Dong, F.; Du, M.; Fu, K. Research Progress and Prospect of Antimony Oxide Ore Beneficiation. *Met. Man Mine* **2021**, *12*, 21–27.
23. Ming, T. Experimental Study on Recovering Gold from Antimony Flotation Tailings. *Non-Ferr. Met. (Miner. Process Part)* **2011**, *406*, 27–29.
24. Wang, J.; Li, L.; Zhang, L.; Li, B.; Deng, R.; Shi, D. Sustainable Applications for Utilizing Antimony Tailing Coarse Aggregate (ATCA) in Concrete: Characteristic of ATCA and Toxicity Risks of Concrete. *Materials* **2021**, *14*, 5480. [CrossRef] [PubMed]
25. Chu, H.; Wang, Y.; Lu, D.; Liu, Z.; Zheng, X. Pre-Concentration of Fine Antimony Oxide Tailings Using an Agitated Reflux Classifier. *Powder Technol.* **2020**, *376*, 565–572. [CrossRef]
26. Liu, Z.; Lu, D.; Wang, Y.; Chu, H.; Zheng, X.; Chen, F. Application of reflux classifier with closely spaced inclined channels in pre-concentrate process of fine antimony oxide particles. *J. Cent. South Univ.* **2020**, *27*, 3290–3301. [CrossRef]
27. Kang, W. Experimental Study on Reconcentration of Fine Antimony Oxide Tailings in Xikuangshan Mining Plant. *China Met. Notif.* **2018**, 230–231.
28. Ren, L.; Wang, L.; Guo, H. Experimental Study on Mineral Processing of a Low Grade Mercury-Antimony Tailings in Northwest China. *Non-Ferr. Met. (Miner. Process Part)* **2020**, 123–126+133. [CrossRef]
29. Gao, W.; Ni, W.; Zhang, Y.; Li, Y.; Shi, T.; Li, Z. Investigation into the Semi-Dynamic Leaching Characteristics of Arsenic and Antimony from Solidified/Stabilized Tailings Using Metallurgical Slag-Based Binders. *J. Hazard. Mater.* **2020**, *381*, 120992. [CrossRef] [PubMed]
30. Li, L.; Wang, J.; Zhang, L.; Deng, R.; Zhou, S.; Wang, G. Strength and Durability Properties of Antimony Tailing Coarse Aggregate (ATCA) Concrete. *Materials* **2021**, *14*, 5606. [CrossRef] [PubMed]
31. Wu, F.; Liu, X.; Qu, G.; Ning, P.; Jin, C.; Cui, Q.; Ren, Y.; He, M.; Yang, Y.; Li, J. Solidification and Stabilization of Harmful Elements in Antimony Tailings and Synergistic Utilization of Multiple Solid Wastes. *Cem. Concr. Compos.* **2022**, *133*, 104718. [CrossRef]
32. Li, Y.; Ni, W.; Gao, W.; Zhang, S.; Fu, P.; Li, Y. Study on Solidification and Stabilization of Antimony-Containing Tailings with Metallurgical Slag-Based Binders. *Materials* **2022**, *15*, 1780. [CrossRef]
33. Wang, K.; Wang, Q.; Chen, Y.; Li, D.; Tian, Q.; Guo, X. Status of solid waste disposal in antimony metallurgy. *Nonferr. Met. Sci. Eng.* **2022**, *13*, 8–17.
34. Luo, S.; Ma, D. Study on the Influence of Slag Composition on Antimony Content in Slag DuringVolatilization Smelting of Antimony Concentrate in Blast Furnace. *Hunan Nonferr. Met.* **2021**, *37*, 28–30+44.
35. Shan, T. Study on the Recovery Process of Antimony Lead from Removal Lead Slag of Smelting Antimony. *Hunan Nonferr. Met.* **2014**, *30*, 36–38+76.
36. Hao, F. Mechanism of Arsenic Fixation by Steel Slag-Based Active Materials and Its Application. Master's Thesis, Kunming University of Science and Technology, Kunming, China, 2020. [CrossRef]
37. Keqiang, Q.; Rongliang, Z. Research on Preparation of Nanometer Antimony Trioxide from Slag Containing Antimony by Vacuum Evaporation Method. *Vacuum* **2006**, *80*, 1016–1020. [CrossRef]
38. Mo, W. The Industrial Practices of Volatility Process for Jamesonite Smelting Slag with Fuming Furnace. *Guangzhou Chem. Ind.* **2012**, *40*, 134–136.
39. He, Q.; Tan, Y. On Zinc and Indium Recycle from Blast Furnace Slag by Fuming Process. *Jiangxi Nonferr. Met.* **2008**, *22*, 29–32. [CrossRef]
40. Luo, H.-L.; Liu, W.; Qin, W.-Q.; Zheng, Y.-X.; Yang, K. Cleaning of High Antimony Smelting Slag from an Oxygen-Enriched Bottom-Blown by Direct Reduction. *Rare Met.* **2019**, *38*, 800–804. [CrossRef]
41. Yao, L.; Liu, D.; Ke, Y.; Li, Y.; Wang, Z.; Fei, J.; Xu, H.; Min, X. Synthesis and Hydration Characteristic of Geopolymer Based on Lead Smelting Slag. *Int. J. Environ. Res. Public Health* **2020**, *17*, 2762. [CrossRef]
42. Wei, Y.; Pan, Y. Study on Lead Recovery from Lead Slag of Antimony Refining byNitric Acid Leaching Process. *Non-Ferr. Met. (Smelt. Part)* **2013**, *8*, 11–13.
43. Long, H.; Zheng, Y.; Peng, Y.; Jin, G.; Deng, W.; Zhang, S.; He, H. Separation and Recovery of Arsenic and Alkali Products during the Treatment of Antimony Smelting Residues. *Miner. Eng.* **2020**, *153*, 106379. [CrossRef]
44. Deng, W.; Chai, L.; Dai, Y. ndustrial Experimental Study on Comprehensive Recoverying Valuable Resources fromAntimony Smelting Arsenic Alkali Residue. *Hunan Nonferrous Met.* **2014**, *30*, 24–27.

45. Long, H.; Zheng, Y.; Peng, Y.; He, H. Recovery of Alkali, Selenium and Arsenic from Antimony Smelting Arsenic-Alkali Residue. *J. Clean. Prod.* **2020**, *251*, 119673. [CrossRef]
46. Tian, J.; Wang, Y.; Zhang, X.; Sun, W.; Han, H.; Yu, Z.; Yue, T. A Novel Scheme for Safe Disposal and Resource Utilization of Arsenic-Alkali Slag. *Process Saf. Environ. Prot.* **2021**, *156*, 429–437. [CrossRef]
47. Jia, X.; Ma, L.; Liu, J.; Liu, P.; Yu, L.; Zhou, J.; Li, W.; Zhou, W.; Dong, Z. Reduction of Antimony Mobility from Sb-Rich Smelting Slag by Shewanella Oneidensis: Integrated Biosorption and Precipitation. *J. Hazard. Mater.* **2022**, *426*, 127385. [CrossRef]
48. Wang, X.; Ding, J.; Wang, L.; Zhang, S.; Hou, H.; Zhang, J.; Chen, J.; Ma, M.; Tsang, D.C.W.; Wu, X. Stabilization Treatment of Arsenic-Alkali Residue (AAR): Effect of the Coexisting Soluble Carbonate on Arsenic Stabilization. *Environ. Int.* **2020**, *135*, 105406. [CrossRef] [PubMed]
49. Sun, Y.; Zhang, P.; Li, Z.; Chen, J.; Ke, Y.; Hu, J.; Liu, B.; Yang, J.; Liang, S.; Su, X.; et al. Iron-Calcium Reinforced Solidification of Arsenic Alkali Residue in Geopolymer Composite: Wide PH Stabilization and Its Mechanism. *Chemosphere* **2023**, *312*, 137063. [CrossRef] [PubMed]