

Article

Utilizing SiO₂ to Break the “Alkali-Lock” Effect for Resource Utilization and Disposal of Arsenic-Alkali Leaching Residue

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Abstract

Arsenic-alkali leaching residue (AAR), generated during antimony smelting, is a hazardous solid waste containing arsenic and antimony. Its safe disposal and resource-oriented utilization are constrained by the strong stabilization of As- and Sb-bearing species in a high-alkali matrix. Herein, we investigated the alkali locking effect during carbothermal roasting of AAR and proposed a SiO₂-assisted roasting strategy to promote the simultaneous volatilization of arsenic and antimony. Thermodynamic calculations indicate that, in a sodium-rich roasting system, representative As- and Sb-bearing species preferentially transform into thermodynamically stable Na₃AsO₄ and Na₃SbO₄, thereby suppressing their reductive conversion into volatile As₂O₃ and Sb₂O₃. Direct roasting experiments confirmed that simply increasing roasting temperature, carbon dosage, or roasting time was insufficient to achieve efficient simultaneous volatilization of As and Sb, which experimentally supports the existence of the alkali-locking effect. The introduction of SiO₂ weakened sodium-induced immobilization by favoring the formation of sodium silicate phases, thereby enhancing the thermodynamic driving force for the generation and release of As₂O₃ and Sb₂O₃. Under the conditions of 900 °C, 90 min, 30% carbon dosage, and 10% SiO₂ addition, the volatilization rates of arsenic and antimony reached 93.25% and 93.80%, respectively. XRD and SEM-EDS revealed that the addition of SiO₂ promoted the reconstruction of Na–Al–Si-bearing phases and the development of porous slag structures, thereby facilitating the mass transfer and volatilization of As/Sb species. Preliminary co-roasting experiments with flotation antimony concentrate suggest the feasibility of using Si-bearing gangue as an in situ additive for AAR treatment. This study provides a thermodynamic and experimental basis for the resource-oriented detoxification of arsenic-alkali leaching residue.



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Keywords: arsenic-alkali leaching residue; alkali-locking effect; SiO₂-assisted roasting; arsenic and antimony volatilization; co-roasting

1. Introduction

Arsenic-alkali residue is a hazardous solid waste generated during the antimony smelting process [1,2]. The crushed residue is metered onto a belt, fed into a sand-blasting

machine for secondary crushing, and then passed into a wet ball mill via a chute for leaching. During leaching, the soluble arsenic, antimony, and alkali components are separated, whereas the insoluble arsenic, antimony, and aluminum silicon components remain in the precipitation, forming arsenic-alkali leaching residue (AAR) [3–5]. The AAR used in this study exhibited a high leaching toxicity of 170 mg/L for arsenic, indicating a significant environmental risk and the necessity of safe disposal or resource-oriented detoxification treatment.

Current disposal methods for arsenic residue include pyrometallurgical arsenic removal, wet leaching-dearsenic technique, and curing landfills [6–8]. Pyrometallurgical roasting leverages the differences in saturated vapor pressures of valent metals and arsenic oxides. Oxidative roasting (for low-valency arsenic compounds such as arsenic sulfide and arsenopyrite) or reduction roasting (for higher-valency compounds such as copper arsenide and iron arsenide) volatilizes arsenic components as As_2O_3 , separating them from valent metals [9–12]. Wet disposal process for arsenic residue mainly includes acid and alkali leaching, in which acid and alkali media are used to selectively separate arsenic and valent metals, and then chemical precipitation is used to effectively and selectively remove arsenic components [13–15]. Curing landfills use curing agents (iron-based) to transform harmful pollutants into low-solubility, low-toxicity solid substrates, which reduce the leaching and migration of harmful substances [16–18]. Obviously, for the AAR system, reusing wet secondary leaching is difficult to achieve effective removal of arsenic and antimony components. During the landfill disposal process, the valuable antimony components in the leaching residue cannot be recovered, resulting in resource loss and posing a risk of secondary pollution. Overall, pyrometallurgy is currently the optimal choice, which is relatively simple to operate with high productivity [10]. However, the economic feasibility of individual pyrometallurgical disposal of AAR is severely constrained by its unique mineralogical composition, specifically the presence of high-alkali components that hinder volatile liberation.

In this study, thermodynamic calculations and controlled roasting experiments were combined to investigate the alkali-locking behavior of AAR and the regulatory effect of SiO_2 [19,20]. The specific objectives were to (i) elucidate the thermodynamic origin of the alkali-locking effect caused by sodium-bearing phases [21]; (ii) evaluate the effect of roasting temperature, carbon dosage, roasting time, and SiO_2 addition on the volatilization behavior of arsenic and antimony [22,23]. (iii) reveal the phase transformation and microstructural evolution of roasted slags by XRD and SEM-EDS [24]; and (iv) preliminarily assess the feasibility of co-roasting AAR with flotation antimony concentrate as an in situ Si-bearing additive [25]. This work provides a theoretical and experimental basis for the resource-oriented detoxification of arsenic-alkali leaching residue and offers a potential pathway for its integration into antimony metallurgical processes.

2. Materials and Methods

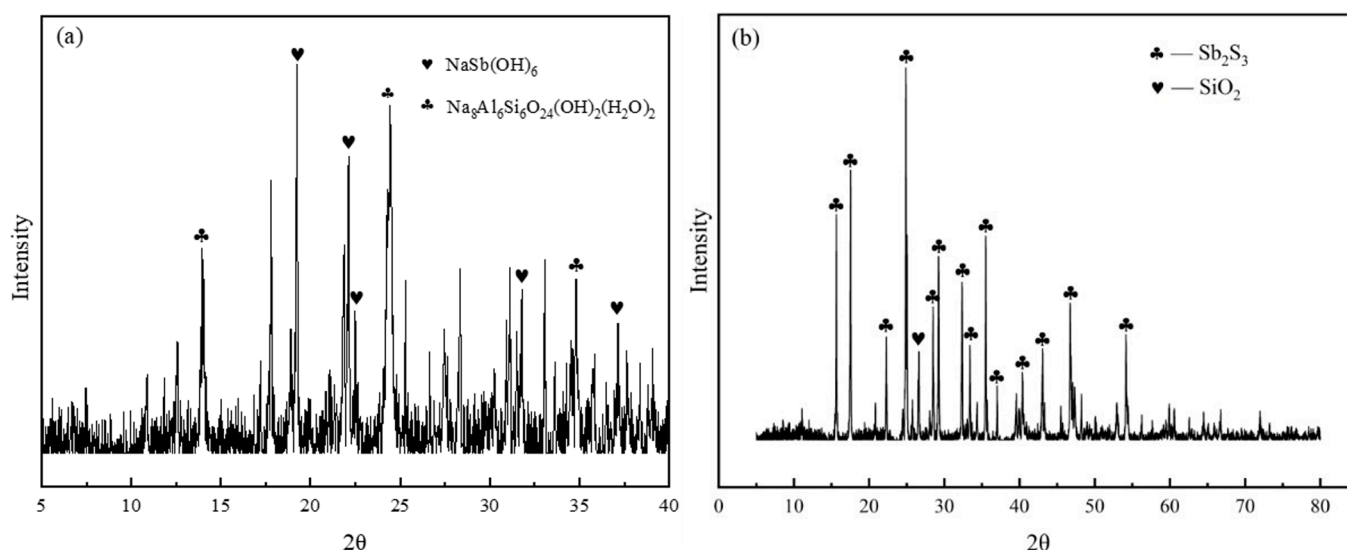
2.1. Materials

The AAR was obtained from the alkaline leaching process of antimony smelting residues at Anti-Du Environmental Protection Co., Ltd. (Loudi, China). Prior to characterization and roasting experiments, the residue was dried, homogenized, and stored in sealed containers to minimize moisture fluctuation and sample heterogeneity. Table 1 shows the elemental composition of AAR determined via X-ray fluorescence spectroscopy (XRF, from Zhuzhou, China). AAR contained high levels of Na, Al, Si, As, and Sb, indicating that it is a typical high-alkali arsenic-antimony-bearing residue.

Table 1. Elemental composition of AAR.

Element	Si	Na	Al	Sb	Fe	Ca	As	S
Content	12.12	21.61	7.094	3.592	2.71	2.501	2.650	2.118

The crystalline phases of raw AAR were identified by X-ray diffraction (XRD, from Changsha, China), as shown in Figure 1a. The major crystalline phases were assigned to NaSb(OH)_6 and a sodalite-type sodium aluminosilicate phase, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2(\text{H}_2\text{O})_2$. The exact formula of the sodium aluminosilicate phase should be kept consistent with the rechecked PDF card throughout the manuscript. Weak diffraction signals related to Sb-bearing phases were observed but were difficult to distinguish because of their low intensity and overlap with the dominant sodium aluminosilicate peaks. In addition, no distinct crystalline arsenate peaks were clearly identified in the XRD pattern, suggesting that part of the As-bearing species may occur as low-content, poorly crystalline, or amorphous phases. Therefore, XRD was mainly used to identify crystalline phases with sufficient abundance and crystallinity, rather than to quantify all As- and Sb-bearing species in AAR.

**Figure 1.** XRD patterns of (a) raw arsenic-alkali leaching residue (AAR) and (b) flotation antimony concentrate.

For the co-roasting experiments, flotation antimony concentrate was used as the antimony-bearing feedstock. Its elemental composition, determined by XRF, is shown in Table 2. The concentrate was mainly composed of Sb and S, with a certain amount of Si, indicating the presence of Si-bearing gangue minerals. The XRD pattern of the flotation antimony concentrate is shown in Figure 1b, in which stibnite (Sb_2S_3) was identified as the major crystalline phase. The presence of Si-bearing gangue was further supported by the XRF result, although the diffraction peaks of SiO_2 were weak, partially overlapped, or below the clear identification limit in the XRD pattern. Therefore, the Si component in the antimony concentrate was discussed based on the combined evidence from XRF and XRD.

Table 2. Elemental composition of antimony concentrate obtained via flotation.

Element	Si	S	Al	Sb	Fe	Ca	As
Content	6.445	22.13	1.03	52.59	2.669	0.235	0.038

The chemical phase distributions of As and Sb in AAR were determined by selective chemical phase analysis, and the results are shown in Tables 3 and 4. The results indicate that As was mainly associated with arsenate-type species, whereas Sb occurred predominantly in oxide-associated and antimonate-related forms. It should be emphasized that these chemical phase distributions were not obtained solely from XRD analysis. The absence of clear As- or Sb-bearing crystalline phases in the XRD pattern can be attributed to low contents, poor crystallinity, amorphous occurrence, and peak overlap with sodium aluminosilicate phases [26].

Table 3. Physical phase distribution of arsenic in AAR.

Arsenic Phase	Arsenic in Arsenic Oxides	Arsenic in Arsenates	Arsenic in Arsenic Sulfide	Arsenic in Residue
Content/%	0.966	1.395	0.095	0.193

Table 4. Physical phase distribution of the antimony in AAR.

Antimony Phase	Antimony in Antimony Ochre	Antimony in Stibnite	Antimonate and Other Antimony
Content/%	2.694	0.523	0.139

Carbon powder and SiO₂ were used as the reducing agent and acidic additive, respectively. The carbon powder and SiO₂ were purchased from Aladdin, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China, with a purity of $\geq 99.0\%$, and were used without further purification. Before roasting, the mixed samples were pressed into briquettes and dried to reduce moisture fluctuation. The briquettes were then placed in a tube furnace, heated to the target temperature at a controlled heating rate, held for the designed roasting time, and cooled to room temperature under controlled conditions before grinding and analysis. The furnace temperature was calibrated using a standard thermocouple before the roasting experiments.

2.2. Experimental Procedures

The roasting experiments were designed to evaluate the volatilization behavior of arsenic and antimony from AAR under different roasting conditions and to clarify the regulatory role of SiO₂ in weakening the alkali-locking effect (as shown in Figure 2). The overall experimental procedure included raw-material weighing, homogeneous mixing, briquetting, drying, preheating, carbothermal roasting, holding at the target temperature, controlled cooling, grinding, and subsequent chemical and phase analyses.

For direct roasting, AAR and carbon powder were mixed at the designed carbon dosage, without the addition of SiO₂ or antimony concentrate. For SiO₂-assisted roasting, AAR, carbon powder, and SiO₂ were mixed according to the preset mass ratios. For co-roasting, AAR, flotation antimony concentrate, and carbon powder were mixed according to the designed AAR-to-concentrate ratio. In this study, “direct roasting” refers to the roasting of AAR with carbon only; “SiO₂-assisted roasting” refers to the roasting of AAR with carbon and externally added SiO₂; and “co-roasting” refers to the roasting of AAR with flotation antimony concentrate and carbon, where the Si-bearing gangue in the concentrate acts as an in situ silica source.

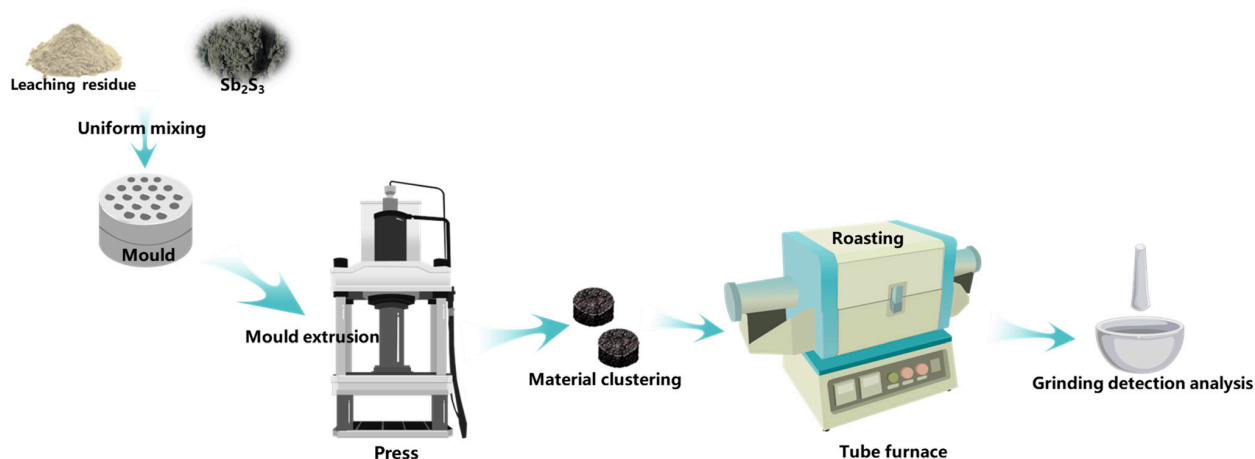


Figure 2. Schematic flowchart of the AAR roasting experiments, including raw-material mixing, briquetting, drying, preheating, roasting, cooling, grinding, and subsequent characterization.

2.3. Elemental Analysis and Solid Characterization

Thermodynamic Research: Thermodynamic calculations were performed using HSC Chemistry to evaluate the standard Gibbs free energy changes (ΔG^θ) of the proposed reactions as a function of temperature. The calculated reactions included representative carbothermal reduction reactions of arsenate- and antimony-bearing species, reactions between As/Sb species and sodium-bearing components, and SiO_2 -assisted displacement reactions involving sodium arsenate and sodium antimonate. These calculations were used to clarify the thermodynamic origin of the alkali-locking effect and the potential role of SiO_2 in weakening sodium-induced immobilization of arsenic and antimony. The software version should be kept consistent throughout the manuscript.

Chemical analysis and volatilization-efficiency calculation: The arsenic and antimony contents in the raw materials and roasted products were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Thermo Scientific, from Changsha, China) after acid digestion of solid samples. Specifically, a representative portion of each sample was accurately weighed, diluted to a fixed volume, and then analyzed by ICP-OES. This revision clarifies that ICP-OES was used to determine the As and Sb contents in the digested solutions of solid samples, rather than in a liquid-phase filtrate generated during roasting.

The volatilization efficiencies of arsenic and antimony were calculated based on the mass balance of As and Sb before and after roasting, according to the following equations:

$$\text{Arsenic volatilization rate (\%)} = \frac{M_1 \times C_{\text{As}1} - M_2 \times C_{\text{As}2}}{M_1 \times C_{\text{As}1}} \times 100$$

$$\text{Antimony volatilization rate (\%)} = \frac{M_1 \times C_{\text{Sb}1} - M_2 \times C_{\text{Sb}2}}{M_1 \times C_{\text{Sb}1}}$$

where M_1 and M_2 are the weight of roasting materials before and after roasting (g); $C_{\text{As}1}$ and $C_{\text{As}2}$ are the arsenic contents before and after roasting; and $C_{\text{Sb}1}$ and $C_{\text{Sb}2}$ are the antimony contents before and after roasting.

XRD characterization: The crystalline phases of raw materials and roasted products were identified by X-ray diffraction (XRD) using a D/max-3B diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The diffraction patterns were collected over a 2θ range of $5\text{--}80^\circ$ at a scanning rate of $5^\circ/\text{min}$. Phase identification was performed using Jade 6.0 and the PDF-2 (2014) database of the International Center for Diffraction Data. It should be noted that XRD was used mainly for identifying crystalline phases with sufficient abundance and crystallinity. Low-content, poorly crystalline, amorphous, or peak-overlapped As/Sb-

bearing species may not be clearly detected by XRD, and therefore XRD results should be interpreted together with chemical analysis and chemical phase analysis.

SEM-EDS characterization. The surface morphology of solid samples was characterized via scanning electron microscopy (SEM, from Loudi, China) and imaged at different magnifications to determine the size and length of crystal particles. The elemental content and distribution on the sample surface were determined via energy-dispersive spectroscopy (EDS, from Loudi, China).

Chemical phase analysis of As and Sb. The chemical phase distributions of arsenic and antimony in AAR were determined by selective chemical phase analysis or sequential extraction analysis, and the results are presented in Tables 3 and 4. This method was used to distinguish different As- and Sb-associated forms, such as oxide-associated, arsenate/antimonate-associated, sulfide-associated, and residual fractions. The dissolved As and Sb in each extracted fraction were determined by ICP-OES after appropriate dilution. It should be emphasized that the chemical phase distributions in Tables 3 and 4 were not obtained solely from XRD analysis. The absence of distinct As- or Sb-bearing crystalline peaks in the XRD pattern can be attributed to low content, weak crystallinity, amorphous occurrence, or overlap with the dominant sodium aluminosilicate phases.

The crystalline phases of raw AAR were identified by X-ray diffraction, as shown in Figure 1a. The major crystalline phases were assigned as $\text{NaSb}(\text{OH})_6$ and a sodalite-type sodium aluminosilicate phase, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2(\text{H}_2\text{O})_2$, according to the rechecked PDF card. No distinct crystalline arsenate peaks were clearly identified in the XRD pattern, suggesting that part of the As-bearing species may occur as low-content, poorly crystalline, or amorphous phases. Therefore, XRD was mainly used to identify crystalline phases with sufficient abundance and crystallinity, rather than to quantify all As- and Sb-bearing species in AAR.

The chemical phase distributions of As and Sb in AAR were determined by selective chemical phase analysis. The results indicate that As was mainly associated with arsenate-type species, whereas Sb occurred predominantly in oxide-associated and antimonate-related forms. It should be emphasized that these chemical phase distributions were not obtained solely from XRD analysis. The absence of clear As- or Sb-bearing crystalline phases in the XRD pattern can be attributed to low contents, poor crystallinity, amorphous occurrence, and peak overlap with sodium aluminosilicate phases.

Accordingly, $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Mg}_3(\text{AsO}_4)_2$, Na_3AsO_4 , and Na_3SbO_4 were selected as representative thermodynamic model phases to evaluate possible reaction tendencies during roasting, rather than as crystalline phases directly confirmed by XRD. Carbon powder was used as the reducing agent in the roasting experiments; therefore, the thermodynamic discussion was mainly focused on carbon-assisted reduction reactions.

3. Results and Discussion

3.1. Thermodynamic Study on the Separate Roasting of AAR

In this section, the thermodynamic behavior of AAR is systematically discussed according to its characteristics. According to the chemical phase analysis, arsenic in AAR was mainly associated with arsenate-type species. However, distinct crystalline arsenate phases such as $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Mg}_3(\text{AsO}_4)_2$, and Na_3AsO_4 were not clearly identified in the XRD pattern, which may be attributed to their low contents, poor crystallinity, amorphous occurrence, or peak overlap with the dominant sodium aluminosilicate phases.

The possible carbothermal reduction reactions of these representative arsenates are listed in Table 5. Carbon powder was used as the reducing agent in the roasting experiments; therefore, the thermodynamic discussion was mainly focused on carbon-assisted reduction reactions. The standard Gibbs free energy changes (ΔG^θ) of the proposed reactions were

calculated using HSC Chemistry software 9.0 as a function of temperature under standard-state conditions. The corresponding results are shown in Figure 3. In general, a more negative ΔG^θ value indicates a stronger thermodynamic driving force for the reaction.

Table 5. Arsenate roasting reactions.

Number	Reaction
(1)	$\text{Ca}_3(\text{AsO}_4)_2 + \text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{CaO} + \text{CO}_2 (\text{g})$
(2)	$\text{Ca}_3(\text{AsO}_4)_2 + 2\text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{CaO} + 2\text{CO} (\text{g})$
(3)	$\text{Mg}_3(\text{AsO}_4)_2 + \text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{MgO} + \text{CO}_2 (\text{g})$
(4)	$\text{Mg}_3(\text{AsO}_4)_2 + 2\text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{MgO} + 2\text{CO} (\text{g})$
(5)	$2\text{FeAsO}_4 + \text{C} = \text{As}_2\text{O}_3 (\text{g}) + \text{Fe}_2\text{O}_3 + \text{CO}_2 (\text{g})$
(6)	$2\text{FeAsO}_4 + 2\text{C} = \text{As}_2\text{O}_3 (\text{g}) + \text{Fe}_2\text{O}_3 + 2\text{CO} (\text{g})$
(7)	$2\text{Na}_3\text{AsO}_4 + \text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{Na}_2\text{O} + \text{CO}_2 (\text{g})$
(8)	$2\text{Na}_3\text{AsO}_4 + 2\text{C} = \text{As}_2\text{O}_3 (\text{g}) + 3\text{Na}_2\text{O} + 2\text{CO} (\text{g})$

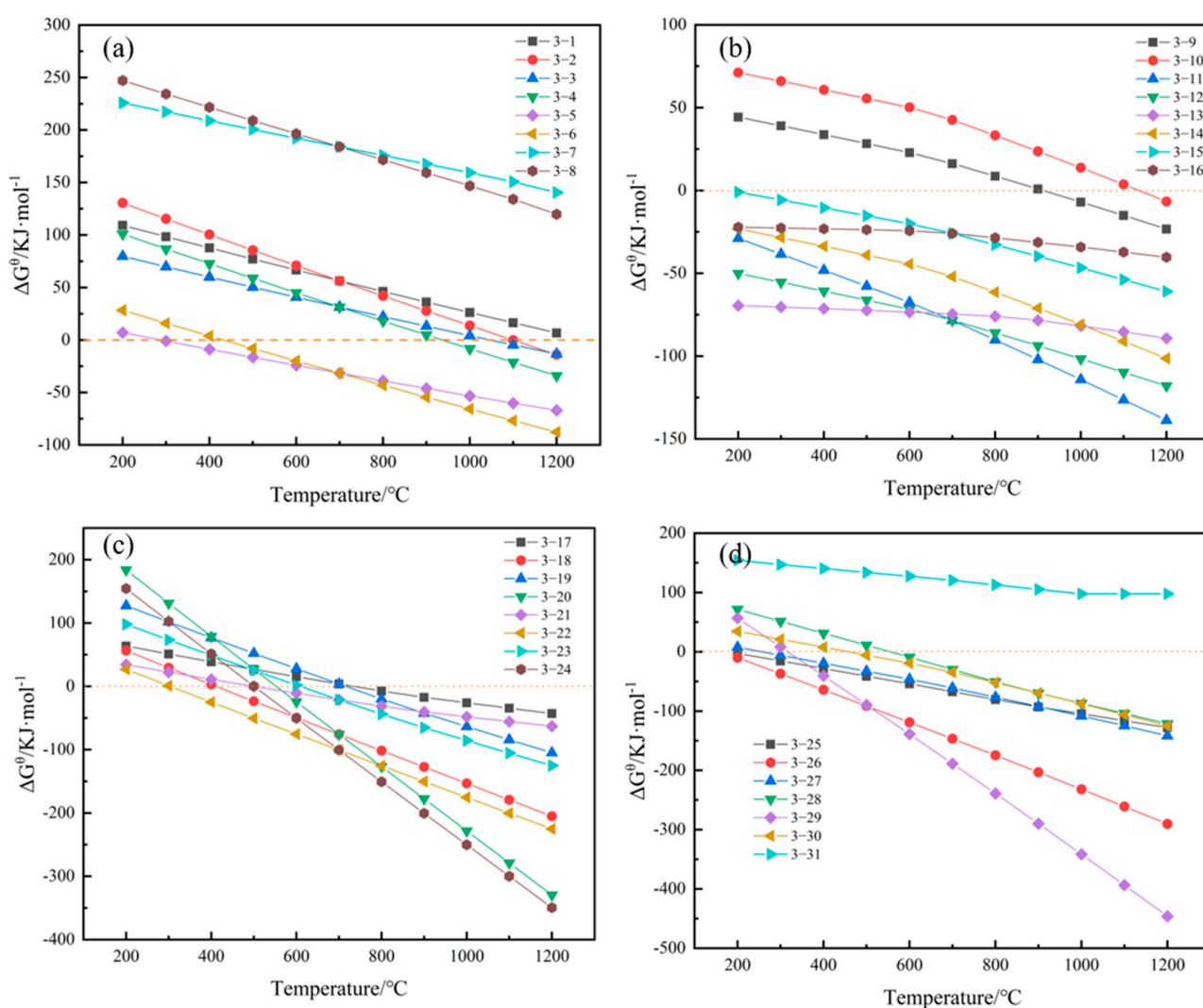


Figure 3. ΔG^θ changes in reactions related to direct AAR roasting: (a) carbothermal reduction in representative arsenate phases; (b) decomposition and carbothermal reduction in representative Sb oxide phases; (c) reactions between representative arsenates and sodium-bearing components; and (d) reactions between representative Sb oxide phases and sodium-bearing components.

As shown in Figure 3a, the FeAsO_4 -related reactions became thermodynamically favorable at relatively lower temperatures, whereas the reduction in Ca- and Mg-arsenates

required higher temperatures to become favorable under the calculated conditions. In contrast, the ΔG^θ values of the Na_3AsO_4 reduction reactions remained positive or much less favorable within the investigated temperature range of 200–1200 °C, indicating that sodium arsenate is more resistant to direct carbothermal decomposition. These results suggest that the ease of reductive volatilization of representative arsenate phases decreases in the order of $\text{FeAsO}_4 > \text{Mg}_3(\text{AsO}_4)_2 \approx \text{Ca}_3(\text{AsO}_4)_2 > \text{Na}_3\text{AsO}_4$. In other words, the formation of sodium arsenate can significantly increase the difficulty of converting arsenic into volatile As_2O_3 during direct roasting.

The thermodynamic behavior of antimony species was also examined. Chemical phase analysis indicated that Sb in AAR was mainly associated with oxide-related and antimonate-related forms. However, valentinite was not clearly identified as a distinct crystalline phase by XRD, probably because of its low content, weak crystallinity, or overlap with other crystalline phases. Considering the available thermodynamic data and the possible occurrence of high-valence Sb species in the oxidized residue, Sb_2O_5 and Sb_2O_4 were selected as representative Sb oxide model phases. The related decomposition and carbothermal reduction reactions are shown in Table 6, and the calculated ΔG^θ –temperature relationships are shown in Figure 3b. CO gas may be used as a reducing agent in an intermediate reaction product.

Table 6. Antimony oxide roasting reaction.

Number	Reaction
(9)	$\text{Sb}_2\text{O}_5 = \text{Sb}_2\text{O}_3 + \text{O}_2 \text{ (g)}$
(10)	$2\text{Sb}_2\text{O}_4 = 2\text{Sb}_2\text{O}_3 + \text{O}_2 \text{ (g)}$
(11)	$\text{Sb}_2\text{O}_5 + 2\text{C} = \text{Sb}_2\text{O}_3 + 2\text{CO} \text{ (g)}$
(12)	$\text{Sb}_2\text{O}_5 + \text{C} = \text{Sb}_2\text{O}_3 + \text{CO}_2 \text{ (g)}$
(13)	$\text{Sb}_2\text{O}_5 + \text{CO(g)} = \text{Sb}_2\text{O}_3 + 2\text{CO}_2 \text{ (g)}$
(14)	$2\text{Sb}_2\text{O}_4 + \text{C} = 2\text{Sb}_2\text{O}_3 + \text{CO}_2 \text{ (g)}$
(15)	$2\text{Sb}_2\text{O}_4 + 2\text{C} = 2\text{Sb}_2\text{O}_3 + 2\text{CO} \text{ (g)}$
(16)	$\text{Sb}_2\text{O}_4 + \text{CO(g)} = \text{Sb}_2\text{O}_3 + \text{CO}_2 \text{ (g)}$

The calculation results indicate that the direct decomposition of high-valence antimony oxides into Sb_2O_3 becomes thermodynamically feasible only at relatively high temperatures, whereas the presence of carbon markedly improves the thermodynamic feasibility of Sb_2O_3 formation. This suggests that a reducing atmosphere is beneficial for the transformation of high-valence Sb oxides into volatile Sb_2O_3 . Nevertheless, in the actual AAR system, the volatilization behavior of Sb cannot be determined solely by the reduction in isolated Sb oxides, because sodium-bearing components may further stabilize Sb in the solid phase.

AAR contains abundant sodium-bearing components, such as Na_2CO_3 and NaHCO_3 , and sodium aluminosilicate phases. These sodium salts may significantly affect the thermodynamic behavior of arsenic and antimony components during roasting. Therefore, it is very necessary to explore the influence of sodium salts on the thermodynamic behavior of arsenate, oxide species, and sodium-bearing components were further considered, as summarized in Table 7 (Equations (17)–(31)). The calculated results in Figure 3c show that the conversion of Ca- and Mg-arsenates into Na_3AsO_4 is thermodynamically favorable over a wide temperature range, particularly in the presence of sodium salts. This indicates that sodium-bearing components can promote the formation of sodium arsenate, thereby stabilizing arsenic in the roasted solid matrix.

A similar tendency was observed for antimony. Figure 3d shows the reactions between representative Sb oxide species and sodium-bearing components, which showed negative ΔG^θ values over a broad temperature range, indicating that the formation of sodium antimonate is thermodynamically favorable. When the ΔG^θ values are ranked, the direction

of the order should be explicitly defined as either increasing or decreasing ΔG^θ , and the interpretation should be based on the principle that a more negative ΔG^θ corresponds to a stronger thermodynamic driving force. Consequently, the thermodynamic calculations indicate that in a highly alkaline environment, Arsenic and antimony are preferentially converted into the thermodynamically more stable compounds Na_3AsO_4 and Na_3SbO_4 . These sodium-containing phases inhibit the reductive conversion of As and Sb into volatile As_2O_3 and Sb_2O_3 , providing a thermodynamic explanation for the alkali-locking effect during the direct roasting of AAR.

Table 7. Roasting reaction between arsenate, antimony components, and alkali components.

Number	Reaction
(17)	$\text{Ca}_3(\text{AsO}_4)_2 + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{CaO} + 3\text{CO}_2(\text{g})$
(18)	$\text{Ca}_3(\text{AsO}_4)_2 + 6\text{NaHCO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{CaO} + 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
(19)	$\text{Ca}_3(\text{AsO}_4)_2 + 3\text{C} + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{CaO} + 6\text{CO}(\text{g})$
(20)	$\text{Ca}_3(\text{AsO}_4)_2 + 6\text{C} + 6\text{NaHCO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{CaO} + 12\text{CO}(\text{g}) + 3\text{H}_2\text{O}$
(21)	$\text{Mg}_3(\text{AsO}_4)_2 + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{MgO} + 3\text{CO}_2(\text{g})$
(22)	$\text{Mg}_3(\text{AsO}_4)_2 + 6\text{NaHCO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{MgO} + 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
(23)	$\text{Mg}_3(\text{AsO}_4)_2 + 3\text{C} + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{MgO} + 6\text{CO}(\text{g})$
(24)	$\text{Mg}_3(\text{AsO}_4)_2 + 6\text{C} + 6\text{NaHCO}_3 = 2\text{Na}_3\text{AsO}_4 + 3\text{MgO} + 12\text{CO}(\text{g}) + 3\text{H}_2\text{O}$
(25)	$\text{Sb}_2\text{O}_5 + 3\text{Na}_2\text{CO}_3 = 2\text{Na}_3\text{SbO}_4 + \text{CO}_2(\text{g})$
(26)	$\text{Sb}_2\text{O}_5 + 6\text{NaHCO}_3 = 2\text{Na}_3\text{SbO}_4 + 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
(27)	$\text{Sb}_2\text{O}_5 + \text{C} + 2\text{NaHCO}_3 = \text{Sb}_2\text{O}_3 + \text{Na}_2\text{O} + 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
(28)	$\text{Sb}_2\text{O}_4 + 6\text{Na}_2\text{CO}_3 = 4\text{Na}_3\text{SbO}_4 + 5\text{CO}_2(\text{g}) + \text{C}$
(29)	$2\text{Sb}_2\text{O}_4 + 12\text{NaHCO}_3 = 4\text{Na}_3\text{SbO}_4 + 11\text{CO}_2(\text{g}) + \text{C} + 6\text{H}_2\text{O}$
(30)	$2\text{Sb}_2\text{O}_4 + \text{C} + 2\text{NaHCO}_3 = 2\text{Sb}_2\text{O}_3 + \text{Na}_2\text{O} + 3\text{CO}_2(\text{g}) + \text{H}_2\text{O}$
(31)	$2\text{Na}_3\text{SbO}_4 + 2\text{C} = \text{Sb}_2\text{O}_3 + 3\text{Na}_2\text{O} + 2\text{CO}(\text{g})$

3.2. Thermodynamic Study on SiO_2 -Assisted Roasting of AAR

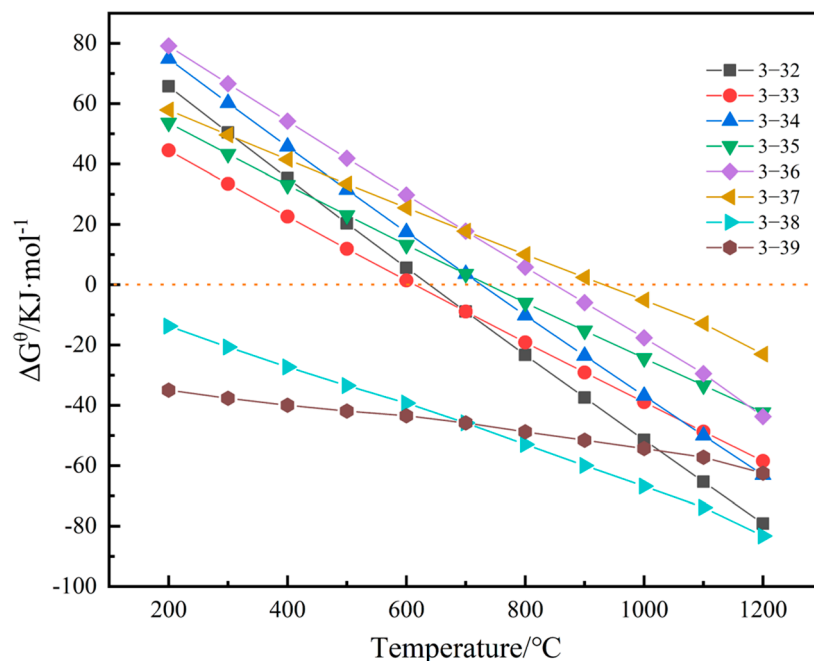
The thermodynamic analysis in Section 3.1 indicates that sodium-bearing components in AAR can stabilize arsenic and antimony by promoting the formation of sodium arsenate and sodium antimonate phases. This sodium-induced stabilization is considered to be the thermodynamic origin of the alkali-locking effect, which inhibits the reductive conversion of As/Sb species into volatile oxides during direct roasting. To weaken this effect, SiO_2 was introduced as an acidic flux and sodium-capturing additive. At elevated temperatures, SiO_2 is expected to react preferentially with sodium-bearing components to form sodium silicate or sodium aluminosilicate phases, thereby reducing the thermodynamic stability of sodium arsenate and sodium antimonate.

To evaluate this hypothesis, the thermodynamic behavior of representative As/Sb-bearing phase– SiO_2 –C systems was calculated. The reactions considered in this section are listed in Table 8. It should be noted that $\text{Ca}_3(\text{AsO}_4)_2$, $\text{Mg}_3(\text{AsO}_4)_2$, Na_3AsO_4 , and Na_3SbO_4 were selected as representative thermodynamic model phases, rather than as crystalline phases directly confirmed by XRD in raw AAR. This treatment is consistent with the chemical phase analysis and the sodium-rich nature of AAR, while avoiding overinterpretation of the XRD results.

The calculated ΔG^θ –temperature relationships are shown in Figure 4. Compared with the direct carbothermal reduction of sodium arsenate and sodium antimonate, the introduction of SiO_2 markedly improves the thermodynamic feasibility of converting these stable sodium-containing phases into volatile oxides. At the selected theoretical roasting temperature of 900 °C, the reactions involving SiO_2 generally show negative or more favorable ΔG^θ values, indicating that the conversion of representative arsenate and antimonate species into $\text{As}_2\text{O}_3(\text{g})/\text{Sb}_2\text{O}_3(\text{g})$ is thermodynamically promoted when sodium is simultaneously incorporated into silicate phases.

Table 8. SiO₂-assisted carbothermal reactions of representative As/Sb-bearing phases.

Number	Reaction
(32)	$\text{Ca}_3(\text{AsO}_4)_2 + 3\text{SiO}_2 + 2\text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{CaSiO}_3 + 2\text{CO}(\text{g})$
(33)	$\text{Ca}_3(\text{AsO}_4)_2 + 3\text{SiO}_2 + \text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{CaSiO}_3 + \text{CO}_2(\text{g})$
(34)	$\text{Mg}_3(\text{AsO}_4)_2 + 3\text{SiO}_2 + 2\text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{MgSiO}_3 + 2\text{CO}(\text{g})$
(35)	$\text{Mg}_3(\text{AsO}_4)_2 + 3\text{SiO}_2 + \text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{MgSiO}_3 + \text{CO}_2(\text{g})$
(36)	$2\text{Na}_3\text{AsO}_4 + 3\text{SiO}_2 + 2\text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{Na}_2\text{SiO}_3 + 2\text{CO}(\text{g})$
(37)	$2\text{Na}_3\text{AsO}_4 + 3\text{SiO}_2 + \text{C} = \text{As}_2\text{O}_3(\text{g}) + 3\text{Na}_2\text{SiO}_3 + \text{CO}_2(\text{g})$
(38)	$2\text{Na}_3\text{SbO}_4 + 3\text{SiO}_2 + 2\text{C} = \text{Sb}_2\text{O}_3(\text{g}) + 3\text{Na}_2\text{SiO}_3 + 2\text{CO}(\text{g})$
(39)	$2\text{Na}_3\text{SbO}_4 + 3\text{SiO}_2 + \text{C} = \text{Sb}_2\text{O}_3(\text{g}) + 3\text{Na}_2\text{SiO}_3 + \text{CO}_2(\text{g})$

**Figure 4.** ΔG^θ changes in SiO₂-assisted carbothermal reactions: conversion of representative arsenates and sodium antimonate into volatile As₂O₃/Sb₂O₃ with simultaneous formation of silicate phases.

The promoting effect of SiO₂ can be attributed to its strong affinity for sodium-bearing components. In the SiO₂–C roasting system, sodium originally associated with arsenate or antimonate can be redistributed into stable silicate phases such as Na₂SiO₃. This process weakens the sodium-induced immobilization of As and Sb and shifts the reaction pathway toward the formation of volatile oxides. Therefore, SiO₂ does not merely act as an inert additive; instead, it participates in the reconstruction of the sodium-containing phase assemblage and provides a thermodynamic driving force for breaking the alkali-locking effect.

Among the calculated reactions, the Na₃SbO₄–SiO₂–C reactions exhibit more negative ΔG^θ values than the corresponding Na₃AsO₄–SiO₂–C reactions under the same temperature range, suggesting that the SiO₂-assisted conversion of sodium antimonate into volatile Sb₂O₃ is thermodynamically more favorable than the conversion of sodium arsenate into As₂O₃. This result is consistent with subsequent roasting experiments, in which Sb volatilization is generally easier to achieve than As volatilization under direct roasting conditions, whereas SiO₂ addition significantly improves the volatilization of arsenic.

It is also worth noting that, according to the thermodynamic comparison between sodium-salt stabilization reactions and SiO₂-assisted displacement reactions, the transformation of representative Ca/Mg arsenates and Sb oxides in the sodium-rich AAR system may proceed through a two-step pathway. First, As- and Sb-bearing species tend to be stabilized as Na₃AsO₄ and Na₃SbO₄ due to the presence of abundant sodium-bearing

components. After SiO_2 addition, sodium is preferentially captured into silicate phases, thereby weakening the stability of sodium arsenate and sodium antimonate and promoting the generation and release of $\text{As}_2\text{O}_3(\text{g})$ and $\text{Sb}_2\text{O}_3(\text{g})$.

3.3. Volatilization Behavior of As and Sb from AAR Under Different Roasting Conditions

Based on the thermodynamic analysis, the direct carbothermal roasting of AAR is limited by sodium-induced stabilization of As- and Sb-bearing species, which may inhibit their conversion into volatile As_2O_3 and Sb_2O_3 . To experimentally verify this behavior and identify suitable roasting conditions, a series of controlled roasting experiments was conducted by varying roasting temperature, carbon dosage, roasting time, and SiO_2 addition. In this section, direct roasting refers to the roasting of AAR with carbon but without externally added SiO_2 , whereas SiO_2 -assisted roasting refers to the roasting of AAR with carbon and added SiO_2 .

For clarity, the fixed conditions for each single-factor experiment are specified as follows. The temperature-optimization experiment was conducted at 700–1100 °C with 30 wt% carbon for 120 min. The carbon-dosage experiment was conducted at 1000 °C for 120 min. The roasting-time experiment was conducted at 1000 °C with 30 wt% carbon. The SiO_2 -dosage experiment was conducted at 900 °C with 30 wt% carbon for 90 min. The volatilization efficiencies and residual grades of As and Sb under these conditions are presented in Figure 5.

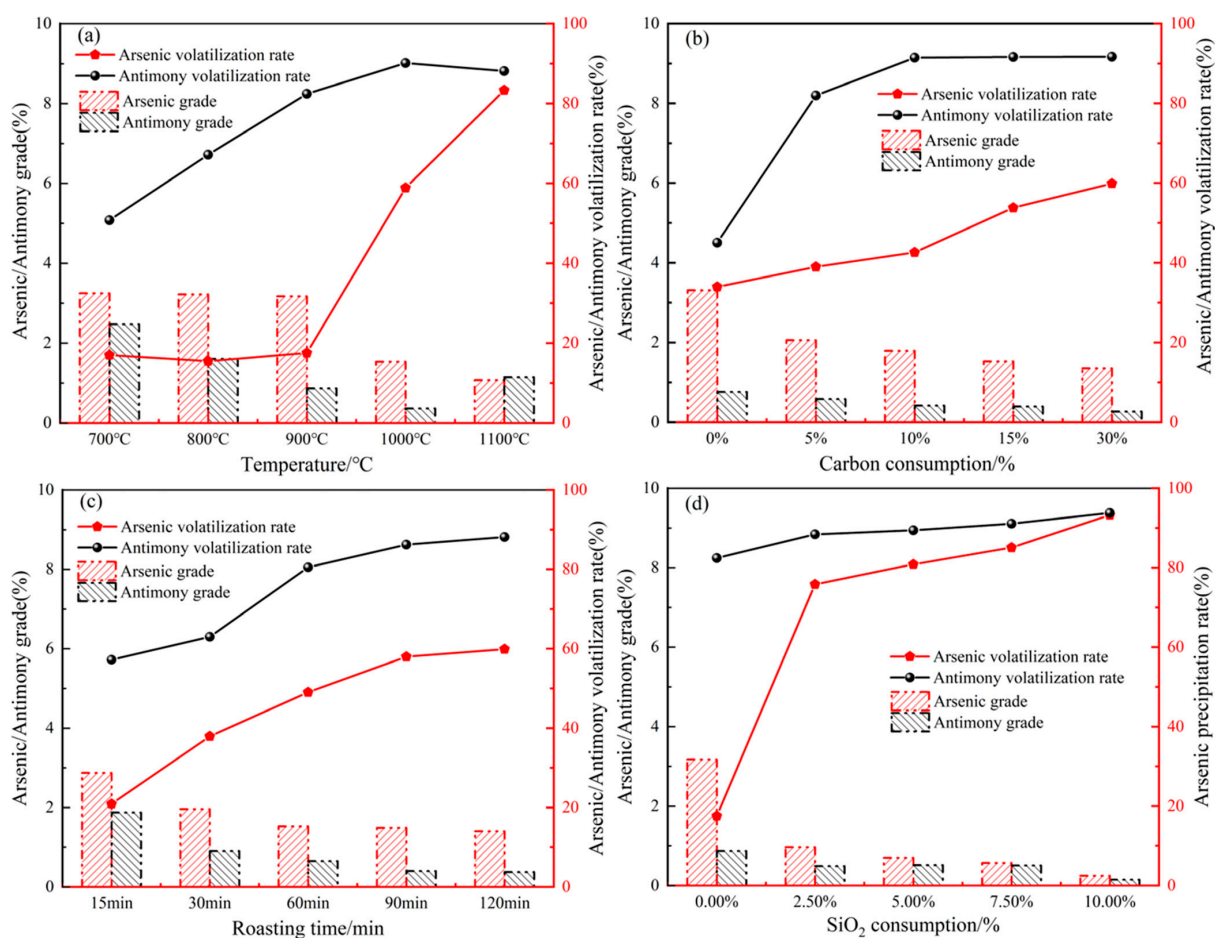


Figure 5. Effects of roasting parameters on As/Sb volatilization from AAR: (a) effect of roasting temperature, 30 wt% carbon, 120 min; (b) effect of carbon dosage, 1000 °C, 120 min; (c) effect of roasting time, 1000 °C, 30 wt% carbon; and (d) effect of SiO_2 dosage, 900 °C, 30 wt% carbon, 90 min.

Figure 5a shows the effect of roasting temperature on As/Sb volatilization during direct roasting. As the temperature increased from 700 to 1100 °C, the volatilization efficiency of Sb 50.78% to 90.15%, indicating that Sb-bearing species were progressively converted into volatile antimony oxides at elevated temperatures. In contrast, As volatilization was much less pronounced at relatively low temperatures and became significant only above 900 °C. When the temperature increased from 900 to 1100 °C, the As volatilization efficiency increased from 17.53% to 83.56%, while the residual As grade in the roasted slag decreased from 3.174% to 1.07%. These results indicate that increasing temperature facilitates the volatilization of both As and Sb, but As volatilization is more strongly restricted than Sb volatilization under direct roasting conditions.

Figure 5b indicates the influence of carbon. Increasing the carbon dosage from 0% to 10% markedly enhanced Sb volatilization from 45.05% to 91.47%, suggesting that a reducing atmosphere promotes the conversion of Sb-bearing species into volatile Sb_2O_3 . Further increasing the carbon addition to 30% improved As volatilization to 59.89%, and the arsenic grade in the slag is 1.349%. However, even under a high carbon content, As volatilization remained incomplete at 1000 °C roasting conditions, indicating that enhancing the reducing atmosphere alone is insufficient to fully overcome the sodium-induced stabilization of arsenic species in AAR.

Figure 5c clearly indicates the influence of roasting time. The volatilization efficiencies of As and Sb increased rapidly during the initial stage of roasting, particularly within the first 60 min, indicating that the conversion and release of volatile species were kinetically promoted at the early stage. As the roasting time was further extended, the volatilization efficiencies gradually approached a plateau. At 90 min, the volatilization rates of As and Sb reached 58.00% and 86.22%, respectively, with the As and Sb contents in the slag were 1.489% and 0.402%. This trend suggests that prolonging the roasting time can improve As/Sb removal to a certain extent, but the subsequent volatilization becomes limited once the readily reducible and releasable species have been consumed.

To weaken the alkali-locking effect, SiO_2 was introduced as an acidic flux and sodium-capturing additive. Thermodynamic analysis shows that SiO_2 can preferentially react with sodium-bearing components to form sodium silicate phases, thereby decreasing the stability of sodium arsenate and sodium antimonate and promoting As/Sb volatilization. Because preliminary observations showed that the briquettes were prone to partial melting or surface sintering at 1000 °C, the SiO_2 -dosage experiment was conducted at a lower temperature of 900 °C, with 30% carbon and a roasting time of 90 min.

As shown in Figure 5d, SiO_2 addition significantly improved As volatilization under these relatively mild roasting conditions. When the SiO_2 dosage increased from 0 to 2.5%, the As volatilization efficiency increased sharply from 17.53% to 75.82%, whereas the Sb volatilization efficiency increased from 82.43% to 88.39%. When the SiO_2 dosage reached 10%, arsenic volatilization further increased to 93.25%, and the residual arsenic content in the slag was reduced to 0.25%. Under the same conditions, Sb volatilization also remained at a high level, reaching 93.80%. These results show that SiO_2 addition can effectively promote the simultaneous volatilization of As and Sb at 900 °C, especially by greatly enhancing As volatilization, which is otherwise strongly inhibited during direct roasting.

The improved volatilization behavior can be attributed to the role of SiO_2 in weakening sodium-induced immobilization. By reacting with sodium-bearing components to form silicate phases, SiO_2 reduces the stability of sodium arsenate and sodium antimonate and facilitates the generation and release of volatile As_2O_3 and Sb_2O_3 . Therefore, the combined action of carbon and SiO_2 does not merely enhance the reducing atmosphere but also reconstructs the sodium-bearing phase assemblage, thereby breaking the alkali-locking effect and enabling efficient As/Sb removal from AAR.

3.4. Phase Evolution of Roasted AAR Under Different Roasting Conditions

During roasting, the phase assemblage of AAR was significantly affected by roasting temperature, carbon dosage, roasting time, and SiO_2 addition, which further influenced the volatilization behavior of arsenic and antimony. To elucidate the phase transformation characteristics of the roasted products, XRD was employed, and the results are presented in Figure 6. It should be noted that XRD mainly identifies crystalline phases with sufficient content and crystallinity. Therefore, As- and Sb-bearing species with low contents, poor crystallinity, amorphous occurrence, or severe peak overlap with Na–Al–Si-bearing phases may not be clearly detected in the XRD patterns.

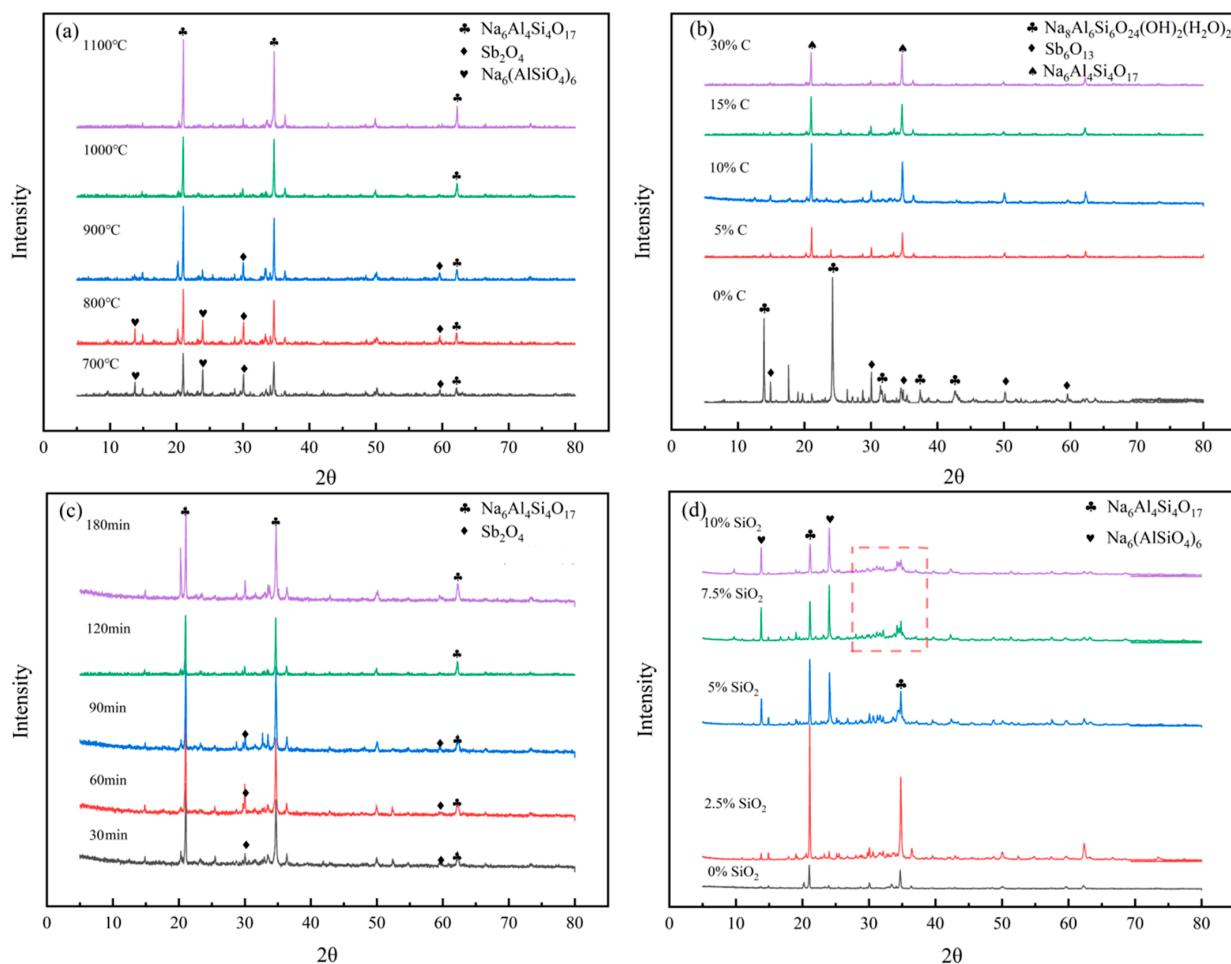


Figure 6. XRD patterns of roasted AAR under different roasting conditions: (a) effect of roasting temperature, 30 wt% carbon, 120 min; (b) effect of carbon dosage, 1000 °C, 120 min; (c) effect of roasting time, 1000 °C, 30 wt% carbon; and (d) effect of SiO_2 dosage, 900 °C, 30 wt% carbon, 90 min.

Figure 6a depicts the phase evolution of roasted AAR at different roasting temperatures. With increasing roasting temperature, the diffraction peaks assigned to Sb_6O_{13} gradually weakened and disappeared above 900 °C. This phenomenon can be attributed to the reduction of high-valence Sb oxides and their subsequent transformation into volatile Sb_2O_3 , which is consistent with the increase in Sb volatilization shown in Figure 5a. In addition, part of the residual Sb may have been incorporated into amorphous or poorly crystalline Na–Al–Si-bearing phases, making it difficult to identify distinct Sb-bearing crystalline phases by XRD. At 1100 °C, the dominant crystalline phase in the roasting slag was assigned to a Na–Al–Si-bearing phase, indicating that high-temperature roasting promoted

the reconstruction of the sodium aluminosilicate matrix. The exact formula of this phase should be kept consistent with the rechecked PDF card throughout the manuscript.

The effect of carbon dosage on phase transformation is shown in Figure 6b. The sample labeled as 0% carbon represents AAR roasted under the same temperature and time conditions without carbon addition, rather than the raw AAR sample. Therefore, its XRD pattern is not expected to be identical to that of the raw AAR. With increasing carbon dosage, the diffraction peaks of Sb_6O_{13} -related phases became progressively weaker, suggesting that a stronger reducing atmosphere promoted the conversion of high-valence antimony oxides into volatile Sb_2O_3 . Meanwhile, the appearance and strengthening of Na–Al–Si-bearing crystalline phases after carbon addition indicate that the local redox environment and phase assemblage of the roasted slag were modified during carbothermal roasting.

Figure 6c shows the XRD patterns of roasted products obtained at different roasting times. As the roasting time increased, the diffraction peaks related to Sb_6O_{13} gradually weakened, which is consistent with the progressive volatilization of Sb observed in Figure 5c. However, the absence of distinct crystalline As-bearing phases in the roasted slag does not necessarily indicate complete arsenic removal. Combined with the chemical analysis results, residual As may exist as amorphous, poorly crystalline, or matrix-incorporated species, especially within the reconstructed sodium aluminosilicate phases. This observation further supports that the high-alkali matrix can retain part of the As/Sb species during direct roasting, which is consistent with the proposed alkali-locking effect.

Figure 6d further illustrates the phase evolution of roasted slag with different SiO_2 additions. The sample labeled as 0% SiO_2 refers to the roasted AAR sample prepared with carbon under the same SiO_2 -dosage experimental conditions but without added SiO_2 , rather than the raw AAR sample. After SiO_2 addition, no distinct crystalline As- or Sb-bearing phases were detected in the XRD patterns. This result, together with the high As/Sb volatilization efficiencies shown in Figure 5d, indicates that SiO_2 addition effectively promoted the release of As and Sb from the roasted matrix. Meanwhile, as the SiO_2 dosage increased, the diffraction features of Na–Al–Si-bearing phases changed markedly, suggesting that SiO_2 participated in the reconstruction of the sodium aluminosilicate framework.

At higher SiO_2 dosages, a broad diffuse hump appeared at approximately $25\text{--}35^\circ$, indicating the formation of partially amorphous or glassy silicate phases. This structural evolution implies that SiO_2 can capture sodium-bearing components and promote the redistribution of Na into silicate phases, thereby weakening the stabilization of As/Sb by sodium salts. Consequently, the phase transformation results support the thermodynamic conclusion that SiO_2 breaks the alkali-locking effect by reconstructing the Na-bearing phase assemblage and facilitating the volatilization of As_2O_3 and Sb_2O_3 . However, the XRD results should be interpreted together with chemical analysis and SEM-EDS characterization because XRD alone cannot fully determine the occurrence state of trace or amorphous As/Sb species.

3.5. Microstructural Evolution of Roasted AAR During SiO_2 -Assisted Roasting

The phase evolution discussed above indicates that SiO_2 addition can reconstruct the Na–Al–Si-bearing phase assemblage of roasted AAR. To further clarify how this phase reconstruction affects the migration and volatilization of arsenic and antimony species, SEM-EDS analysis was performed to compare the microstructures of directly roasted AAR and SiO_2 -assisted roasted AAR. The samples were prepared under the same roasting conditions of 900°C , 30 wt% carbon, and 90 min. The directly roasted sample contained no externally added SiO_2 , whereas the SiO_2 -assisted sample contained 2.5% SiO_2 . The corresponding SEM images and EDS spectra are shown in Figure 7.

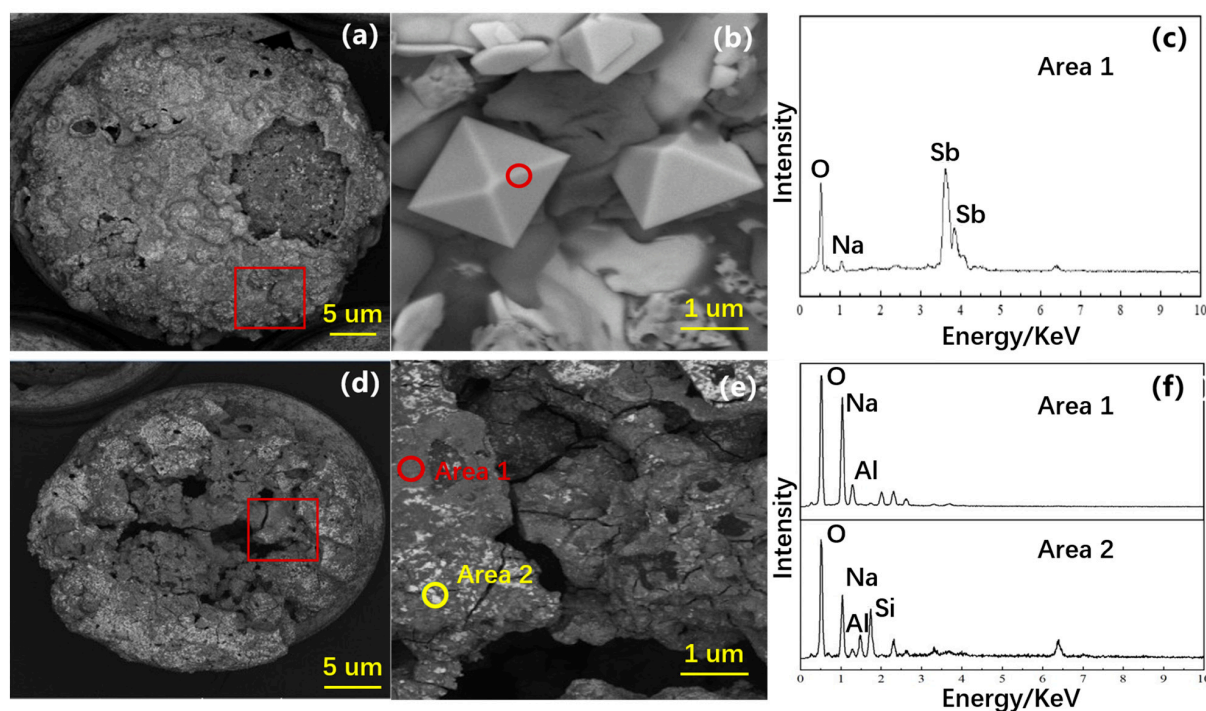


Figure 7. SEM images and EDS spectra of roasted AAR samples: (a–c) directly roasted AAR without SiO_2 ; (d–f) SiO_2 -assisted roasted AAR with 2.5 wt% SiO_2 . Roasting conditions: 900 °C, 30 wt% carbon, and 90 min. Rectangles indicate the enlarged regions, and circles indicate the EDS analysis positions. Magnifications and scale bars should be provided in each SEM image.

As shown in Figure 7a,b, the directly roasted AAR exhibited a dense and partially sintered surface morphology, accompanied by local glassy-phase encapsulation. The enlarged SEM image in Figure 7b corresponds to the region marked by the rectangle in Figure 7a. This compact microstructure would increase the diffusion resistance for gaseous As_2O_3 and Sb_2O_3 , thereby restricting their outward migration during roasting. In addition, cubic or blocky crystals were observed on the surface of the directly roasted slag. The EDS spectrum collected from the circular position in Figure 7b is shown in Figure 7c, which indicates local enrichment of Sb-bearing species. This suggests that some of the Sb-bearing components may have been retained on or within the compact slag matrix, probably due to sintering, glassy-phase encapsulation, and insufficient gas-release channels.

In contrast, the SiO_2 -assisted roasted sample showed a markedly different microstructure. As shown in Figure 7d,e, SiO_2 addition promoted the formation of cracks, pores, and a looser slag texture, rather than the dense and compact structure observed in the directly roasted sample. The enlarged region in Figure 7e corresponds to the rectangle marked in Figure 7d, and the EDS spectra in Figure 7f were collected from the marked circular positions. Compared with the directly roasted sample, the SiO_2 -assisted roasted slag exhibited a more open framework, which could provide effective pathways for the diffusion and escape of volatile As_2O_3 and Sb_2O_3 [27]. This microstructural feature is consistent with the enhanced As/Sb volatilization observed in the SiO_2 -dosage experiment.

EDS results further support the role of SiO_2 in regulating the slag structure. The SiO_2 -assisted roasted matrix was mainly enriched in O, Na, Al, and Si, indicating the formation or reconstruction of sodium aluminosilicate/silicate phases. In contrast, the signals of As and Sb were weak or not evident at the selected EDS positions, suggesting that most As/Sb species had been volatilized or were present at levels below the local detection capability of EDS. Because EDS is a local and semi-quantitative technique, these

results should be interpreted together with the chemical analysis and XRD results rather than as direct evidence of the complete absence of residual As/Sb.

3.6. Synergistic Roasting of Antimony Concentrate and AAR

The results above demonstrate that SiO_2 can weaken sodium-induced immobilization and promote As/Sb volatilization from AAR by facilitating silicate-phase formation. From the perspective of metallurgical solid-waste utilization, externally added SiO_2 may be partly replaced by Si-bearing gangue naturally present in flotation antimony concentrate. Therefore, co-roasting experiments were conducted to preliminarily evaluate whether flotation antimony concentrate could serve as an in situ silica source for regulating the alkali-rich AAR roasting system.

In this section, co-roasting refers to the simultaneous roasting of AAR and flotation antimony concentrate with carbon. The objective was not to establish a complete industrial process, but to assess the feasibility of integrating AAR detoxification with antimony concentrate roasting. During co-roasting, Si-bearing gangue in the concentrate may react with sodium-bearing components in AAR to form silicate phases, thereby weakening the alkali-locking effect and promoting the release of volatile As_2O_3 and Sb_2O_3 . Meanwhile, the AAR-to-concentrate mass ratio may affect slag viscosity, local sintering, pore structure, and gas-diffusion pathways.

As shown in Figure 8, the AAR-to-concentrate mass ratio had a clear influence on As/Sb volatilization at 800 °C and 900 °C. At 800 °C, As volatilization remained higher than 95% for all investigated ratios, suggesting that co-roasting with flotation antimony concentrate favored As release under relatively mild conditions. Sb volatilization was more sensitive to the feed ratio. At an AAR-to-concentrate ratio of 3:1, Sb volatilization reached the highest level among the tested ratios, probably because the roasted slag maintained a relatively porous structure that facilitated the diffusion of volatile Sb_2O_3 . However, further increasing the concentrate proportion decreased Sb volatilization, which may be associated with changes in slag viscosity, heat transfer, and incomplete release of Sb-bearing volatile species.

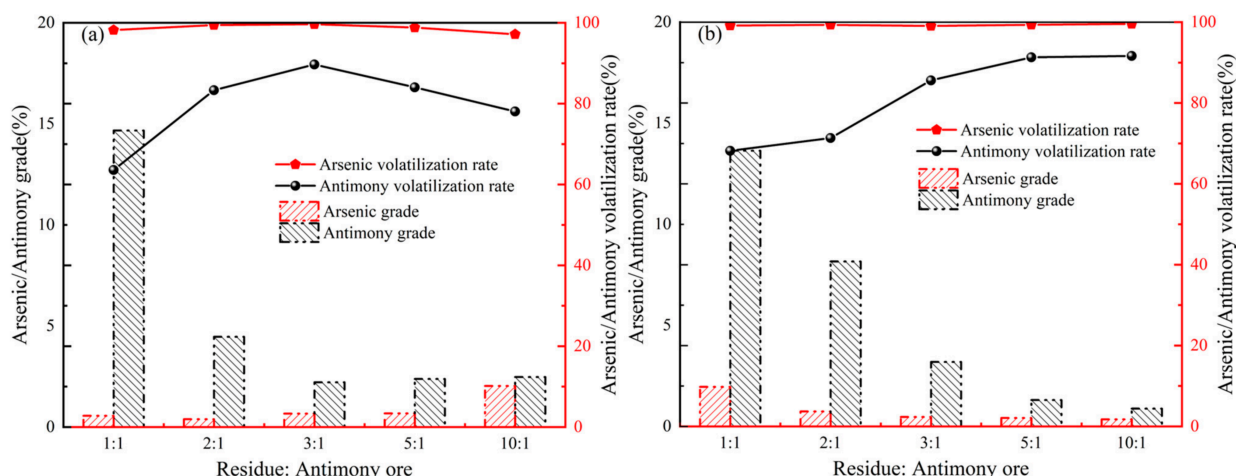


Figure 8. Effect of AAR-to-flotation antimony concentrate mass ratio on As/Sb volatilization during co-roasting at (a) 800 °C and (b) 900 °C.

At 900 °C, the higher thermal input promoted the reaction, but local glassification and surface sintering became more pronounced at certain ratios. Compact sintered layers may increase the diffusion resistance of As_2O_3 and Sb_2O_3 , thereby hindering their outward migration. When the AAR-to-concentrate ratio reached 10:1, Sb volatilization increased to

91.66%, indicating that an appropriate feed ratio may mitigate excessive sintering while maintaining gas-release channels [28].

4. Conclusions

In this study, the alkali-locking behavior of arsenic-alkali leaching residue (AAR) during carbothermal roasting and the regulatory role of SiO₂ were investigated. The main conclusions are as follows:

- (1) Thermodynamic calculations indicate that sodium-bearing components in AAR tend to react with representative As- and Sb-bearing species to form thermodynamically stable sodium arsenate and sodium antimonate phases, such as Na₃AsO₄ and Na₃SbO₄. These sodium-containing phases increase the stability of As and Sb in the solid matrix and suppress their conversion into volatile As₂O₃ and Sb₂O₃, which provides a thermodynamic explanation for the alkali-locking effect.
- (2) Direct roasting by increasing temperature, carbon dosage, or roasting time only partially promoted As/Sb volatilization. In contrast, SiO₂ addition weakened sodium-induced immobilization by promoting sodium silicate or sodium aluminosilicate formation, thereby enhancing As/Sb release. Under the optimized conditions of 900 °C, 90 min, 30 wt% carbon, and 10 wt% SiO₂, the volatilization efficiencies of As and Sb reached 93.25% and 93.80%, respectively.
- (3) XRD and SEM-EDS results show that SiO₂ promoted Na–Al–Si phase reconstruction and porous slag formation, providing favorable pathways for gaseous As₂O₃/Sb₂O₃ migration. Preliminary co-roasting experiments further suggest that flotation antimony concentrate can serve as an in situ Si-bearing additive for AAR treatment. However, further optimization of the feed ratio, slag-melting behavior, and volatile-product collection is still required before industrial application.

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