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Appendix

1 Experimental procedures

The leaching experiments were conducted using a beaker immersed in a thermostat-regulated water bath. 30 g of arsenic-alkali residue and a certain amount of deionized water (30-120 mL) were added to the beaker and heated with the function of agitation. Hydrogen peroxide was added to the bottom of the beaker using a syringe. After the required reaction time, liquid and solid were separated and a part of the filtrate was taken out to determine As and Sb contents. Using ICP-OES, the leaching efficiency of arsenic and antimony was calculated. The leaching residue and crystallization products were analyzed using XRD, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy-energy dispersive spectrometry (SEM-EDS).

The crystallization products with carbon powder were manually mixed using a mortar and pestle to ensure thorough mixing. The mixture was transferred into a porcelain boat. The boat containing the sample was placed to heating zone of a pipe furnace. A protecting gas (highly pure argon) was introduced into the container at a velocity of 0.1 L/min, and heating for 15 min. The roasting temperature ranged from 500 to 900 °C, and the roasting time ranged from 0.5 to 3.0 h. After roasting, the roasted samples were taken out and cooled to room temperature in air. Afterward, each sample was weighed, ground, and analyzed to determine As content. ICP-OES was used to calculate the removal efficiency of arsenic.

2 Analytical and characterization methods

The phase composition of the solid samples was examined by X-ray powder diffractometry (XRD) augmented with a Cu-K_{α} radiation source (wavelength: 0.15418 nm). The surface morphology and elemental distribution of the solid particles were characterized by SEM-EDS (MLA650, FEI, USA). The accurate element amounts in the solid phase were analyzed using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8000 Leeman, USA). The valence state of the relative elements was analyzed by XPS (ESCALAB Xi+, Thermofischer, USA) using Al-K_{α} X-ray as excitation source. The mass loss of the crystallization product was analyzed using a thermogravimetric analyzer (STA449F5) from Germany NETZSCH with a heating rate of 2 °C/min.

The leaching efficiencies (η) of As and Sb were calculated using the formula, $\eta = [CV/(\alpha M)] \times 100\%$, where *C* represents the concentration of As and Sb in the leaching solution; *V* represents the volume of the leaching solution; α is the content of As and Sb in arsenic-alkali residue; and *m* is the mass of arsenicalkali residue. The removal efficiency (η_0) of As was calculated using the formula, $\eta_0=1-((X_0m_0)/(X_1m_1))\times$ 100%, where m_0 and m_1 are the mass of samples before and after roasting, respectively; X_0 and X_1 are the arsenic content of samples before and after roasting, respectively.

3 Thermodynamic analysis of arsenic-alkali mixed salts carbothermal reduction

The possible reactions in the roasting process are presented as Eqs. (1)–(12). The corresponding dependency of Gibbs free energy ($\Delta_r G^{\Theta}$) on temperature was calculated using HSC chemistry software 6.0 (Outokumpu, Finland) under standard state conditions and shown in Figure S1.

 $2Na_3AsO_4 = As_2O_5 + 3Na_2O \tag{1}$

 $4Na_3AsO_4+5C=5Na_2CO_3+As_4(g)+Na_2O$ (2)

 $4Na_3AsO_4+5C=5CO_2(g)+6Na_2O+As_4(g)$ (3)

 $6Na_3AsO_4+3C=4NaAsO_2+As_2O_3+3Na_2CO_3+4Na_2O_3$

$$2Na_3AsO_4+C=2NaAsO_2+Na_2CO_3+Na_2O$$
 (5)

 (Λ)

 $2Na_3AsO_4 + C = As_2O_3 + Na_2CO_3 + 2Na_2O$ (6)

$$Na_2As_4O_{11} = 2As_2O_5 + Na_2O \tag{7}$$

$$Na_2As_4O_{11}+5C=Na_2CO_3+As_4(g)+4CO_2(g)$$
 (8)

 $Na_2As_4O_{11}+2C=2NaAsO_2+As_2O_3+2CO_2(g)$ (9)

$$Na_2As_4O_{11}+4C=2NaAsO_2+As_2O_3+4CO(g)$$
 (10)

$$4NaAsO_2+3C=As_4(g)+2Na_2O+3CO_2(g)$$
 (11)

$$2As_2O_3+3C=As_4(g)+3CO_2(g)$$
 (12)

Equations (1)–(6) present the possible reactions

during the reduction of Na₃AsO₄, as seen in Figure S1(a). Equation (1) relates to the selfdecomposition reaction of Na₃AsO₄. The $\Delta_r G^{\Theta}$ is far larger than 0 within the temperature range investigated, indicating that Na₃AsO₄ does not decompose. The values of $\Delta_r G^{\Theta}$ in Eqs. (3)–(6) are far larger than 0 within the temperature range investigated, while the value in Eq. (2) becomes negative at approximately 750 °C and keeps decreasing. Therefore, intermediate oxides such as NaAsO₂ or As₂O₃, during the reductive roasting of Na₃AsO₄ are thermodynamically denied, indicating that the only possibility of the gaseous arsenic product is the free element arsenic in the form of As₄. Equations (7)–(10) present the possible reactions during the reduction of Na₂As₄O₁₁, as seen in Figure S1(b). Equation (7) relates to the selfdecomposition reaction of Na₂As₄O₁₁, the $\Delta_r G^{\Theta}$ is far larger than 0 within the temperature range



investigated, indicating that Na2As4O11 will not decompose. The $\Delta_r G^{\Theta}$ of Eqs. (8)–(10) becomes increasingly negative as the temperature rises above 370, 180 and 440 °C, respectively, which indicates that Na₂As₄O₁₁ will be reduced to NaAsO₂, As₂O₃, or As₄ by carbon. The relationship between $\Delta_r G^{\Theta}$ and T in Eqs. (11) and (12) are shown in Figure S1(c). Equation (11) relates to the reduction of NaAsO₂; $\Delta_{\rm r} G^{\Theta}$ is far larger than 0 within the temperature range investigated, indicating that NaAsO₂ cannot be reduced. Equation (12) relates to the reduction of As₂O₃; $\Delta_r G^{\Theta}$ becomes more and more negative as the temperature increases above 120 °C, which indicates a great reaction tendency. According to the analysis of the thermo-dynamics results, it can be concluded that the crystallization product has two reduction paths: Na₂As₄O₁₁ and Na₃AsO₄ are directly reduced to As₄, and Na₂As₄O₁₁ is first reduced to As₂O₃ and then reduced to As₄.



Figure S1 Diagram of Gibbs free energy ($\Delta_r G^{\Theta}$) in function of temperature for reactions occurring during the roasting process: (a) Equations (1)–(6); (b) Equations (7)–(10); (c) Equations (11) and (12)