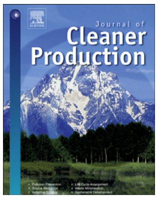
Journal of Cleaner Production xxx (2015) 1–6

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



One-step extraction of antimony from low-grade stibnite in Na_2CO_3–NaCl binary molten salt

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A R T I C L E I N F O

Article history:
Received 8 June 2014
Received in revised form
6 January 2015
Accepted 8 January 2015
Available online xxx

Keywords:
Stibnite
Molten salt smelting
Low-carbon
Cleaning metallurgy

A B S T R A C T

The extraction of antimony from low-grade stibnite in eutectic Na_2CO_3–NaCl molten salt using ZnO as a sulphur-fixed agent was studied. The results of the experiments on the reaction mechanism indicate that the reaction courses of antimony and sulphur were $Sb_2S_3 \rightarrow Sb_2O_3 \rightarrow Sb$ and $Sb_2S_3 \rightarrow ZnS$. Sulphur was fixed in the form of ZnS, while molten salt did not react with other components, serving only as the reaction medium. The influencing factors, including the smelting temperature, reaction time, and dosage of ZnO, salt and carbon, were investigated in detail by single factor experiments. The optimum conditions were determined as follows: temperature 1123 K, time 1 h, $W_{salt}/W_{ore} = 5:1$, $W_{ZnO}/W_{theory} = 1.0$, and $W_{carbon} = 10\% W_{ore}$, where W represents weight. Under those optimum conditions, the average direct recovery ratio of antimony reached 92.88%. It is suggested that an increase in the temperature and the dosage of salt and carbon powder is beneficial for the improved direct recovery rate of antimony.

1. Introduction

Antimony is primarily used for the production of alloys, flame retardants and brake pads (Uexküll et al., 2003). For industrial production, the pyrometallurgical methods involving volatilisation and reduction of sulphide ores were the primary means to extract antimony, which are high temperature (>1473 K) and high energy consumption ($>3.6 \times 10^{10}$ J/t) processes (Habashi, 1997). It is known that antimony and its oxides are easy to volatilise (Cui et al., 2008a,b), and both exhibit significant vapour pressure above 1073 K. In addition, arsenic is often associated with antimony ore due to their similar chemical properties; in addition to being toxic, arsenic is also volatile (Chen et al., 2012; Awe and Sandström, 2010). Thus, smelting at high temperature will result in environmental pollution and hazards. In addition, determining how to extract antimony more efficiently from a declining grade of antimony ore is a challenge.

Hydrometallurgical methods can be used for both simple and complex antimony ore. Normal industrial antimony hydrometallurgical practices consist of a two steps of process of leaching and electrodeposition using agents such as alkaline sulphide and acidic chloride (Anderson, 2012; Awe et al., 2013). The alkaline sulphide system has been used industrially in the former Soviet Union, China, Australia and America (Yang and Wu, 2013; Awe and Sandström, 2013). However, the fatal shortcoming of the hydrometallurgical process is the low current efficiency of Sb electrodeposition.

Alkaline smelting was first proposed by scholars of the former Soviet Union (Smirnov, 1990) and was used for lead sulphide extraction in molten NaOH; this process featured a low smelting temperature and less pollution. Subsequently, Margulis exploited low temperature smelting to recycle lead form lead metallic scrap (Margulis, 2000). Molten salt have excellent thermal stability and solvent properties which have led to their use in materials preparation (Chen et al., 2000), solar power plants (Zhou et al., 2012) and removing paints from the surface of metal (Long et al., 2013). Recently, this process was adapted to the smelting of antimony and bismuth using NaOH and mixed molten salts in the NaOH–Na_2CO_3 system (Yang et al., 2011, 2011; He et al., 2013). However the alkaline system, particularly NaOH, has a strong activity at a high temperature, which makes it easy to react with sulphide and gangue, resulting in difficulties in regeneration. To address the issues, we propose instead, as the reaction medium, Na_2CO_3–NaCl molten salt, which exhibits alkalescence and has a low temperature eutectic composition, to replace the NaOH system as the reaction medium. In addition, the new process also added zinc oxide as a desulphurisation agent, which provides the outstanding

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http://dx.doi.org/10.1016/j.jclepro.2015.01.018
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Please cite this article in press as: Ye, L., et al., One-step extraction of antimony from low-grade stibnite in Na_2CO_3–NaCl binary molten salt, Journal of Cleaner Production (2015), http://dx.doi.org/10.1016/j.jclepro.2015.01.018

advantages of eliminating SO_2 discharge while utilising the larger zinc ash resources (Wei et al., 2013). The present work investigated the effects of the main variables contributing to the yield of antimony and considered the relevant reaction mechanism. The purpose of this work is to examine the feasibility of smelting low-grade stibnite at low temperatures and the stability of the molten salt system. Compared to the conventional two-step process, the proposed clean approach is simplified and can produce crude antimony directly in one-step.

2. Materials and methods

The low-grade stibnite (Sb 37.21%, Fe 13.27%, Cu 0.085%, Pb 0.18%, As 0.034%, S 30.60%, SiO_2 7.14%, Al_2O_3 2.26%, CaO 0.079%) used in this study was obtained from the Hunan Chenzhou Mining Group, PRC. Antimony occurs in the form of 51.85% Sb_2S_3. All other reagents included Sb_2S_3, ZnO and carbon used in mechanism experiment were analytical grade. Na_2CO_3 and NaCl were dried in an oven at 543 K for 24 h. According to the phase diagram shown in Factsage, the melting temperature at the eutectic composition of $n(Na_2CO_3)/[n(Na_2CO_3)+n(NaCl)] = 0.423$ is 908 K (Jun et al., 2007; Iwasawa et al., 2001), where n represents mole. The dried Na_2CO_3 and NaCl were charged in a corundum crucible and were heated to melt completely at 973 K for 10 min, and then the melt was cooled to room temperature naturally. Finally, the cooled solids were ground to a powder via mechanical ball milling, and then the resulting powder was sealed and kept in a dryer.

In the smelting experiments, the mass of raw ore was kept at 100 g, and the amount of mixed salt and carbon added were expressed as multiple and percentage of the ore content. The amount of ZnO required to covert the sulphur released from stibnite in the form of ZnS was calculated based on stoichiometry ($Sb_2S_3 + 3ZnO = 2Sb + 3ZnS$). After mixing to improve homogeneity, the mixture was charged in an alumina crucible. When the furnace reached the required temperature, the crucible was located in the hot zone. After the predetermined reaction time, the crucible was quickly taken out and quenched to room temperature. Sb metal could be easily separated at the bottom of quenched crucible, and the content of Sb in crude antimony was determined by titrimetric analysis.

X-ray diffraction (XRD) studies were performed using a Rigaku D/max 2550VB + 18 kW powder diffractometer. The XRD patterns were recorded at a scan rate of $5^\circ\ min^{-1}$ and a sampling interval of 0.01°. The samples used for XRD detection were from 5 g mixtures calcined at different time and temperature. The TG-DSC analysis was performed using a thermo-gravimetric analyser of Universal V4.0C TA instrument with SDT Q600 V8.0 Build 95 in a nitrogen flow of 100 ml/min and at a heating rate of 10 K/min, and about 15 mg of the mixtures were proceeded every times. The direct recovery rate of Sb was calculated using the following equation

$$Direct\ recovery\ rate = \frac{W_2 \cdot x_2\%}{W_1 \cdot x_1\%} \times 100\% \qquad (1)$$

where W_1 is the initial mass of stibnite, g; W_2 is the mass of crude antimony, g; and x_1 and x_2 are the Sb contents in raw ore and crude antimony, respectively.

3. Results and discussion

3.1. Mechanism of the reaction

3.1.1. Thermodynamic calculation

One-step smelting of stibnite was conducted in molten Na_2CO_3—NaCl salt with the addition of a reductant and a sulphur fixing agent. The principal products were antimony and ZnS. The main chemical reactions can be described as follows:

$$Sb_2S_3 + 3ZnO + 3C = 2Sb + 3ZnS + 3CO(g) \qquad (2)$$

$$Sb_2S_3 + 3ZnO + 3CO(g) = 2Sb + 3ZnS + 3CO_2(g) \qquad (3)$$

$$Sb_2S_3 + 3Na_2CO_3 + 6C = 2Sb + 3Na_2S + 9CO(g) \qquad (4)$$

$$Sb_2S_3 + 3Na_2CO_3 + 3CO(g) = 2Sb + 3Na_2S + 6CO_2(g) \qquad (5)$$

$$Na_2S + ZnO + CO_2(g) = Na_2CO_3 + ZnS \qquad (6)$$

Equation (7) represents the Gibbs free energy function. By calculating $\Delta G^{\theta}{}_T$ at different temperatures, all of the above reaction $\Delta G^{\theta}{}_T$ values can be obtained. If $\Delta G^{\theta}{}_T < 0$, then the relevant reaction can be spontaneously completed. Conversely, if $\Delta G^{\theta}{}_T > 0$, then the reaction cannot occur. Equation (7) is expressed as follows:

$$\Delta G^{\theta}{}_T = \left[\Delta H^{\theta}_{298} + \int_{298}^{T} \Delta C_p dT\right] - T\left[\Delta S^{\theta}_{298} + \int_{298}^{T} \frac{\Delta C_p}{T} dT\right] \qquad (7)$$

where ΔH^{θ}_T and ΔH^{θ}_{298} are the standard enthalpy change at T(K) and 298 K, respectively; ΔS^{θ}_T and ΔS^{θ}_{298} are the standard entropy change at T(K) and 298 K, respectively; Δc_p is the heat capacity change; T is the temperature in Kelvin. All of the data are from the thermodynamic handbook (Brain et al., 1972). Fig. 1 shows the relationships between $\Delta G^{\theta}{}_T$ and the temperature of reactions (2)–(6).

As shown in Fig. 1, Eqs. (2), (3) and (6) can be spontaneously completed when the reaction temperature is maintained between 800 K and 1300 K because all the values of $\Delta G^{\theta}{}_T < 0$. Thus, Sb_2S_3 can easily react with ZnO and carbon to yield Sb. In addition, Na_2S can be regenerated into Na_2CO_3 by reaction (6) spontaneously. Meanwhile, the $\Delta G^{\theta}{}_T$ values of reactions (4) and (5) are greater than zero below 1000 K, so both of these reactions are difficult to complete. Therefore, the overall reaction to extract Sb from Sb_2S_3contained in stibnite can be denoted as reactions (2) and (3).

3.1.2. Reaction of Sb_2S_3—ZnO system

The results of TG/DTA analysis of Sb_2S_3 and ZnO at mole rate of 1:3 are shown in Fig. 2. The DTA curve shows an endothermic peak at 518.97 K, which is ascribed to the phase transition of antimony

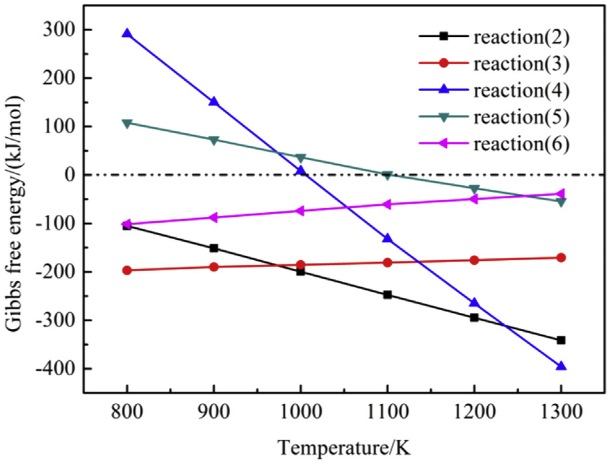

Fig. 1. Relationship between $\Delta G^{\theta}{}_T$ and T of the reactions (2)–(6).

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