Separation and Recovery of Antimony from High Arsenic-bearing Flue Dusts through Selective Oxidation Using MnO_2

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The recovery of antimony from high arsenic-bearing flue dusts was carried out by a selective oxidation roasting process using MnO_2 , in which the arsenic was removed through a volatilization and antimony was oxidized to Sb_2O_4 staying in the roasted products. In a certain range, the MnO_2 additive has an active effective on the arsenic volatilization for the reason that structures of some complicated As-Sb phases were destroyed after the Sb_2O_3 being oxidized to Sb_2O_4 and this part of arsenic continued to volatile. About 90.06% arsenic and only about 6.89% antimony went into smoke under the condition of roasting temperature of 723.0 K, MnO_2 amount of 20.5%, and roasting time of 90 min. The MnO_2 selective oxidation provided a good separation of arsenic from high arsenic-bearing flue dusts. The left antimony existing in the roasted products can be reclaimed through a process of reduction roasting and dust collection.

KEY WORDS: high arsenic-bearing flue dusts; separation of arsenic and antimony; selective oxidation; MnO_2 ; waste utilization.

1. Introduction

Flue dusts are generated in many pyrometallurgical processes of metal extraction, which represent not only secondary resources of many valuable metals but also potential risks of environmental contamination.^{1–3)} Among them, an arsenic-bearing flue dust is one of the most important secondary resources, which contains a large amount of valuable metals, such as lead, antimony and indium.^{4–7)} Composition of arsenic-bearing dusts varies mainly according to the type of reactor and the raw material used. During the smelting and converting process, around 60% of As and 30–40% of Sb from the raw material are transferred into the flue dust.⁸⁾ These dusts can not be directly recycled to the smelters or converters, because of the increase of required energy for smelting or converting process.^{9,10)} It is necessary to treat the flue dust separately to recover valuable metals.

Based on distinctions of volatility and water-solubility of arsenic and antimony compounds, there are many studies on treating arsenic-bearing materials by pyrometallurgy or hydrometallurgy process.^{4–7,11–14)} Pyrometallurgy processes containing methods of oxidation roasting, reduction roasting and chlorination roasting, usually lead to secondary arsenic pollution and high energy consumption.^{15,16)} Most research focused on treatment of arsenic-bearing materials by hydrometallurgical methods. The dusts were firstly leached with water, different acid solutions,¹⁷⁾ NaOH solution, mixed

solution of NaHS/NaOH^{18,19)} or sodium-sulfide solution,²⁰⁾ and then hydrocyclone classification was executed on the obtained residues. Generally, the solidification process of arsenic through the formation of a stable and insoluble ferric arsenate compound in the leaching is the conventional thought for the separation of As from other elements, and it is more economical.¹⁵⁾ Obviously, the hydrometallurgy processes have drawbacks such as complex process flows, high consumption of chemical reagents and high cost in operation.

In this paper, an effective and environmental friendly method separating arsenic through a method of selective oxidation using MnO_2 is proposed. Further, the effects of different process parameters on the separation of arsenic were initially investigated in order to determinate the optimal conditions for increasing separation rate.

2. Experimental

2.1. Materials and Methods

The high arsenic-bearing flue dust used in this study was provided by a plant for treating tin anode slime using a pyrometallurgy process locating in Yunnan province, China. The dust was crushed, ground, and screened using a 200 mesh sieve. The chemical composition (mass%) of it is depicted in **Table 1**. Table 1 shows that the major elements are arsenic and antimony, and the antimony content is of 28.72%, being well worth to be reclaimed. “Others” in Table 1 is mainly composed of “O” (existing as As_2O_3 and Sb_2O_3 etc.). **Figure 1** shows that the main phases

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are As_2O_3 , Sb_2O_3 , As_4O_6 and $(\text{Sb,As})_2\text{O}_3$, and **Fig. 2** and **Table 2** also show that the dust mainly contains phases of arsenic and antimony. Specifically, most arsenic-containing phases occur independently in the form of As_2O_3 , and most antimony is embedded in arsenic-containing complicated phases. Deduced from Table 2, the main compositions of altered red sulfur arsenic antimony sodium ore, altered allemontite and varieties white arsenic in Fig. 2 are As_2O_3 and Sb_2O_3 , and they mainly exist in the phase of $(\text{Sb,As})_2\text{O}_3$ as shown in Fig. 1. The chemicals used in all experiments were analytical reagent grade, manufactured by Tianjin Fengchun Chemical Reagent Co., Ltd.

Table 1. Chemical composition of the high arsenic-bearing flue dust (% mass).

Elements	As	Bi	Cu	Fe	Pb	Sb	Others
Contents	36.28	0.68	0.24	1.13	2.06	28.72	30.89

Fig. 1. XRD pattern of the high arsenic-bearing flue dust.

The roasting experiments were conducted in an electric furnace, as shown in **Fig. 3**. Where, the furnace plug made of ceramics was used to make the temperature in constant temperature area relatively stable, and the furnace cover fixed with a flange was used to sealing up the furnace. A Pt/Pt–Rh thermocouple in an alumina sheath was introduced into the furnace to monitor the temperature. The furnace was heated to a fixed temperature under a continuous flow of nitrogen $5.00 \times 10^{-6} \text{ m}^3/\text{s}$. 5 g of high arsenic-bearing flue dust samples were used in every experiment, and addition amount of MnO_2 reagent was calculated based on the quality ratio of it to the high arsenic-bearing flue dust used. After mixed carefully, mixtures of high arsenic-bearing flue dusts and MnO_2 were roasted in a tube furnace in the range of 573–823.0 K under N_2 atmosphere. The off-gas from the reaction tube was continuously passed through a water-cooled condenser, which collected the volatile matter, and then was directed to solutions of 1 M NaOH to remove harmful components (Fig. 3). After a proper time held, the reactor was cooling down in the furnace tube under N_2 atmosphere to room temperature, and then pulled out for analysis.

2.2. Instrumentation

The thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC) of the samples were performed on a thermal analyzer (NETZSCH, STA 449 F3). The typical measurements were performed at a heating rate of 0.083 K/s under N_2 atmosphere. The chemical composition and mineralogy of the samples were characterized by chemical analysis, scanning electron microscope (SEM), and electron probe microanalysis (EPMA). Phase compositions of all samples were detected by X-ray diffraction (The emission target of XRD was Cu-K α , the step width was 0.01° , the

Fig. 2. Mineral phase's distribution obtained by EPMA. (Online version in color.)

Table 2. EPMA point analysis of samples shown in Fig. 2 (% mass).

Point	Na_2O	As_2O_3	SiO_2	SO_3	FeO	CuO	Sb_2O_3	Cr_2O_3	PbO
1	0.038	34.883	0.290	0.000	0.000	0.838	34.802	0.070	29.079
2	0.000	99.073	0.249	0.130	0.004	0.077	0.311	0.149	0.006
3	0.060	56.766	0.104	0.176	1.948	0.000	40.422	0.215	0.309
4	0.188	49.540	0.364	0.230	0.176	0.204	44.931	0.085	4.283
5	0.056	50.253	0.013	0.165	3.279	0.032	44.573	0.071	0.658
6	0.019	45.536	0.160	0.014	0.198	0.523	50.045	0.182	3.324
7	0.186	40.098	0.360	0.136	0.080	0.068	54.858	0.302	3.912

Fig. 3. Experimental apparatus. 1. Flowmeter; 2. Pressure valve; 3. Furnace cover; 4. Furnace plug; 5. Silicon carbide bar; 6. Corundum boat; 7. thermocouple; 8. Electric furnace; 9. Control cabinet; 10. Water-cooled condenser; 11. Alkali vessel. (Online version in color.)

Fig. 4. TG-DSC curves for high arsenic-bearing flue dusts, MnO_2 , and mixture of MnO_2 and high arsenic-bearing flue dusts (MnO_2 amount of 15.00%). (Online version in color.)

scanning rate was $8^\circ/\text{min}$ and 2θ was $10\text{--}90^\circ$, D/max-3B, Rigaku Corporation of Japan). The thermodynamic data of species were given by FactSage thermochemical software. Mathematical expressions of the arsenic and antimony volatilization rates were separately defined as:

$$R = \left(1 - \frac{M_T \times W_0}{M_C \times W_C} \right) \times 100\% \quad \text{..... (1)}$$

$$R' = \left(1 - \frac{M_T \times W_0'}{M_C \times W_C'} \right) \times 100\% \quad \text{..... (2)}$$

Where, M_C stands for the mass of the high arsenic-bearing flue dust used, W_C and W_C' for the arsenic and antimony contents in the origin high arsenic-bearing flue dust, M_T for total mass of the roasted residue, W_0 and W_0' for the arsenic and antimony contents in the roasted residue. FactSage

Fig. 5. XRD pattern of the roasted product of MnO_2 at roasting temperature of 723 K.

was used to calculate the mineral phase composition during roasting of mixtures of high arsenic-bearing flue dusts and MnO_2 , and calculation parameters were set at 1 atm pressure of shielding gas.

3. Thermo-chemical Behavior of the Mixture of MnO_2 and High Arsenic-bearing Flue Dusts

Figure 4 shows TG-DSC curves of high arsenic-bearing flue dusts, MnO_2 , and mixture of them (MnO_2 addition amount of 15.00%) under N_2 atmosphere. Two endothermic peaks at 552.0 K (A and B points) are detected in the DSC measurements for high arsenic-bearing flue dusts and the mixture, which are related to the melting of As_2O_3 in the raw material. At 712.2–805.7 K, two noticeable endothermic peaks (P and Q points) are detected in the DSC measurement for MnO_2 , and each of them corresponds to a weight-loss stage. They are attributed to the decomposition of MnO_2 , generating Mn_2O_3 (**Fig. 5**) and O_2 . There is another endothermic peak (R point) as a shoulder appearing near 836.6 K, which is also related to the MnO_2 decomposition. Different from that for MnO_2 , the DSC curve for the mixture shows an obvious exothermic peak (C point) at 713.4–790.5 K. It may be related to the oxidation of high arsenic-bearing flue dusts (especially for phases of As and Sb) by MnO_2 or O_2 generated from MnO_2 decomposition. In addition, the obvious difference of decrease in weight between high arsenic-bearing flue dusts and the mixture indicates that MnO_2 can oxidize the flue dust distinctly with

temperature being higher than 713.4 K.²¹⁾

4. Results and Discussion

4.1. Effect of Roasting Temperature

In order to investigate the effect of roasting temperature on the separation efficiency of arsenic and antimony, experiments were performed at 573.0–823.0 K while keeping other parameters constant as: roasting time 120 min, N₂ flow rate 5.00*10⁻⁶ m³/s, and MnO₂ addition amount of 12.5%.

Figure 6 shows arsenic and antimony volatilization rates both increase with roasting temperature with or without MnO₂ addition. Temperature has an effect mainly on vapor pressures of volatile species shown as Fig. 7 and they increase with temperature, causing increase of volatilization rates of arsenic and antimony in Fig. 6. The As₂O₃ and Sb₂O₃ could be both oxidized to high valence oxides by MnO₂ (Eqs. (3)–(4)) during the roasting process, and volatilization rates of them should be decreased with MnO₂ addition from the point of view of thermodynamics. The standard Gibbs free energy changes of Eqs. (3)–(4) at different roasting temperatures are shown in Table 3. But for As, it is different seen from Fig. 6. Though the vapor pressure of As₂O₅ is low and its volatilization is hard to be carried out at the roasting temperature, evaporation of

As₂O₃ appears earlier than it being oxidized to As₂O₅ for its strong volatility. Meanwhile, structures of some As-Sb complicated phases (Fig. 2 and Table 2) might be destroyed after the Sb₂O₃ being oxidized to Sb₂O₄ (Fig. 8), causing this arsenic continues to volatile and the arsenic volatilization rate increases. For the purpose of increasing separation efficiency of arsenic and antimony, the roasting temperature is determined as 723.0 K.

4.2. Effect of Amount of MnO₂ Addition

The MnO₂ addition amount is one of the most important parameters in the selective oxidation process. Antimony and arsenic volatilization rates were examined by varying the MnO₂ addition amount from 12.5% to 30.5%.

Most arsenic evaporates during the roasting process at 723.0 K seen from Fig. 6, and the binary phase diagram of MnO₂–Sb₂O₃ was used to calculate phase composition of the roasted product theoretically.²²⁾ It can be seen from Fig. 9 that the phase diagram is segmented into 20 regions and the MnO₂ content affects obviously on the phase composition. But for the temperature, it plays an inconspicuous effect. Specially, the “Sb₂O₄(s)” is transformed to “SbO₂(s)” at about 788.0 K, from region “3” to “4”, “8” to “7” and “15” to “16”, respectively. When the roasting temperature is 723.0 K, Fig. 9 and Table 4 show that with increasing content of MnO₂, Sb₂O₃ is firstly oxidized to Sb₂O₄, and then to Sb₂O₅. Simultaneously, the reduction product Mn₃O₄ gradually vanishes and Mn₂O₃ is formed. The XRD patterns of roasted samples with different MnO₂ addition amounts are presented in Figs. 8 and 10. They show that the main phases

Fig. 6. Effect of roasting temperature on arsenic and antimony volatilization rates. (Online version in color.)

Fig. 7. Vapor pressures of As₂O₃ and Sb₂O₃ change with temperature. (Online version in color.)

Table 3. The standard Gibbs free energy changes of Eqs. (3)–(4) with temperature (kJ/mol).						
T/K	573.0	623.0	673.0	723.0	773.0	823.0
Eq. (3)	–91.552	–89.010	–85.861	–82.587	–79.198	–75.694
Eq. (4)	–219.872	–220.349	–220.658	–220.777	–220.689	–220.375

Fig. 8. XRD pattern of the roasted product at roasting temperature of 723 K and MnO₂ amount of 12.5%.

of antimony and manganese are Sb_2O_4 and Mn_3O_4 respectively. From a comparison of mineral phases calculated by FactSage between those from XRD, it is found that Sb_2O_3 is not detected in the XRD patterns, the reason for which may be that the Sb_2O_3 has evaporated and been separated from the roasted residues. In addition, some part of As_2O_3 can be oxidized and immobilized in the form of MnAsO_4 when MnO_2 amount is excessive (Fig. 10), resulting in decrease of arsenic volatilization rate (Fig. 11). Figure 11 shows that the

Fig. 9. Binary phase diagram of MnO_2 - Sb_2O_3 . (Online version in color.)

Table 4. Phase composition in the binary phase diagram of MnO_2 - Sb_2O_3 .

1: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_3\text{O}_4(\text{s}) + \text{Sb}_2\text{O}_3(\text{s})$	11: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$
2: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_3\text{O}_4(\text{s}) + \text{Sb}_2\text{O}_3(\text{s})$	12: $\text{Sb}_2\text{O}_5(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_4(\text{s})$
3: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_3\text{O}_4(\text{s}) + \text{Sb}_2\text{O}_3(\text{s})$	13: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
4: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_3\text{O}_4(\text{s}) + \text{Sb}_2\text{O}_3(\text{s})$	14: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
5: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_3\text{O}_4(\text{s}) + \text{Sb}_2\text{O}_3(\text{s})$	15: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
6: $\text{Sb}_2\text{O}_3(\text{liq}) + \text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$	16: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
7: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$	17: $\text{Sb}_2\text{O}_3(\text{g}) + \text{O}_2(\text{g}) + \text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s})$
8: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$	18: $\text{O}_2(\text{g}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
9: $\text{Sb}_2\text{O}_4(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$	19: $\text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_2\text{O}_2(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$
10: $\text{Sb}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Mn}_3\text{O}_4(\text{s})$	20: $\text{Mn}_2\text{O}_2(\text{s}) + \text{Mn}_2\text{O}_3(\text{s}) + \text{Sb}_2\text{O}_5(\text{s})$

arsenic volatilization rate decreases from 93.48% to 85.58% and that for antimony decreases from 30.18% to 11.11% with increasing MnO_2 amount from 12.5% to 30.5%. Giving consideration on increasing separation efficiency of arsenic and antimony, the MnO_2 addition amount of 20.5% is determined as the optimal condition.

4.3. Effect of Roasting Time

Volatilization rates of arsenic and antimony phases were distinguished due to the vapor pressure difference between them. Figure 12 shows variations of arsenic and antimony volatilization rates as a function of roasting time. The arsenic volatilization rate increases gradually in the primary 90 min, from 25.62% to 90.06%, and then remains nearly constant. Comparatively, that for antimony always increases, from 3.18% to 20.33% with the roasting time from 30 min to 150 min. To decrease the antimony loss and improve arsenic removal rate, the roasting time is fixed at 90 min.

For the purpose of increasing separation and recovery rates of antimony, the above results suggest that the selective oxidation roasting of high arsenic-bearing flue dusts using MnO_2 should be carried out at roasting temperature of 723.0 K, MnO_2 amount of 20.5%, and roasting time of 90 min. Under the optimal conditions, the volatilization rate of arsenic is about 90.06% and for antimony is only about 6.89%, indicating that arsenic can be separated effectively

Fig. 11. Effect of MnO_2 addition amount on arsenic and antimony volatilization rates. (Online version in color.)

Fig. 10. XRD patterns of the roasted products at roasting temperature of 723 K with MnO_2 amount of 24.5% and 27.5%.

Fig. 12. Effect of roasting time on arsenic and antimony volatilization rates. (Online version in color.)

from high arsenic-bearing flue dusts through a low temperature roasting using MnO_2 as an additive. Then the antimony in the roasted products can be reclaimed through a reduction roasting and dust collection process.²³⁾

5. Conclusions

A selective oxidation roasting process was developed for the separation and recovery of antimony from high arsenic-bearing flue dusts. Though As_2O_3 could be oxidized to As_2O_5 by MnO_2 from the point of view of thermodynamics during the roasting process, the evaporation for As_2O_3 appeared earlier than it being oxidized attributed to strong volatility of it and most arsenic volatilized. Meanwhile, the MnO_2 has a positive effect with it amount in a certain range for the arsenic volatilization, for the reason that structures of some As-Sb complicated phases were destroyed after the Sb_2O_3 being oxidized to Sb_2O_4 by MnO_2 and this arsenic continued to volatile. The MnO_2 selective oxidation provided a good separation of arsenic and antimony under the conditions of roasting temperature of 723.0 K, MnO_2 amount of 20.5%, and roasting time of 90 min, with which about 90.06% arsenic and only about 6.89% went into the smoke. The

residual antimony existing in the roasted products, mainly in the form of Sb_2O_4 , could be reclaimed through a process of reduction roasting and dust collection.

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