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Article

Arsenic Removal from Arsenopyrite-Bearing Iron Ore and Arsenic Recovery from Dust Ash by Roasting Method

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Abstract: In most cases, arsenic is an unfavorable element in metallurgical processes. The mechanism of arsenic removal was investigated through roasting experiments performed on arsenopyrite-bearing iron ore. Thermodynamic calculation of arsenic recovery was carried out by FactSage 7.0 software (Thermfact/CRCT, Montreal, Canada; GTT-Technologies, Ahern, Germany). Moreover, the arsenic residues in dust ash were recovered by roasting dust ash in a reducing atmosphere. Furthermore, the corresponding chemical properties of the roasted ore and dust ash were determined by X-ray diffraction, inductively coupled plasma atomic emission spectrometry, and scanning electron microscopy, coupled with energy-dispersive X-ray spectroscopy. The experimental results revealed that the arsenic in arsenopyrite-bearing iron ore can be removed in the form of $As_2O_3(g)$ in an air or nitrogen atmosphere by a roasting method. The efficiency of arsenic removal through roasting in air was found to be less than that in nitrogen atmosphere. The method of roasting in a reducing atmosphere is feasible for arsenic recovery from dust ash. When the carbon mass ratio in dust ash is 1.83%, the arsenic removal products is almost volatilized and recovered in the form of $As_2O_3(g)$.

Keywords: arsenopyrite; arsenic removal; mechanism; roasting; arsenate; dust ash; arsenic recovery

1. Introduction

Arsenic content in the earth's crust is up to 5 mg·kg⁻¹, and more than 300 arsenic species occur in nature. Arsenic is mainly associated with minerals such as pyrite, arsenopyrite, or enargite [1,2]. In most cases, arsenic is an unfavorable element in metallurgical processes. For example, arsenic reduces the quality of raw materials, affects the extraction of metal, interferes with the purity of the product, and poses serious environmental hazards [1]. Arsenic has an adverse effect on steel; for instance, the surface hot shortness increases, and the reduction of area and impact toughness decrease with the increase of arsenic content in steel [3–6]. Under the hot rolling or welding conditions, the arsenic in the steel leads to the increase in the content of arsenic at grain boundaries and the expansion of welding cracks [4,7–9]. Moreover, as the oxidability of arsenic is less than that of iron, it is difficult to remove arsenic from molten iron by using excessive Al and Ca–Fe alloys or rare earth elements, but it also needs deep deoxidation and desulfurization before arsenic removal can be achieved, so the cost of arsenic removal is too high to be feasible in realistic production [10]. However, the price of arsenic-bearing iron ore is cheaper than that of high-grade iron ore.



decreasing greatly in the earth, and arsenic-bearing ore needs to be comprehensively utilized through ore blending. Some metallurgical enterprises at home and abroad, such as Peru, Chile, Philippines, France, Mexico, and China, have adopted some arsenic-bearing ore in the metallurgical industry [11]. When these arsenic-bearing ores are used, they are faced with the problem of arsenic removal from ores and the problem of arsenic-bearing dust treatment from the point of view of environmental protection.

Arsenic can be removed from arsenic-bearing ore by a roasting or sintering method due to the volatile nature of arsenic and its compounds [12]; thus, some scholars have explored the appropriate arsenic removal conditions by performing roasting or sintering experiments. Yin et al. and Lu et al. studied arsenic removal from copper–silver ore using a roasting method [13,14], and the impact of different parameters (e.g., temperature, atmosphere, and roasting time) on the arsenic removal ratio was also evaluated. Lu et al. investigated arsenic removal from arsenic-bearing iron ore during the sintering process [15,16]. The effects of temperature, bed depth, gas pressure, and coal ratio on arsenic removal during the sintering process were studied, and the reasonable technical parameters were obtained. In addition to the arsenic removal tests by roasting and sintering methods, a number of scholars also carried out thermodynamic calculations on arsenic removal, and discussed the arsenic-bearing products and suitable conditions for arsenic removal. Chakraborti and Lynch analyzed the As-S-O vapor system [17] and further identified the importance of bed depth in the rapid release of arsenic from arsenical materials under an oxidizing atmosphere. Contreras et al. evaluated the impact of various factors, such as trace element concentration, flue gas composition, temperature, and pressure, on the equilibrium composition based on the arsenic interactions in the co-combustion processes [18]. Nakazawa et al. and Zhang et al. studied the thermodynamics of arsenic removal from arsenic-containing copper ore during roasting [19] and arsenic-bearing iron ores during sintering [20–23], respectively, and obtained the equilibrium components containing arsenic and the arsenic removal rate.

The arsenic removed by roasting is mixed in the dust ash. For arsenic existing in dust, chemical adsorption of gaseous arsenic by CaO or CaCO₃ can effectively control arsenic content in flue gas and prevent arsenic pollution [24–26], but arsenate is easy to remain in dust, which is not conducive to the use of dust ash as raw material for sintering or roasting ore. Therefore, recovery of As₂O₃ is another feasible method.

Although arsenic removal experiments and thermodynamic calculations have been carried out by many scholars [12–23], and the volatilization behavior of arsenic in the process of roasting has also been explored [13,22], the mechanism of arsenic removal by roasting has never been reported. Exploration of the mechanism of arsenic removal by a roasting process and investigation of the residual form of arsenic in the roasted ore are important for controlling the arsenic removal efficiency and the arsenic component. Moreover, it is important to recover arsenic from dust ash to prevent further mobilization of arsenic and arsenic contamination. Therefore, these problems were attempted in this research.

2. Materials and Methods

2.1. Experiment on Arsenic Removal from Roasting Iron Ore

The composition of mixed ore used in the test is listed in Table 1.

Table 1. Composition and proportion of roasting ore.

Ore Name		Buene entire no /0/						
	Fe ₂ O ₃	SiO ₂	CaO	Al ₂ O ₃	MgO	FeAsS	S	
Iron ore	71.36	10.64	0.40	7.39	0.31	0.05	0.06	90
Arsenopyrite	/	/	/	/	/	92.71	/	10
Mixed ore	64.22	9.58	0.36	6.65	0.28	9.37	0.05	100

Note: "/" Represents "the chemical composition is not determined".

The mixed ore can be obtained by mixing 90% iron ore with 10% arsenopyrite. Mixed ore was crushed by an F77-1 sealed sample grinder for 1 min, then screened by a 75 mesh sieve. The ore powder larger than 75 mesh was crushed again until all powders were less than 75 mesh, and then the crushed powder was mixed. Mixed ore was blended with water to make iron ore balls with a diameter of 10 \pm 2 mm. Furthermore, the iron ore balls were heated in an oven at 110 °C for 3 h, until they were completely dry. Then, the balls were taken out and reserved for further experiments.

The roasting test was carried out in a horizontal resistance furnace with 60 mm i.d. quartz tube, and the constant temperature zone of the resistance furnace was controlled using a thermocouple. The experiments were carried out in an air atmosphere and nitrogen atmosphere (1 L·min⁻¹, STP), respectively. The roasting temperature was 700, 800, 900, and 1000 °C, respectively, and the roasting time was 60 min. The porcelain boat loaded with the ore ball was put into the constant temperature zone of the tube furnace. When the roasting time was over, the power was turned off, and the sample was cooled down to room temperature and analyzed by various techniques. The schematic illustration of the roasting method is shown in Figure 1.



Gas inlet Resistance furnace Thermocouple Beaker

Figure 1. Schematic illustration of roasting test.

2.2. Experiment on Recovery of Arsenic by Roasting Dust Ash

The composition of dust ash of roasting iron ore from an iron plant is shown in Table 2. After adding 10% As₂O₃ chemically pure powder to the dust ash, the XRD pattern of the mixed dust ash powder is shown in Figure 2.

Fe	CaO	MgO	SiO ₂	Al ₂ O ₃	TiO ₂	S	K ₂ O	Na ₂ O	Cl-
42.34	7.08	0.82	4.80	3.04	0.72	0.65	1.16	0.15	1.06

Table 2. Composition of dust ash from roasted iron ore.

The arsenic recovery experiment by roasting was carried out in two different atmospheres with 10% As₂O₃ powder in the dust ash. The experiment was carried out in a horizontal resistance furnace with a 60 mm i.d. quartz tube. The dust ash was first placed in the constant temperature zone of the quartz tube. When the roasting experiment was carried out under an anaerobic atmosphere, the quartz tube was evacuated and washed with high-purity nitrogen 3 times before heating up the furnace. The test process was protected by 100 mL/min of high-purity nitrogen. The dust ash was heated to 600 °C and then cooled to room temperature after an hour of constant temperature. The experimental steps of roasting in a reducing atmosphere with 2% graphite powder as raw material are the same for the anaerobic atmosphere. When the roasting time was over, the sample was cooled down to room temperature and analyzed by the following various tests.



Figure 2. XRD spectra of the mixed dust ash powder.

2.3. Sample Analysis and Testing

The phase composition of iron ore was evaluated by PANalytical XPert PRO MPD XRD (Panaco, Almelo, Netherlands) with Cu target, K radiation, and 40 kV operating voltage. The chemical component of roasted ore was determined by IRIS Advantage Radial inductively coupled plasma atomic emission spectrometry (ICP-AES, Thermo Elemental, Massachusetts, America), and the physicochemical properties of the roasted ore were analyzed by FEI Nova NanoSEM400 (FEI, Hillsboro, America) scanning electron microscopy (SEM), coupled with energy-dispersive X-ray spectroscopy (EDS, FEI, Hillsboro, America).

3. Results

The white volatile that condensed in the cold beaker at the end of the quartz tube during the roasting process is shown in Figure 3a, b, and its XRD pattern is presented in Figure 3c. The XRD pattern and ICP-AES analysis indicated that the white volatiles corresponded to As_2O_3 powder with 89.12% purity, which confirms that the arsenic removal in an oxygen atmosphere is mainly carried out via Equation (1). The arsenic content in the ore after roasting at different temperatures is listed in Table 3.

$$2FeAsS + 5O_2(g) = Fe_2O_3 + As_2O_3(g) + 2SO_2(g)$$
(1)



Figure 3. (a) Arsenic removal from mixed ore by roasting in resistance furnace with quartz tube under air atmosphere and 1000 °C; (b) Collected As₂O₃ powers condensed in cold beaker; (c) XRD spectra of collected As₂O₃ powers condensed in cold beaker.

Temperature/°C	Arse	nic Removal I Atmosphere/	Rate in Air wt %	Arsenic Removal Rate in Nitrogen Atmosphere/wt %				
	Before Roasting	After Roasting	Arsenic Removal Rate	Before Roasting	After Roasting	Arsenic Removal Rate		
700	4.31	3.78	12.30	4.31	1.000	76.80		
800	4.31	3.86	10.44	4.31	0.186	95.68		
900	4.31	0.88	79.58	4.31	0.051	98.82		
1000	4.31	0.57	86.77	4.31	0.027	99.37		

Table 3. Arsenic removal rate of ore subjected to roasting.

Table 3 summarizes how arsenic can be removed from arsenopyrite-bearing iron ore by roasting in an air atmosphere or nitrogen atmosphere. The arsenic removal rate increases with the increase of temperature from 700 to 1000 °C. The arsenic removal rate by roasting method in an air atmosphere is less than that in the nitrogen atmosphere. The arsenic removal rate in the air atmosphere is poor at 700–800 °C, and the arsenic removal rate is about 12%, while the rate is 76.8–95.68% in the nitrogen atmosphere.

4. Discussion

4.1. Thermodynamic Calculation of Mixed Ore Subjected to Roasting

In order to explain the reason for the increase in arsenic removal rate with increasing temperature during roasting, the thermodynamic calculations of the roasting mixed ore in the air atmosphere were carried out by FactSage 7.0 (version 7.0, Thermfact/CRCT, Montreal, Canada, GTT-Technologies, Ahern, Germany) thermodynamic software. The effect of partial pressure of oxygen on the residual arsenic rate at different temperatures was calculated as shown in Figure 4. The results show that arsenate is the residual product in air roasting of arsenic-bearing ores at 700–1000 °C. Figure 4 shows that excessive partial pressure of oxygen is not beneficial to arsenic removal. Moreover, with the decrease of roasting temperature from 1000 to 700 °C, arsenic removal requires lower partial pressure of oxygen, which is the reason why the arsenic removal rate at 700 °C is lower than that at 1000 °C.



Figure 4. Effect of partial pressure of oxygen on residual rate at different temperatures.

The arsenic removal rate by roasting method in the air atmosphere is poor, which is probably attributed to the reaction between As_2O_3 and oxygen to generate As_2O_5 , and then the As_2O_5 reacts with other oxides (Fe₂O₃, Al₂O₃, CaO) via Equations (2) to (4) to generate arsenate. Thus, the roasting product contains a variety of arsenic residues. The arsenic removal rate at 900–1000 °C increases to 79.58–86.77% in air; the formation rate of As_2O_3 is accelerated at high temperature, and a large amount of gas escapes rapidly.

$$As_2O_3(g) + O_2(g) + Fe_2O_3 = 2FeAsO_4$$
 (2)

$$As_2O_3(g) + O_2(g) + Al_2O_3 = 2AlAsO_4$$
 (3)

$$As_2O_3(g) + O_2(g) + 3CaO = Ca_3(AsO_4)_2$$
 (4)

4.2. X-Ray Diffraction Analysis of the Roasted Ore and Dust in Different Atmospheres

The XRD spectra of the roasted ore in air and nitrogen atmospheres are shown in Figure 5a,b, respectively. In the raw material ore, arsenic exists in the form of FeAsS (Figure 5a, bottom). Figure 5a shows the disappearance of peaks of FeAsS due to its decomposition when the ore was roasted at 700–1000 °C, and a small amount of peaks of AlAsO₄ at 800 °C and As₂O₃ at 1000 °C appear for the roasted ore, indicating that FeAsS underwent decomposition via Equation (1) and As₂O₃(g) underwent reaction via Equation (3). Figure 5b demonstrates that the arsenic removal by roasting in the nitrogen atmosphere is more thorough, and the peaks of arsenates and As₂O₃(s) are not found in XRD spectra of roasted ore. The reaction of arsenic removal is mainly carried out via Equation (1). The investigation of the mechanism on arsenic removal by roasting method proves that arsenic is mainly removed in the form of gaseous As₂O₃(g) in the oxidation or nitrogen atmosphere, while the residual arsenic is mostly arsenate.



Figure 5. XRD spectra of the roasted ore and dust in: (a) Air and (b) nitrogen atmosphere.

4.3. Mechanism Research on Arsenic Removal by Roasting Method and Scanning Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy Analysis

Arsenic removal efficiency in the air atmosphere was found to be poor. Therefore, the arsenic residual form in the roasted sample under an air atmosphere was further studied by SEM coupled with EDS. Figure 6 shows the SEM images of the roasted ore under an air atmosphere at different roasting temperatures. Chemical composition of the raw ore and roasted ore is shown in Table 4. Figure 6a demonstrates that arsenic and sulfur occur simultaneously in the raw material, and arsenic is present

in the form of FeAsS. Figure 6b shows that arsenic is found in the samples roasted at 700 °C; however, sulfur is not found, which indicates the decomposition of FeAsS, where arsenic is present in FeAsO₄ and Ca₃(AsO₄)₂. Figures 5 and 6c show that the arsenic in the roasted ore is present as AlAsO₄ and FeAsO₄ at 800 °C, respectively. The results exhibited in Figure 6d,e are similar to those shown in Figure 6c. The abovementioned SEM and EDS results further confirm that arsenic is removed in the form of As₂O₃(g) by roasting in the air atmosphere, and the residual arsenic reacts with oxide in the ore to generate arsenates.

Element Nie	D • • • • •	Atomic Ratio of Elements/at %											
Figure No.	Point No.	Mg	Al	Ca	Cr	Si	S	Mn	Fe	Ni	As	Nb	0
	А	-	-	-	-	5.40	-	-	33.53	-	-	-	61.08
	В	5.97	-	-	-	10.86	-	-	22.20	-	-	-	60.98
62	С	-	9.18	-	-	6.73	-	-	22.75	-	-	-	61.35
oa (row oro)	D	-	-	-	-	7.50	0.26	0.43	28.61	-	1.64	-	61.57
(law ole)	E	-	-	-	-	-	-	-	40	-	-	-	60
	F	-	-	-	-	-	5.91	-	32.42	-	0.48	-	61.18
	G	-	-	-	-	7.23	2.14	-	22.82	-	5.08	-	62.73
	А	-	-	-	-	7.30	-	-	24.31	-	0.082	4.36	63.21
	В	-	-	-	-	11.16	-	1.15	24.35	0.80	0.70	-	61.84
6b	С	-	-	-	-	3.12	-	-	35.84	-	0.42	-	60.62
(700 °C)	D	-	-	0.46	-	10.45	-	-	25.06	0.42	1.70	-	61.92
(700 C)	Е	-	-	0.64	-	8.38	-	-	28.03	-	0.81	-	61.65
	F	-	-	-	0.36	7.73	-	-	29.08	-	1.28	-	61.55
	G	-	-	-	-	2.10	-	-	37.48	-	-	-	60.42
	А	-	-	-	0.36	10.00	-	0.38	27.33	-	-	-	61.92
	В	-	-	-	0.34	8.42	-	-	29.56	-	-	-	61.68
	С	-	-	-	-	22.59	-	-	12.55	-	0.34	-	64.52
6c	D	-	-	-	-	11.86	-	-	25.76	-	-	-	62.37
(800 °C)	Е	-	-	-	-	8.02	-	3.49	27.58	-	-	-	60.91
	F	2.59	-	-	-	19.04	-	-	15.08	-	-	-	63.29
	G	-	-	-	-	24.37	-	0.40	9.85	-	0.58	-	64.79
	Н	-	-	-	-	12.95	-	-	19.00	-	0.25	3.72	64.08
	А	-	-	-	-	9.79	-	-	28.25	-	-	-	61.96
	В	-	-	-	-	7.12	-	-	23.55	-	2.00	4.22	63.11
6d	С	-	-	-	-	9.72	-	-	25.08	-	3.25	-	61.94
(900 °C)	D	-	7.01	-	0.39	3.87	-	-	27.95	-	-	-	60.77
	E	-	-	-	0.46	6.49	-	-	31.75	-	-	-	60.30
	F	-	-	-	0.34	5.44	-	-	32.65	-	0.49	-	61.09
	А	-	-	-	0.96	7.34	-	-	30.23	-	-	-	61.47
	В	-	1.16	-	-	1.75	-	-	36.74	-	-	-	60.35
6 -	С	-	2.93	-	-	2.50	-	-	26.14	-	-	5.66	62.76
(1000 °C)	D	-	1.46	-	-	-	-	-	38.54	-	-	-	60.00
(1000 C)	E	-	-	-	-	2.45	-	-	35.38	-	1.68	-	60.49
	F	-	0.89	-	0.49	16.73	-	-	18.54	-	-	-	63.35
	G	-	-	-	1.02	8.67	-	-	26.13	-	2.44	-	61.73

Table 4. Chemical composition of the raw ore and roasted ore.

Note: "-" Represents "below the detection limit".



Figure 6. SEM images of the roasted ore in air atmosphere and at different roasting temperatures: (**a**) Raw material; (**b**) 700 °C; (**c**) 800 °C; (**d**) 900 °C; (**e**) 1000 °C.

4.4. Route for the Recovery of Arsenic from Arsenic-Bearing Dust Ash

The arsenic recovery experiment by roasting in the atmosphere of air, anaerobic and reducing, was carried out with the dust ash containing 10% As₂O₃ powder [20]. The experiment confirms that arsenic recovery from dust ash by roasting in the atmosphere of air or an anaerobic atmosphere is difficult, and that arsenate easily remains in the dust ash. Figure 7 shows the effect of temperature on arsenic-containing products in dust ash by reduction roasting. Thermodynamic calculation of arsenic recovery by roasting under a reduction environment shows that arsenic is not easy to be removed from dust and that arsenate is easy to be formed when the roasting temperature is below 390 °C. The arsenic is easily volatilized and recovered when the dust is roasted above 390–890 °C, but it is easy to produce arsenate when the dust ash is roasted above 890 °C, which affects the recovery of arsenic.



Figure 7. Effect of temperature on arsenic-containing products in dust ash by reduction roasting.

4.5. Effect of Carbon Mass Ratio on Arsenic Removal Products of Dust Ash by Roasting

According to the dust ash in Table 2, the thermodynamic calculation of the effect of carbon powder on arsenic removal products was done using FactSage 7.0. Figure 8 shows the results of the effect of carbon ratio on arsenic removal products of dust ash by roasting using thermodynamic calculations. When the arsenic-bearing dust ash was roasted with a carbon mass ratio increasing from 0 to 1.83%, the percentage of residual solid AlAsO₄(s) in dust ash gradually decreased from 100% to 0, and the percentage of gaseous $As_2O_3(g)$ gradually increased to 100%. When the arsenic-bearing dust ash was roasted with a carbon mass ratio was below 1.63%, the arsenic removal products were the majority of AlAsO₄(s) and a small amount of $As_2O_3(g)$. When the carbon mass ratio was 1.83%, the arsenic removal product was almost volatilized in the form of $As_2O_3(g)$. Subsequently, with the increase of carbon mass ratio, the percentage of volatile $As_2O_3(g)$ gradually decreased, while the percentages of $As_2(g)$ and $As_4(g)$ gradually increased. When the carbon mass ratio increased to 5%, arsenic was almost removed by volatilization of $As_2(g)$ and $As_4(g)$.



Figure 8. Effect of carbon ratio on arsenic removal products of dust ash by roasting.

The arsenic recovery experiment by roasting in the reducing atmosphere was carried out with dust ash containing 2% carbon powder. Figure 9a shows the recovered products condensed on the edge wall of the quartz tube. Figure 9b exhibits the XRD spectrum of the recovered products. The recovered products are almost $As_2O_3(g)$. Figure 9c is the XRD spectrum of the roasted dust ash, and the peak of arsenic is almost invisible in the XRD spectrum. By comparing dust ash before roasting in Figure 2, it can be seen that almost all arsenic in the dust ash has been volatilized and recovered in the low-temperature section at the end of the quartz tube. Thermodynamic calculation of Figure 8 shows that arsenic volatilized in the form of gaseous $As_2O_3(g)$ when dust ash was roasted with 2% carbon. The results demonstrate that the thermodynamic calculation results are in good agreement with the experimental results.



Figure 9. (a) Volatile compounds photograph, (b) XRD spectrum of volatile compounds collected during roasting dust ash, and (c) the dust ash after roasting.

5. Conclusions

- (1) Arsenic in arsenopyite-bearing iron ore can be removed by roasting method in an air or nitrogen atmosphere;
- (2) The mechanism of arsenic removal by roasting method indicates that the efficiency of arsenic removal by roasting in air is less than that in nitrogen atmosphere. The poor arsenic removal efficiency at low temperature and in an air atmosphere is due to the formation of arsenates by the reaction of As₂O₃(g) with other oxides in the strong oxidizing atmosphere. Lower partial pressure of oxygen is required to ensure an effective arsenic removal rate when arsenic-bearing ore is roasted at lower temperatures. Arsenic is removed in the form of As₂O₃(g) by the roasting method, and residual arsenic reacts with oxides in the ore to generate arsenates.
- (3) The arsenic recovery from dust ash by roasting in the atmosphere of an air or anaerobic atmosphere is difficult, and arsenic easily reacts with oxides to form arsenate and remains in the dust ash. The method of roasting in a reducing atmosphere is feasible for arsenic recovery from dust ash. When the arsenic-bearing dust ash is roasted with a carbon mass ratio below 1.63%, the arsenic removal products are the majority of AlAsO₄(s) and a small amount of As₂O₃(g). When the carbon mass ratio is 1.83%, the arsenic removal product is almost volatilized and recovered in the form of As₂O₃(g).

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