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Fundamental study on utilization of tin and zinc-bearing iron concentrate by selective chlorination①

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Abstract: The feasibility and technologies of comprehensive recovery of tin, zinc, arsenic and iron from the complex iron ores by selective chlorination roasting were studied by thermodynamic analysis and roasting experiments. Investigation shows that the product pellets with the compression strength of 2 625 N/P, the tumble index of 97.26%, the abrasion index of 1.35%, tin, arsenic and zinc residue of 0.043%, 0.046% and 0.058% respectively can be achieved if balling a concentrate containing 0.39% tin, 0.40% arsenic and 0.28% with addition of 8% coke breeze and 0.5% $CaCl_2$ and roasting the pellets at 1 060 - 1 080 ℃ for 40 min. The volatilization of tin, arsenic and zinc is 91.75%, 93.42% and 81.12% respectively. The performances of the product pellets are able to meet the requirements of blast furnace ironmaking.

Key words: selective chlorination; comprehensive recovery; tin; zinc; complex iron ore
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1 INTRODUCTION

China is rich in iron ore resources, but most of these ores are low-grade, polymetallic refractory ones[1, 2]. With the rapid development of iron and steel industry, the comprehensive utilization of these ores is becoming more and more important. The complex iron ores containing tin and zinc are typical intractable ones, great reserves of which are found in Inner Mongolia, Guangdong, Guangxi and Hunan of China. Huanggang Iron Mine of Inner Mongolia is a large-size complex iron ore deposite associated with nonferrous elements of tin, arsenic, zinc and so on[3, 4], among which the reserve of iron is above 1.1×10^8 t, and the reserves of tin, arsenic and zinc are respectively about 4×10^5, 5.6×10^5 and 2.5×10^5 t. It is very difficult to efficiently recover and utilize iron, tin, arsenic and zinc from these ores because of the complex association of these elements. The literatures indicate that a lot of research has been done since 1970, but the methods are mainly limited to reduction roasting to produce metallic pellets[5]. Furthermore, these methods with high production costs and low efficiency lack systematical research and have not been put into commercial production. Therefore, these ores have not been efficiently utilized hitherto.

Because of the low melting point and high volatility of most metal chlorides, chlorination volatilization has been adopted in extractive metallurgy. The metal elements accompanied are easy to be transferred into their chlorides, selectively volatilized into gaseous phase and recovered in the dust collecting system[6-8]. In this investigation, a new process of tin and zinc recovery and preparation of pellets for blast furnace from tin and zinc containing iron concentrate by chlorination roasting is developed.

2 EXPERIMENTAL

2.1 Characteristic of material

The iron concentrate containing tin and zinc used in this investigation is taken from Inner Mongolia Autonomous Region of China. The mass percent of particles below 0.075 mm of the concentrate is found to be 61.16%, and the chemical composition is listed in Table 1.

It can be seen from Table 1 that the iron con-

Table 1 Chemical composition of iron concentrate (mass fraction, %)

TFe	FeO	Sn	As	Zn	SiO_2	Al_2O_3
64.79	28.59	0.39	0.40	0.28	3.35	0.70

CaO	MgO	Pb	P	S	Ignition loss
2.19	0.21	0.017	0.022	0.25	1.23

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centrate belongs to magnetite type[9]. The contents of tin and zinc are 0.39% and 0.28% respectively, each of which exceeds the limitation of iron-making[10]. And the contents of SiO_2 and Al_2O_3 are 3.35% and 0.70% respectively. Moreover, there is 0.40% of arsenic in the sample, which needs to be removed or recovered.

Optical microscope (OM) and scanning electronic microscope (SEM) observations (Fig. 1) show that tin in the concentrate mostly occurs as SnO_2 in fine intergrowth or inclusion and a little in monomer, and partial SnO_2 is adherent to magnetite or encapsulated by silicate and fluorite. And arsenic in the concentrate almost occurs as $FeAsS_2$, and closely adheres to magnetite. The primary existence minerals of zinc are sphalerite and calamine(including a little of zinc oxide), part of which are embedded in the gangue alone and metasomaticly intergrow with magnetite and gangue. The other metallic minerals hardly contain zinc.

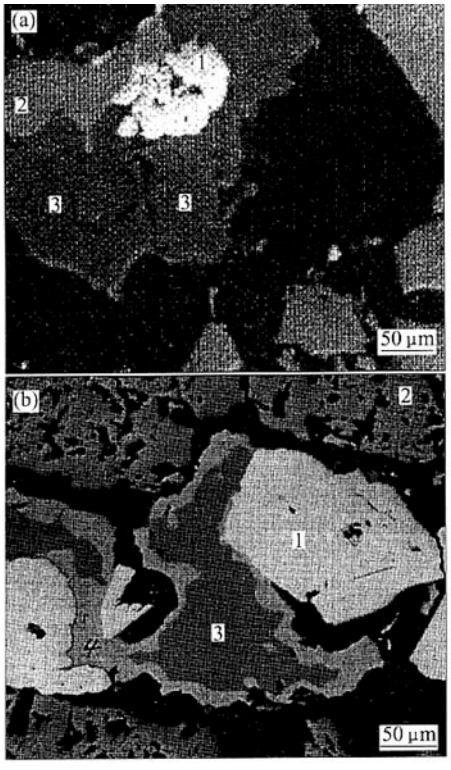


Fig. 1 Existence forms of tin, arsenic and zinc in concentrates
(a)—1—SnO_2, 2—Fe_3O_4, 3—CaF_2;
(b)—1—$AsFeS_2$, 2— Fe_3O_4, 3—ZnS

In this investigation coke breeze is used as internal reductants. The mass percent of coke particles below 0.15 mm and 0.075 mm is 100% and about 80% respectively, and the industrial analyses of coke breeze are listed in Table 2.

Table 2 Industrial analysis of coke breeze (mass fraction, %)

Fixed carbon	Percent volatile	Percent ash
84.55	1.47	13.98

Fuel ratio (the ratio of fixed carbon to percent volatile) is an important criterion of coal combustibility, which is closely correlated to the coal reactivity[11]. The greater the fuel ratio is, the worse the combustibility and reactivity are, and the more obvious the lingering combustion is. From Table 2, it can be calculated that the fuel ratio of coke breeze is 57.52, which indicates that the combustibility and reactivity of coke breeze are inferior, so it can offer durative combustion and feeble reduction atmosphere.

2.2 Research methods

The experimental process includes mixing, balling, drying, preheating, roasting and so on. The green ball is prepared in the disc pelletizer of 1 m in diameter. The bench-scale experiments of preheating and roasting are carried out in a vertical electrically heated tube furnace with an internal and external diameter of 80 mm and 100 mm respectively. The mixture of N_2 and CO_2, with a ratio of 2 : 1, and the flow-rate of 10 L/min and 5 L/min respectively, is led into from the bottom of the furnace. The experimental flowsheet is shown in Fig. 2.

3 CHLORINATION THERMODYNAMICS OF IRON, TIN, ARSENIC AND ZINC

Thermodynamic analysis indicates that the standard formation free enthalpy of FeO and SnO_2 is approachable, and the reduction balance curves of SnO_2(s) and SnO(g) are also proximate[12]. Therefore, it is difficult to realize the effective volatilization of tin in the form of SnO(g) by selective reduction under the condition of the only existence of carbon. But effective separation of Sn from Fe becomes easy in the coexistence of carbon and chlorides. On one hand, carbon is easily compatible with O_2, so the partial pressure produced by chlorination reactions is decreased; and on the other hand, SnO_2 is easily inverted into SnO(g) and Sn(l) in the presence of carbon[8]. Therefore, there will be the following chlorination reactions:

$$SnO_2(s)+2Cl_2+2C=SnCl_4(g)+2CO \quad (1)$$

$$\Delta G^{\ominus}/J=-160\,900-232.06T$$

$$SnO(g)+Cl_2=SnCl_2(g)+1/2O_2 \quad (2)$$

$$\Delta G^{\ominus}/J=38\,284-75.88T$$

$$Sn(l)+Cl_2=SnCl_2(g) \quad (3)$$

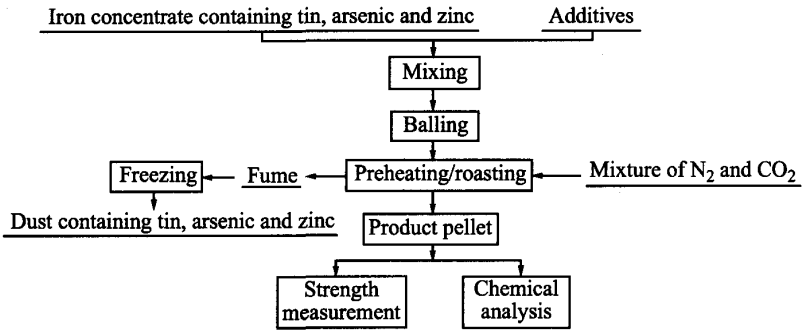


Fig. 2 Experimental flowsheet

$\Delta G^{\ominus}/J = -251\,458 + 30.21T$

$\Delta G^{\ominus}$ for the above three reactions is below zero when the temperature is between 800 ℃ and 1 200 ℃. It is obvious that $SnO_2(s)$, $SnO(g)$ and $Sn(l)$ will easily form $SnCl_4(g)$ or $SnCl_2(g)$ and can be volatilized from the ores.

For arsenic, the following reaction will take place at first during chlorination roasting:

$$4FeAsS_2 + 14O_2 = 2Fe_2O_3 + As_4O_6 + 8SO_2 \quad (4)$$

As_4O_6 exists steadily between 25 ℃ and 900 ℃, and will be decomposed if the temperature is higher[8]:

$$As_4O_6 = 2As_2O_3 \quad (5)$$

As_2O_3 can be chlorinated into $AsCl_3$, but As_2O_3 has a higher steam pressure because of a low boiling point (about 460 ℃) at the chlorination roasting temperature. Therefore, once As_2O_3 is formed, it will be volatilized into gaseous phase in which a little of it may be chlorinated into $AsCl_3$. So, arsenic is mostly volatilized in the form of As_2O_3.

As far as ZnO and FeO are concerned, there will be the following reactions in the presence of chlorides:

$$ZnO(l) + Cl_2 = ZnCl_2(g) + 1/2O_2 \quad (6)$$

$\Delta G^{\ominus}/J = -800 - 72.8T$

$$FeO(l) + Cl_2 = FeCl_2(g) + 1/2\,O_2 \quad (7)$$

$\Delta G^{\ominus}/J = -41800 + 20.0T$

But seen from the $\Delta G^{\ominus}-T$ chloride curves of MeO-Cl_2[12-14], in the three curves of FeO-Cl_2, ZnO-Cl_2 and SnO-Cl_2, the curve of FeO-Cl_2 lies in the upper side, ZnO-Cl_2 in the middle, and the curve of SnO-Cl_2 in the lower side. It shows FeO(l) is most difficult to be chlorinated among the three oxides, and SnO(g) is easy to be transferred into $SnCl_2$. Therefore, if only the proper chloride content and given volatile conditions are controlled, tin, arsenic and zinc can be chlorinated and volatilized step by step, and iron will not be chlorinated and remain in the roasted pellets.

Practical chlorination agent is calcium chloride, and through the activation of gangues, such as SiO_2 and Al_2O_3, $CaCl_2$ reacts with O_2 and H_2O to form Cl_2 or HCl in the following chlorination reactions:

$$CaCl_2 + SiO_2 + 1/2O_2 = CaO \cdot SiO_2 + Cl_2 \quad (8)$$

$\Delta G^{\ominus}/J = 65\,960 - 34.89T$

$$CaCl_2 + Al_2O_3 + 1/2O_2 = CaO \cdot Al_2O_3 + Cl_2 \quad (9)$$

$\Delta G^{\ominus}/J = 140\,400 - 56.23T$

$$CaCl_2 + SiO_2 + H_2O = CaO \cdot SiO_2 + 2HCl \quad (10)$$

$\Delta G^{\ominus}/J = 175\,200 - 103.55T$

$$CaCl_2 + Al_2O_3 + H_2O = CaO \cdot Al_2O_3 + 2HCl \quad (11)$$

$\Delta G^{\ominus}/J = 199\,700 - 124.89T$

Compared with no existence of SiO_2 and Al_2O_3 gangues, the trend of oxidation and hydrolyzation of $CaCl_2$ is apparently increased and the reaction equilibrium constant multiples 10^4 in the existence of the two gangues[15, 16]. Furthermore, the melting point of $CaCl_2$ is only 772 ℃, and CaO generated in the oxidation and hydrolyzation reactions of $CaCl_2$ is easy to dissolve in the melting $CaCl_2$, so the activity of CaO is reduced. Thus, $CaCl_2$ actually acts an accelerator of the formation of $CaO \cdot SiO_2$ or $CaO \cdot Al_2O_3$ and the chloride volatile reactions can proceed.

4 EXPERIMENTAL RESULTS AND DISCUSSION

In batch-scale experiments, the mixture of N_2 and CO_2 is led into the roasting furnace during whole roasting in order that the internal reductants in the pellets react with CO_2 at high temperature and are gasified into CO to maintain feeble reduction atmosphere for the roasting procedure. In this test, coke breeze is used as an internal reduction agent.

4.1 Effect of reductant dosage

The test conditions are fixed as follows: the roasting temperature 1050℃, time 60 min, and $CaCl_2$ dosage 4%. The effect of internal coke breeze dosage on the roasting results is studied and

illustrated in Fig. 3.

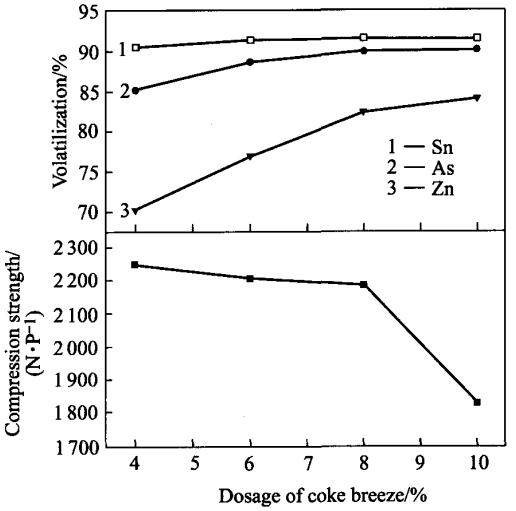


Fig. 3 Effect of coke dosage on roasting results

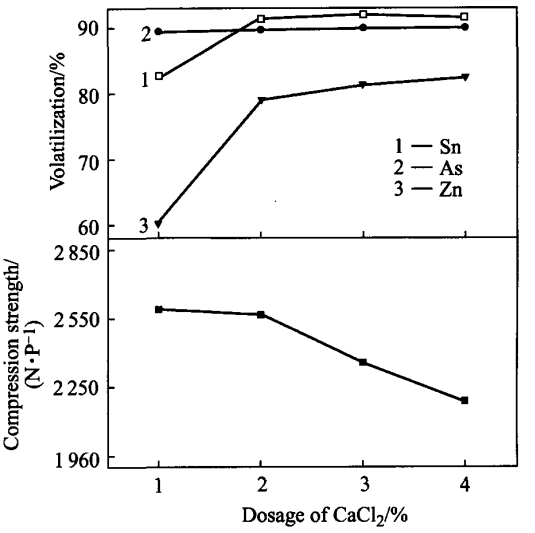


Fig. 4 Effect of dosage of $CaCl_2$ on roasting results

It can be seen from Fig. 3 that the compression strength of pellets presents a downward trend, but all of them are above 2 100 N/P with the increase of coke breeze dosage from 4% to 8%. When the dosage is increased to 10%, the compression decreases obviously. The possible reason is that there will be more pores formed inside the pellets after roasting with increasing dosage of internal coke breeze, which results in a looser structure.

Fig. 3 also shows that tin volatilization, which remains above 90%, is nearly unchanged and the remains of tin are below 0. 06% when the dosage of coke breeze varies from 4% to 10%. It can be concluded that compounds of tin can be easily chlorinated and volatilized effectively in the coexistence of coke breeze and $CaCl_2$. Arsenic volatilization is increased continuously with the increase of coke dosage. The volatilization of arsenic is 90. 03% and the remaining arsenic is below 0. 08% when the coke dosage is 8%. Furthermore, zinc volatilization is also enhanced with the increase of coke breeze dosage. Volatilization of zinc is also increased with the increase of coke breeze dosage. When the coke breeze dosage is in excess of 8%, zinc volatilization is above 82%, and the remains of zinc is below 0. 06%.

4. 2 Effect of $CaCl_2$ dosage

The test conditions are as follows: roasting at 1 050 ℃ for 60 min, and 8% internal coke breeze dosage. Effects of the dosage of $CaCl_2$ are shown in Fig. 4.

It is illustrated in Fig. 4 that the compression strength of roasted pellets is reduced gradually with the increase of $CaCl_2$. The possible reason is that some low-melting-point compounds (such as $CaO \cdot SiO_2$) are formed. It also can be seen that the volatilizations of tin and zinc are enhanced with the increase of $CaCl_2$ dosage. When the dosage of $CaCl_2$ is below 2%, the volatilizations of tin and zinc increase markedly with the dosage. And when the dosage exceeds 2%, the volatilization of tin keeps almost unchanged and remains above 90%. As far as arsenic is concerned, the change of $CaCl_2$ dosage hardly has effect on arsenic volatilization, which is between 89. 4% and 90. 4% when the dosage of $CaCl_2$ is from 1% to 4%. However, the volatilization of zinc still keeps increasing.

4. 3 Effect of roasting temperature

The test conditions are: the roasting time of 40 min, coke breeze dosage of 8%, and $CaCl_2$ dosage of 2%. Effects of roasting temperature on the roasting results are shown in Fig. 5.

From Fig. 5, it can be concluded that roasting temperature has great effect on the results. With the rising of roasting temperature, the compressive strength keeps increasing. But the compression strength exceeds 2 000 N/P only when the temperature gets to 1 100 ℃. When the temperature reaches 750 ℃, tin has been volatilized notably. When the temperature exceeds 850 ℃, over 80% tin has been volatilized, and the remains of tin in the pellets are below 0. 08%. When the temperature gets to 950 ℃, the volatilization increases slowly. Volatilization of arsenic is kept above 85. 83% and changes a little with the temperature when it surpasses 850 ℃. The volatilization of zinc is continuously increased with the rising of temperature(750 - 1100℃). When the pellets are roasted at 1 100 ℃, zinc volatilization is 82. 55% with the

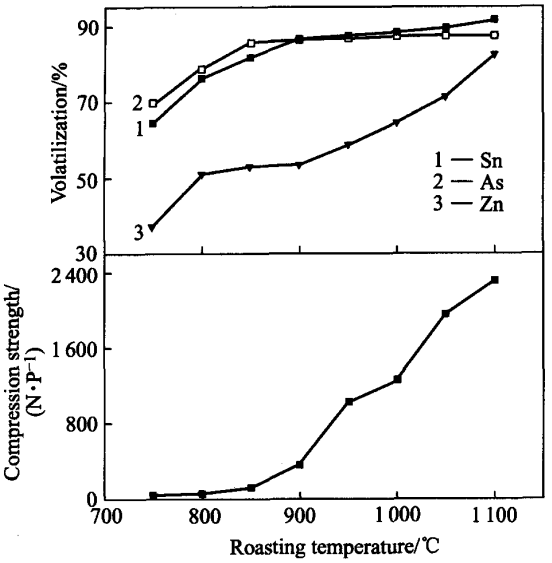


Fig. 5 Effect of roasting temperature on roasting results

remains of 0.058% zinc in the finished pellets. Therefore, the suitable roasting temperature should be between 1 050 ℃ and 1 100 ℃.

4.4 Effect of roasting time

Effect of roasting time on the roasted results is shown in Fig. 6. Experimental conditions are kept at 8% coke breeze, 2% $CaCl_2$ and 1 100 ℃ roasting temperature.

It can be seen from Fig. 6, the compression of the roasted pellets and the volatilization of tin and zinc are continuously increased with the increase of roasting time. When time is over 30 min, the compression strength is greater than 2 100 N/P. When roasting time increases from 10 min to 20 min, the volatilizations of tin, arsenic and zinc increase quickly and about 90% of tin, 85% of arsenic and 80% of zinc are volatilized into gaseous phase in 20 min. With the further increase of roasting time, the volatilization is increased slowly. When the time is above 40 min, remaining contents of tin, arsenic and zinc are all under 0.08%.

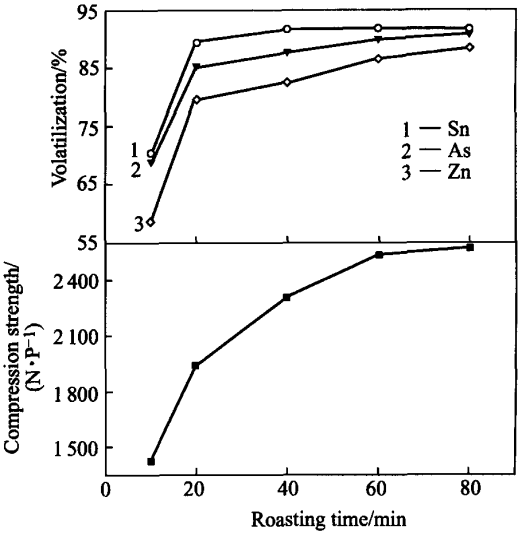


Fig. 6 Effect of roasting time on roasting results

Seen from the results and discussion, the suitable roasting time is between 30 and 40 min.

4.5 Dynamic roasting experiment

Previous tests are conducted in a static furnace. The dynamic experiment is performed in an intermittent rotary kiln with a diameter of 1 m. The experimental conditions are that the pellets with coke breeze (8%) and $CaCl_2$ (0.5% and 2%) are roasted for 40 min and the temperature is controlled between 1 060 ℃ and 1 080 ℃. The performances of the product pellets are presented in Table 3.

The results in Table 3 indicate that the compression strength of the product pellets is greater than 2 500 N/P, the tumble index is higher than 97%, and the contents of tin, arsenic and zinc in the pellets are all less than 0.06%. All the indexes of the pellets meet the requirement of ironmaking in blast furnaces. It is found that the dosage of $CaCl_2$ can be greatly reduced to 0.5% from 2%, which may be due to the improved dynamic conditions for tin, arsenic and zinc volatilization in the rotary kiln.

Table 3 Performances of product pellets by roasting in rotary kiln

$CaCl_2$ dosage/%	Pellet strength			Primary chemical compositions of product pellets/%				Volatilization/%		
	Compression strength/(N/P)	Tumble index/(+6.3 mm, %)	Abrasion index/(−0.5 mm, %)	Sn	As	Zn	TFe	Sn	As	Zn
0.5	2 625	97.57	1.24	0.045	0.056	0.060	67.96	91.02	90.46	81.45
2.0	2 573	97.26	1.35	0.043	0.050	0.058	67.53	91.49	90.53	82.22

Since tin, arsenic and zinc are easily volatilized into gaseous phase, they can be selectively recovered in the dust collecting system. As well known, the traditional chlorination processes often use over 4% chlorinating agent and anticorrosive process has been successfully applied in the whole production. This process, only using 0.5% $CaCl_2$, possesses a promising perspective.

5 CONCLUSIONS

1) SEM analysis shows that the symbiosis of valuable metals in tin, zinc-bearing iron concentrates are so complex that it is difficult to effectively recover them by beneficiation and traditional sintering and pelletizing process.

2) The thermodynamic analyses show that tin, arsenic, zinc and iron can be separated from one another by selective chlorination. Tin, arsenic and zinc can be chlorinated and volatilized selectively and iron will remain in the roasted product by properly controlling chloride dosage and roasting conditions.

3) The static bench-scale experiments show that appropriate conditions of comprehensive recovery of tin, arsenic and zinc containing iron concentrates are balling the concentrate with 8% coke breeze and 2% $CaCl_2$, and roasting at 1 050 - 1 100 ℃ for 40 min.

4) The dynamic rotary kiln experiments show that the dosage of $CaCl_2$ can be reduced to 0.5%, and the product pellets with the compression strength of 2 625 N/P, the tumble index of 97.57%, the abrasion index of 1.24%, tin, arsenic and zinc residues of 0.045%, 0.056% and 0.060% are achieved. The performances of the pellets meet the requirements of ironmaking.

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