Sr speciation in producing SrCO₃ with celestite

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Abstract Strontium speciation transferring in strontium residue and mixing strontium ore are investigated with extracting experiment, X-ray powder diffraction (XRD), X-ray fluorescence spectrometer (XRF) and Atomic Absorption Spectroscopy (AAS). The results show that there are strontium carbonate, strontium sulfate, strontium sulfide, and a little amount of strontium silicate and strontium ferrite in strontium residue. Impurities in strontium residue mainly contain carbonate and oxide of calcium, iron, magnesium and aluminum etc. The amount of strontium sulfide in strontium residue is larger than that in strontium ore. And a little strontium silicate and strontium ferrite are found in strontium ore. It is concluded that acid soluble method is used firstly in the process of producing strontium carbonate from mixing strontium ore. In addition, mechanical smash method and surface active treatment to strontium samples are beneficial to the ratio-leaching increase of strontium. The research achievement helps to save energy and decrease pollutants emission in strontium processing industry.

Key words strontium speciation; celestite; strontium residue; strontium ore; impurity

1 Introduction

Strontium carbonate is a significant inorganic chemical raw material, and mainly applied to the production of color kinescope, magnetic materials, glass, electronics ceramics, metallurgy, metal strontium and strontium salt (Wu and Wang, 2008). In recent years, the demand for strontium carbonate increase with the vigorous development of domestic automobile, computer and home appliance manufacture, attracting much attention. China has a large amount of strontium carbonate and strontium sulfate in strontianite and celestite resources. Celestite is mostly seen in Chongqing, Sichuan, Yunnan, Hubei, Qinghai, Jiangsu, and Xinjiang provinces. And a great deal of strontium minerals is medium-grade (30%-60%), which is explored and used in industry. The old ore-processing technology and the low leaching utilization ratio of strontium ore lead to huge waste of strontium resources and serious environmental pollution. Scientists pay intensive attention to the extraction improvement of preparing strontium carbonate from strontium ore in recent years (Xu et al., 2008, 2010; Liu et al., 2011, 2012; Zhu and Luo, 2011; Wang et al., 2010; Kang et al., 2011; Rangel et al., 2009). While, there are few reports of elements speciation analysis and characteristics of strontium ore and strontium residue. The effece of coexisting elements on the leaching rate of strontium were systemically researched in the work.

2 Main instruments and methods

2.1 Instruments

XRF-1800 (Shimadzu), AAS (WFX-110, Beijing Rayleigh Analytical Instrument Co., Ltd), XRD-6000 (Shimadzu).

2.2 Methods

Strontium ore and strontium residue were from the Dazu Mine, Chongqing. The residue and ore were powdered and sieved ~75 μ m. The sample was dried at 105–110°C in oven. Components of the residue and ore were tested by XRF. 0.50 g strontium residue and 40 mL water were added into a 150 mL beaker, micro-boiled for 20–30 minutes until the suspension volume was about 20 mL and filtered. The content of soluble strontium was tested by AAS. The residue was used for the following determinations. The content of strontium carbonate in residue was analyzed according to HG/T2428-93. The content of strontium sulfate was examined after conversing strontium sulfate into strontium carbonate (Jin et al., 2002). Strontium silicate was detected by the method of Jin (2011). The phases of strontium residue were measured with XRD.

3 Results and discussion

3.1 Elements analysis of strontium ore and strontium residue

The components of strontium residue and strontium ore are listed in Table 1. It shows that only 24.3% of strontium was effectively used in preparing strontium carbonate from strontium ore, and a large amount of strontium remains in the residue (equivalent to a grade of 52.7% ore, the raw ore was the grade of 69.7%). The contents of Ca, Fe, Mg, and Al in strontium residue are larger than that in strontium ore, and the presence of them would disturb the dissolution of strontium in strontium ore.

3.2 Strontium speciation in strontium ore and strontium residue

The XRD pattern of strontium residue is shown in Fig. 1. The main phase of strontium residue involved in SrSO₄, CaCO₃, SrCO₃, SiO₂, FeS, Fe₃O₄, Fe_2O_3 , CaS, CaSO₄, MgO, MgCO₃, Al₂O₃, and 2Al₂O₃-3SiO₂ are shown in the Figure.

The average contents of different strontium data in strontium residue and strontium ore are listed in Table 2. The result shows that there were strontium carbonate, strontium sulfate, strontium sulfide, and a little amount of strontium silicate and strontium ferrite in strontium residue. The main component of strontium ore was strontium sulfate, often associated with strontianite. Strontium ore contains soluble strontium, carbonate, sulfate and residual state, and strontium silicate and strontium ferrite barely exist in strontium ore. The strontium speciation in strontium ore is simpler than that in strontium residue.

The reduction reaction usually happens on the surface or inner layers of ore instead of center location for the limit condition of temperature or time. Thus, there was high content of strontium carbonate and strontium sulfate remaining in strontium residue. SrS was formed on the surface of strontium sulfate particles as the reaction went on. The total reaction rate slowed down as the increase of impact of ash layer diffusion. High temperature and small particle size were conducive to improving the productive rate and to shortening reaction time. SrS was oxidized finally in the carbon-reduction process, thus, the forming ratio of soluble strontium was decreased (Meng et al., 2009). The grade of strontium residue was equivalent to 50%-60% strontium ore, namely, low utilization of strontium was illustrated.

 Table 1
 Components and contents of strontium residue and strontium ore (%)

Component	Sr	Fe	Al	Mg	Ca	0	S	Si	Ba	Κ	Ti	Mn	Р
Ore	33.25	0.94	1.30	1.66	6.45	33.66	10.42	5.61	0.84	0.61	0.13	/	/
Residue	25.16	3.87	2.21	2.74	13.47	37.06	7.14	6.74	0.58	0.47	0.33	0.04	0.03

 Table 2
 Main speciation, relative content, extraction rate of strontium in waste residues and strontium ore (%)

Sample		Stro	Total	RE	Extraction					
Sample	Carbonate	Sulfate	Sulfide	Ferrate	Silicate	Residue	content	KL	ratio	
S _{1 A}	15.13	5.22	2.45	0.69	0.81	0.81	25.11	-0.19	96.58	
В	8.95	21.44	1.98	0	0	0.83	33.20	-0.15	97.35	
S _{2 A}	15.10	5.24	2.48	0.68	0.82	0.78	25.10	-0.24	96.66	
В	8.93	21.45	2.00	0	0	0.82	33.20	-0.15	97.38	
S _{3 A}	15.12	5.25	2.47	0.70	0.80	0.79	25.13	-0.13	96.74	
В	8.95	21.45	1.98	0	0	0.82	33.20	-0.15	97.38	
S4 A	15.12	5.26	2.46	0.69	0.81	0.77	25.11	-0.19	96.74	
В	8.94	21.44	1.99	0	0	0.83	33.20	-0.15	97.35	
S5 A	15.11	5.21	2.48	0.71	0.79	0.81	25.11	-0.19	96.58	
В	8.94	21.44	1.97	0	0	0.84	33.19	-0.18	97.29	
Smean A	15.12	5.24	2.47	0.69	0.81	0.79	25.11	-0.19	96.66	
В	8.94	21.44	1.98	0	0	0.83	33.20	-0.15	97.35	

Note: A. Waste residue; B. strontium ore; RE%=[(strontium total content-strontium real content)/strontium real content]×100%; extraction ratio=(extraction total content/strontium real content)×100%.



Fig. 1. The XRD pattern of waste residue.

3.3 Effect factors on leaching rate of strontium

High temperature carbon reducing method is the main method in industry. However, there are a variety of side effects in the process of preparing strontium carbonate from strontium ore at high temperature. And large amount of carbon is consumed, making effective carbon in the ratio of carbon and strontium reduced, and the reaction of strontium compounds partly reduced.

Coexisting elements Ca, Fe, Mg and Al are involved in reaction, which affects the leaching rate of strontium. The calcium content in Table 1 is the largest of companying metal elements in both strontium residue and strontium ore. Calcium in strontium ore exists mainly in the state of aragonite with a few of calcite, dolomite and gypsum. Impurities calcium compounds cause side reactions in carbon reducing reaction and consume much carbon. As a result, calcium compounds decompose and form calcium sulfide and calcium oxide (Zhang et al., 2010). The conclusion is proved by Fig. 1. Namely,

 $CaSO_4+2C=CaS+CO_2\uparrow \\CaS+3CaSO_4=4CaO+4SO_2\uparrow \\2CaSO_4+C=2CaO+2SO_2\uparrow+CO_2\uparrow \\$

Iron element existed mainly in Fe_2O_3 , Fe_3O_4 , FeO, $Fe_2O_3 \cdot nH_2O$, FeCO₃ and FeS₂ in ore. In the carbon reduction, impurity iron compounds also involved in reaction (Gong et al., 2006). So there were Fe_2O_3 , Fe_3O_4 and a little strontium ferrite in strontium residue. (Fig. 1).

$$3Fe_2O_3+CO=2Fe_3O_4+CO_2$$

 $Fe_3O_4+CO=3FeO+CO_2$
 $1/4Fe_3O_4+CO=3/4Fe+CO_2$
 $SrCO_3+Fe_2O_3=SrFe_{12}O_{19}$

Magnesium mainly exists as magnesite and dolomite in strontium ore. Fig. 1 also shows the spectra of magnesium oxide and magnesium carbonate. The result is consistent with the reference (Jin, 2011). Kaolinite is one associated mineral in strontium ore. After high temperature carbon reducing, Al_2O_3 and $Al_6Si_2O_{13}$ remain in strontium residue.

The decomposition reactions of calcium, iron, magnesium, and aluminum compounds in strontium ore happen at high temperature, so that energy consumption and the product cost increas, while the product quality become low.

In the strontium leaching process, SDS shows strong chemical adsorption with strontium. It indicates in two aspects: (1) on the celestite (SrSO₄) surface, SDS and celestite exchange their cation to generate $C_{12}H_{25}$ -OSO₃-Sr. This could float celestite effectively. (2) SDS reacts with water to form alcohol in the acidic solution. The existence of alcohol improves the surface activity of SDS. This is the role of helper leaching agent. It can effectively increase the leaching rate of strontium.

The above discussions demonstrate that preparing strontium carbonate directly from strontium ore brings a serious of environmental problems and great waste of mineral resource if the ore is not treated ahead of the process. It proves acid soluble method should be used firstly to extract strontium carbonate, and then mechanical smash method and surface active treatment are adopted to strengthen the depth of the carbon reduction reaction or the reduction degree of strontium sulfate.

4 Conclusions

(1) There are strontium carbonate, strontium sulfate and strontium sulfide, including a little strontium silicate and strontium ferrite in the strontium residue. Strontium silicate and strontium ferrite hardly exist in strontium ore. There was about 25% strontium remain in strontium residue, and the grade of strontium residue is 50%–60% (relative to strontium ore). The utilization rate of strontium is low.

(2) Calcium, iron, magnesium, and aluminum compounds in strontium ore would cause side reactions at high temperature. The side reactions not only increase energy consumption and product cost, but also reduce the product quality.

(3) Acid soluble method could be used to extract strontium carbonate at first, and mechanical smash method and surface active treatment are adopted to increase extraction rate of strontium ore. The improving process is good to reduce pollutants emission and save energy in industrial strontium carbonate production. Acknowledgements We were in appreciation of the Brainstorm Project Foundation by Scientific and Technological Committee of Chongqing (CSTC, 2010AC7180).

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