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Preparation of Chromium-iron Metal Powder from Chromium Slag by Reduction Roasting and Magnetic Separation

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Abstract: Chromium slag (CS) has become one of the most hazardous solid waste containing chromium and iron. Based on its characteristics, the technology of reduction roasting and magnetic separation was employed to treat CS. The major impurity element of CS is magnesium and it exists in magnesium ferrite phase, which is hard to recover iron in the absence of additives. During reduction roasting, additives (Al_2O_3 and CaF_2) could destroy the structure of magnesium ferrite and improve the iron grade and recovery. The final product, i. e. chromium-iron powder, contains 72.54% Fe and 13.56% Cr, with the iron recovery of 80.34% and chromium recovery of 80.70%.

Key words: chromium slag; reduction roasting; magnetic separation; chromium-iron metal powder

As a residue of chromate and metallic chromium production, chromium slag (CS) is one of the 47 kinds of hazardous waste listed in China. About 7 t CS is produced when 1 t metallic chromium is manufactured, while about 1.7－4.2 t CS is discharged when 1 t sodium dichromate is manufactured[1,2]. In China, it is estimated that about 0.8 Mt CS is generated every year and about 6 Mt CS are stacked[3,4]. Heavy metal ions usually seep from the landfill site or pipelines into ground or underground water, which causes environmental problems. In the meantime, CS is a solid waste containing chromium, iron, and other valuable metals, which causes the waste of resources.

There are many methods to treat CS, such as stabilization, pyrometallurgical, hydrometallurgical and biometallurgical process[5,6]. Stabilization is favorable abroad but consumes a great deal of cement and energy[7-9]. The hydrometallurgical methods have a high cost of reducing reagents which could lead to a secondary pollution, and the biological methods have a low efficiency because of long reaction time[10,11]. The pyrometallurgical process, such as the technology of reduction roasting and magnetic separation, is an effective way to recycle valuable metals from secondary resources containing iron[12,13]. Therefore, the technology of reduction roasting and magnetic separation was developed to treat CS in this paper.

1 Experimental

1.1 Materials

CS samples were provided by a plant in Hubei, China. CS samples were ground before the experiment and their particle size is 80% passing through 0.074 mm. The chemical compositions of CS samples are shown in Table 1.

Table 1 Chemical compositions of CS samples

mass%

Total Fe	Total Cr	MgO	SiO_2	Al_2O_3	Na_2O	CaO	MnO	CuO
31.49	5.86	20.83	8.13	7.26	6.13	2.69	0.45	0.22

The X-ray diffraction (XRD) pattern of CS is given in Fig. 1. Chromium and iron in CS mainly exist in the phases of $FeCr_2O_4$, Fe_2SiO_4, $MgFe_2O_4$, and Fe_3O_4.

Anthracite was used as reductant and the proximate analysis results are given in Table 2. The particle size of anthracite is 70.84% passing through 0.125 mm. Analytical reagent grade Al_2O_3 and CaF_2

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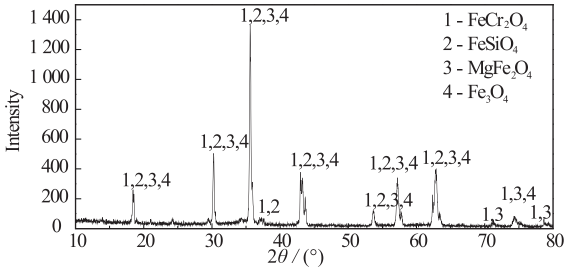


Fig. 1 XRD pattern of chromium slag

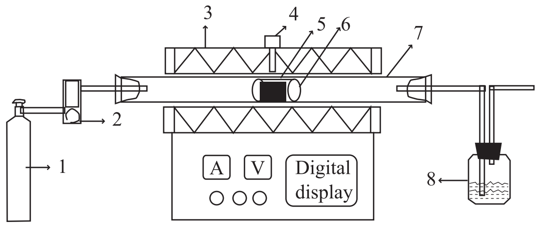
Table 2 Proximate analysis of anthracite mass%

Fixed carbon	Ash	Volatile	S	H_2O
80.36	10.54	8.52	0.41	8.15

were employed as the additives.

1.2 Instrumentation

The experimental equipment is shown in Fig. 2. The heating element of the tube furnace is silicon molybdenum rod with the highest heating temperature of 1 673 K. The quartz tube of 70 mm in diameter and 1 600 mm in length was used as a reaction vessel.



1—N_2 bottle; 2—Flow meter; 3—Furnace; 4—Thermocouple; 5—Sample; 6—Graphite crucible; 7—Quartz tube; 8—Water.

Fig. 2 Experimental equipment

1.3 Methods

1.3.1 Methods of analysis

The chemical compositions of CS samples and final product were analyzed by X-ray fluorescence (XRF) spectrometer of Thermo Fisher Scientific. The crystalline phase of CS samples was investigated by XRD technique, using Ni-filtered Cu Kα, operated at 40 kV and 100 mA and scanning rate of 4 (°)/min from 10° to 80°. The structures and element distribution of final product were analyzed by JSM-6490LV scanning electron microscope (SEM) with energy dispersive system (EDS).

1.3.2 Reduction roasting and magnetic separation

The main process of the experimentis presented in Fig. 3. For every batch, 100 g CS and 30 g anthracite were used and mixed with some additives. The mixture was pressured by self-made mold of 20 mm in diameter and 20 mm in height; then, the briquettes were dried at 378 K for 4 h in the oven.

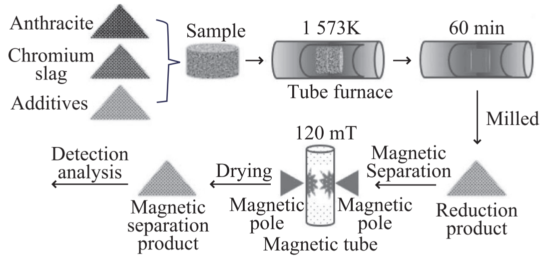


Fig. 3 Main process of the experiment

The graphite crucible containing dried briquettes was put into the quartz tube when temperature reached 1 573 K. N_2 was introduced into the quartz tube to expel the air for 1 min and then the graphite crucible was put in the flat-temperature zone, followed by roasting for 60 min. N_2 was introduced into quartz tube to cool down when reduction roasting was finished, and the reduced briquettes were obtained.

The magnetic separation was performed in the magnetic tube after the reduced briquettes were ground in the cone ball mill. The product was obtained after magnetic separation at the grinding fineness of 80% powder passing through 0.074 mm. The model of cone ball mill is XMQ240×90 and the laboratory magnetic equipment is Davis tube of XCGS-73.

The grade and recovery of iron and chromium of product were considered as the evaluating indexes. The recovery of iron and chromium was calculated by Eq. (1).

$$R_x = \frac{m_2 \times w_x}{[m_{cs}/(m_{cs}+m_{an}+m_{ad})] \times m_1 \times w_{x,cs}} \qquad (1)$$

where, R_x is the recovery of x (x=Fe or Cr); w_x is the mass fraction of x in product; m_1 is the mass of briquettes; m_2 is the mass of product; m_{cs}, m_{an} and m_{ad} are the mass of CS, anthracite and additives in mixture, respectively; and $w_{x,cs}$ is the mass fraction of x in CS.

1.4 Experimental mechanism

According to the XRD result of CS, the direct reduction reactions of the minerals containing iron or chromium in the CS mainly include the following equations:

$$1/4\,Fe_3O_4 + C = 3/4Fe + CO\uparrow \qquad (2)$$

$$Fe_2SiO_4 + 2C = 2Fe + SiO_2 + 2CO\uparrow \qquad (3)$$

$$FeO \cdot Cr_2O_3 + C = Fe + Cr_2O_3 + CO\uparrow \qquad (4)$$