



Novel method to prepare sodium chromate from carbon ferrochrome



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Abstract: An oxidizing roasting process of carbon ferrochrome to prepare sodium chromate in the presence of sodium carbonate and air was investigated. The effects of reaction temperature, reaction time, mole ratio of sodium carbonate to carbon ferrochrome were studied, and thermodynamics and kinetics of the reaction were also discussed. It was observed that there was a sudden increase in reaction rate when the temperature rose to a certain value, and the sample with a smaller grain size could start the sudden increase at a lower temperature. The chromium recovery rate increased with the increase of mole ratio of sodium carbonate to carbon ferrochrome, and it reached up to 99.34% when mole ratio of sodium carbonate to carbon ferrochrome increased to 1.2:1. The chromium residue yielded from this method was only about 1/3 of the product. Moreover, the content of Fe in the residue was as high as 60.41%. Therefore, it can be easily recovered to produce sponge iron, realizing complete detoxication and zero-emission of chromium residue.

Key words: carbon ferrochrome; sodium chromate; oxidizing roasting; chromium residue; zero-emission

1 Introduction

Chromate compounds are important chemical products, which have been widely used in metallurgy, chemistry, material and leather-making. Normally, the chromate products are achieved via a soda–ash roasting process, which is now under enormous pressure due to the environmental problems [1]. In this soda–ash roasting process, lime with about 100% (mass fraction) of the chromite ore was incorporated in the charge to control the siliceous and acid gangue minerals in the ore. But the addition of lime generates a large quantity of highly alkaline chromite ore processing residue (COPR), which contains hexavalent chromium of 1%–2% (mass fraction). It also results in the generation of CaCrO_4 , which is volatile and airborne, causing a major threat to human, animal, and plant health. The remediation of the COPR is either too expensive or not thorough [2,3]. Although the lime-free roasting process can reduce the COPR and restrict the generation of CaCrO_4 , the necessity for high grade chromite ores with silica content of less than 1% restricts its wide application [4].

Carbon ferrochrome (CrFeC) is a kind of intermediate product of chromium metallurgy, which is

mainly used for producing stainless steel, tool steel, ball-bearing steel, heat resistant steel, and so on [5]. CrFeC is produced from chromite ore through a electric furnace reduction process, and thanks to the strong reducing atmosphere, the slag yielded from this process has no hexavalent chromium, therefore, it nearly has no threat to the environment. Because the factories for producing CrFeC are always built in areas where electric power and mineral resources are rich, there are only fewer economic disadvantages using CrFeC as raw material than using chromite ore. Accordingly, a novel method to prepare Na_2CrO_4 from CrFeC through an oxidizing roasting process was proposed. The residue emitted from this process was very little, and mainly consisted of iron oxides, which could be easily recovered to produce sponge iron. Therefore, the target of zero-emission of chromium residue can be realized, and the chromium residue pollution problem can be resolved completely.

2 Experimental

CrFeC specimen originated from Africa was provided by Jiafei New Material Co., Ltd., Hunan Province, China. The particle size of the CrFeC

specimen is 12.6 μm (median diameter). The chemical components and the phase compositions are shown in Table 1 and Fig. 1, respectively.

Table 1 Chemical components of CrFeC (mass fraction, %)

Cr	Na	Fe	S	C
60.6	0.013	27.9	5.0×10^{-3}	8.7
Mn	V	Mg	Pb	Co
1.9	0.06	0.12	3.2×10^{-3}	0.14
Si	Ni	Al	Ti	
0.24	0.11	0.14	0.095	

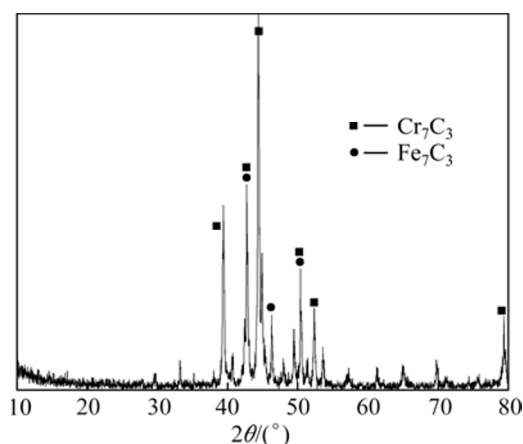
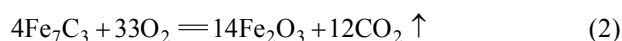
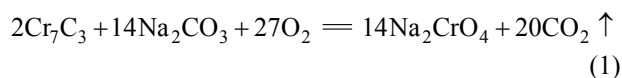


Fig. 1 XRD pattern of CrFeC

According to the chemical analysis results in Table 1 and the XRD pattern in Fig. 1, the main components of CrFeC are Cr_7C_3 and Fe_7C_3 . During the roasting process, Cr_7C_3 is oxidized to Na_2CrO_4 in the presence of O_2 and Na_2CO_3 , while the component of Fe_7C_3 is converted to Fe_2O_3 . The equations of the main reactions are as follows [6]:



The experiments were carried out in a muffle furnace. Temperature was precisely controlled by a programming temperature controller. CrFeC was mixed homogeneously with a certain amount of Na_2CO_3 in a porcelain mortar. Then, the mixture was loaded in a corundum boat and put into the muffle furnace when temperature of the muffle furnace rose to the specified value. When time was up, the roasted product was taken out and cooled quickly. The roasted product was leached in distilled water at 313 K with the liquid-to-solid ratio of 5:1 (mass fraction), and then washed three times under the same condition. At last, it was filtered to get a chromate solution and a solid residue. The solution was analyzed for Cr and other impurities. The conversion rate

was calculated according to the following formula:

$$r = \frac{m_r}{m_o} \times 100\% \quad (3)$$

where r is the conversion rate of Cr; m_r is the total quantity of Cr in the solution and m_o is the total quantity of Cr in CrFeC. While the residue was analyzed for Cr(VI) to determine the quantity of Cr(VI) remaining in the residue.

The leaching solution was analyzed by inductively coupled plasma-optical emission spectrometer (ICP-OES, PE Optima 5300DV, Perkin Elmer), and the residues were analyzed with a volumetric titration method. The phase identification was carried out on an X-ray diffraction (XRD, Phillips PW223/30). The particle size distribution was measured by a particle size analyzer (LS230, Beckman, Coulter). SEM (scanning electron microscopy) images were taken on a JSM-35CF SEM equipment (Japan Electron Optics Laboratory Co., Ltd.). Thermoanalysis was performed on a universal V4.0C TA instrument (SDT Q600 V8.0 Build 95).

3 Results and discussion

3.1 Thermodynamical analysis

The standard Gibbs energy changes ($\Delta_r G^\ominus$) and standard enthalpy changes ($\Delta_r H^\ominus$) of Reaction (1) are shown in Figs. 2 and 3, respectively. They are calculated using the method in Ref. [7] following the assumptions below:

- 1) All the components in Reaction (1) are pure substances.
- 2) The gases of oxygen and carbon dioxide are all in standard state.
- 3) Cr_7C_3 is solid, and its activity is equal to 1. Na_2CrO_4 and Na_2CO_3 can be in liquid or solid state, depending on the roasting temperature, and their activities are equal to 1.

The highly negative values of $\Delta_r G^\ominus$ shown in Fig. 2

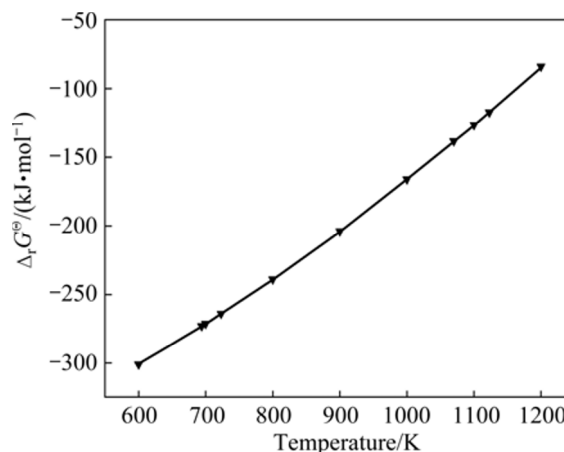


Fig. 2 $\Delta_r G^\ominus$ of Reaction (1) at 600–1200 K

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