

Green metallurgical processing of chromite

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Abstract

A new green metallurgical process for chromite ore has been proposed and developed to solve the serious environmental problem in the traditional production process of chromate. In the new process, the oxidation of chromite ore is carried out in sub-molten potassium hydroxide at 300 °C. Compared with the traditional roasting process in a rotary kiln at 1200 °C, the oxidation and mass transfer are greatly intensified in the new process. Chemical conversion of chromium is above 99% and the recovery of chromium is raised by more than 20% while the reaction temperature is dropped by 900 °C. Thus the energy consumption is decreased. Furthermore, as no limestone or dolomite additives are required, the amount of chromium-containing residue is decreased from 2.5 tonnes to 0.5 tonnes with the production of 1.0 tonne of product in the new process. As all reactions and separating operations are performed in liquid media, pollution due to toxic dust is prevented.

With the change of reaction medium, the new process achieves higher resource and energy utilization efficiency. At the same time, the new process also changes the physical and chemical properties of other components co-existing in the chromite ore. The process provides the possibility for virtually complete utilization of chromite and zero emission of residue. Thus, the clean production of chromate can be realized.

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1. Introduction

Chromate production from chromite ore is an important basic metallurgical process but is usually a source of severe pollution. The traditional chromate production process used in China presently consists of three procedures: roasting of chromite ore, water leaching, and multi-stage evaporation and crystallization. In the process of roasting, chromite is mixed with sodium carbonate and a large amount of limestone and dolomite additives, and then calcined at 1200 °C in a rotary kiln.

The utilization of reagents and energy in the calcination process is quite low. In particular, a large amount of chromium-containing residue, chromite dusts and waste gases are discharged from chromate plants, which results in serious pollution problems all over the world. The key reaction of chromate production is the oxidation of chromium from Cr(III) to Cr(VI) by the oxygen in air. In the conventional process, limestone and dolomite additives are applied to avoid agglomeration of chromite particles and enhance the mass transfer of oxygen through thickening reaction products around the chromite particle. The amount of additives used in the process can be twice as much as that of the chromite ore, which causes a large amount of chromium-containing residue. Many new methods, such as acid leaching

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(Amer, 1992; Amer and Ibrahim, 1996; Geveci et al., 2002), alkali leaching at atmospheric pressure (Zhang et al., 1998a,b; Hundley and Nilsen, 1985) or at higher pressures (Farrow and Burkin, 1975), as well as various investigations on soda-ash roasting have been reported (Arndt et al., 1996; Chandra et al., 1996; Arslan and Orhan, 1997; Kowalski and Mazanek, 1998; Tathavadkar et al., 2001; Weber et al., 1993; Bellinghausena et al., 1998). But many difficulties still exist in their industrialization and the pollution problem has not been completely resolved.

Prompted by urgent social needs, a green metallurgical process for chromite ore has been developed by the Institute of Process Engineering, Chinese Academy of Sciences (Zhang, 2001; Cui and Zhang, 2000; Zhang et al., 1998a,b; Zheng and Zhang, 1999) according to the principles of green chemistry and cleaner production (Trost, 1991; Allen and Shonnard, 2001; Grossmann and Westerberg, 2000). The key point of the new process is a continuous liquid phase oxidation of chromite ore in the sub-molten salt medium at 300 °C. This paper describes the reaction kinetics, thermodynamics and mechanism of the system as well as the industrial results of a demonstration plant.

2. Green chemistry of the metallurgical process of chromite

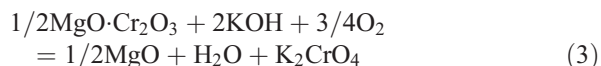
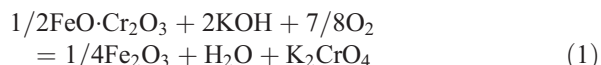
2.1. Efficiency of the chemical reaction in the sub-molten salt medium

Compared with the gas–solid reactions of chromite with sodium carbonate and oxygen at high temperature (1200 °C), the reaction and separation in the new process can be controlled quantitatively and easily. This is because O^{2-} exchange in the sub-molten salt medium is similar to that in the solvent, and the heat and mass transfer in the sub-molten salt medium are enhanced. Hence, the efficiency and selectivity of chromite oxidation are improved significantly along with a great reduction in energy consumption.

2.2. Thermodynamic analysis

The major chromium-bearing mineral can be ideally represented as $FeO \cdot Cr_2O_3$. However, it rarely exists in nature as pure iron oxide and chromic oxide and FeO is always replaced in part by isomorphous crystals, such as Al_2O_3 and MgO . The general formula of the chromium-bearing mineral is $(Mg_xFe_{1-x})O \cdot (Al_yCr_{1-y})_2O_3$. Silica co-exists with chromite ores as a gangue mineral. When reacting with oxygen (or air) in the fluid medium of

potassium hydroxide, chromite ore will undertake the following main chemical reactions:



The relationship between the standard Gibbs free energy change ($\Delta_r G^\circ$) and temperature for main reactions (1), (2), and (3) is shown in Fig. 1, and that of the traditional roasting process is shown in Fig. 2. Since $\Delta_r G^\circ$ of the main reaction (1) has a large negative value, trivalent chromium is easily oxidized to hexavalent chromium. Under the same reaction conditions, the thermodynamic tendency of the reaction is: $FeO \cdot Cr_2O_3 > Cr_2O_3 > MgO \cdot Cr_2O_3$. Thermodynamically, the reaction of $FeO \cdot Cr_2O_3$ with sub-molten potassium hydroxide is much more favorable than with sodium carbonate in the traditional roasting of chromite. The change of standard Gibbs free energy, $\Delta_r G^\circ$, is much lower than that of the traditional roasting process. Since the liquid phase oxidation of chromite in sub-molten potassium hydroxide is an exothermic reaction, it is favorable for lowering the energy consumption.

2.3. Experimental

Low-grade massive chromite specimens from Vietnam were used. The samples were crushed, ground and dry-sieved to different narrow size fractions. Table 1 gives the chemical analysis results of the chromite ore.

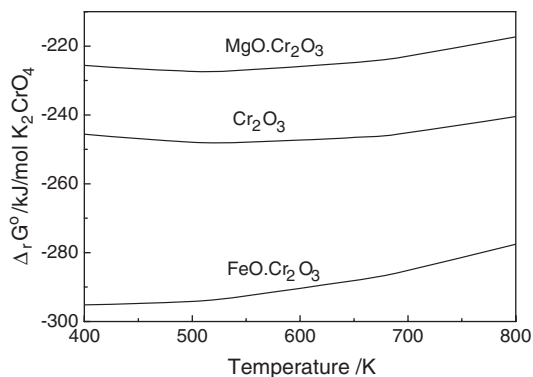


Fig. 1. Standard Gibbs free energy change vs. temperature in the sub-molten KOH phase oxidation process.

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