

Decomposition of chromite ore by oxygen in molten NaOH–NaNO₃

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ABSTRACT

An optimized process production of chromate by oxygen was proposed. The tests are executed by introducing NaNO₃ to the decomposition process of chromite ore in molten NaOH to decrease the decomposition temperature. An interesting result is that the reaction temperature could decrease from above 500 °C to about 400 °C, and sodium nitrate has no consumption in the oxidation process, while the Cr yield is above 99%. Mechanism analysis shows that chromite ore is firstly oxidized by NaNO₃, where NaNO₂ is generated as a reduction product, and then is oxidized to NaNO₃. NaNO₃ plays the role of oxygen carrier, which can reduce the mass transfer resistance of oxygen. The kinetic study shows that the decomposition process was an internal diffusion controlled, with an apparent activation energy of 106 kJ/mol. Effects of liquid-to-ore ratio, chromite ore particle size, and reaction temperature on the decomposition of chromite ore were also studied.

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1. Introduction

Chromite ore is the most important mineral for chromate production (Ding and Ji, 2003). Traditionally, chromite ore is processed by roasting with sodium carbonate at 1200 °C in a rotary kiln with the addition of limestone and dolomite, yielding only 75% of Cr in the ore. Furthermore, the residue discharged (2.5–3.0 ton per ton chromate product) contains hexavalent chromium causing significant environmental pollution. Although improved roasting technologies, the use of less or none of calcium-containing chemicals, have been developed to improve Cr yield to nearly 90% and reduced the hazardous residue to 0.8 ton per ton chromate product. The low Cr yield, high energy consumption due to high temperature roasting, as well as the environmental pollution by hexavalent chromium-containing residue has remained unsolved.

Liquid-phase oxidation of chromite ore as an alternate approach for chromate production has been studied since 1970s, in which chromite ore is oxidized in the liquid medium, such as molten NaOH, KOH. Kashiwase et al. (1974a,b) investigated such oxidation reaction in molten NaOH and NaNO₃ at a temperature range of 270–350 °C, in which sodium nitrate was reduced to nitrite. The technology was not economic due to the consumption of expensive sodium nitrate, and the disposal of sodium nitrite remained a problem. In addition, the high alkali-to-ore ratio (30:1) also limited its industrial application.

In other studies, chromite ore was oxidized by oxygen or air in molten sodium hydroxide at a reaction temperature of above 500 °C with an alkali-to-ore of 4:1 (Hundley et al., 1985; Chandra et al., 1996; Arslan and Orhan, 1997; Charles et al., 1974). Many efforts have been made to decrease the reaction temperature including mechanical activation of the chromite ore in sodium hydroxide at temperatures below 240 °C under pressurized oxygen (10 bar). This led to 98% chromium extraction in 120 min (Amer and Ibrahim, 1996). Recently, a novel process of oxidizing chromite ore using high-concentration of potassium hydroxide solution by air was proposed (Yang, 1996; Zhang et al., 1998, 2005; Zheng, 2000; Xu et al., 2005; Zheng et al., 2006; Sun et al., 2007). In this process, Cr yield could be raised to 99% at a temperature of 300 °C with an alkali-to-ore ratio of 4:1. The residue of the process was reduced to one-fifth of the traditional roasting process and could be used as high valued desulphurization agent, which eliminated the pollution of Cr-containing residue. A demonstration plant has been built in China and runs well. Though, it can only produce potassium-containing chromate products (such as K₂CrO₄ and K₂Cr₂O₇) instead of sodium dichromate as products, which are utilized larger than potassium-containing products in industries.

In this paper, an optimized process for sodium chromate production is proposed. NaNO₃ was introduced to the process of chromite oxidation with oxygen or air in molten sodium hydroxide to intensify the reaction. It seems that sodium nitrate serves as an oxygen carrier rather than chemical oxidant. The thermodynamics, macro-kinetics of the process with NaNO₃ added, as well as the behavior of sodium nitrate were investigated in this paper.

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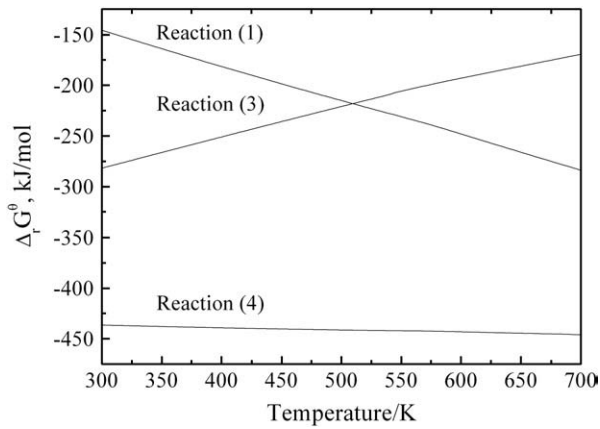
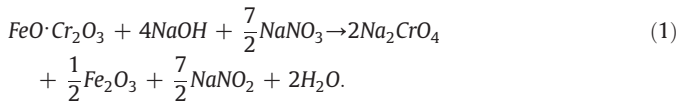


Fig. 1. $\Delta_r G^\circ$ for Eqs. (1), (3) and (4) at 300–700 K.

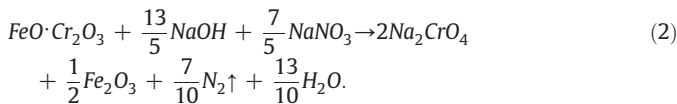
2. Description of the proposed process

2.1. Thermodynamics

The chromite ore can be ideally represented as $FeO \cdot Cr_2O_3$. Previous study showed that chromite can be oxidized by sodium nitrate, which is thereby reduced to either sodium nitrite or nitrogen depending on the reaction temperature (Kashiwase et al., 1974a,b). Below 673 K, sodium nitrate is reduced to sodium nitrite, as follows:

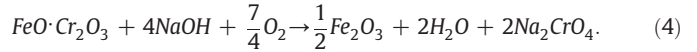


Above 673 K, sodium nitrate is reduced to nitrogen, as follows:



Keeping the reaction temperature below 673 K, the reduction product $NaNO_2$ in Eq. (1) exists in the molten salts, but not released to the environment as nitrogen from Eq. (2). In the presence of oxygen,

the oxidation of $NaNO_2$ may occur according to Eq. (3), thus the consumption of sodium nitrate being avoided. Oxygen can also oxidize $FeO \cdot Cr_2O_3$ directly without $NaNO_3$ according to Eq. (4). The thermodynamics study was made to analyze the possibility. Fig. 1 shows the Gibbs free energy changes for Eqs. (1), (3) and (4), indicating that they all occur readily in the temperature range of 300 to 700 K.



2.2. Proposed flow sheet

Based on theoretical and experimental results, a new process for chromate production from chromite ore by oxygen with molten $NaOH-NaNO_3$ is proposed. The new process is schematically plotted in Fig. 2.

After the liquid oxidation decomposition of chromite in molten salts, the reaction slurry is diluted to 50% sodium hydroxide solution. Then the filtration is carried out to separate the alkali liquor and the mixtures of ferrite-enriched residue and Na_2CrO_4 crystal. The filter cake is leached by water to dissolve Na_2CrO_4 , and then the residue is separated from Na_2CrO_4 solution. Na_2CrO_4 solution is crystallized to obtain Na_2CrO_4 crystal. Specially, the alkali liquor and the crystallization mother liquor which mainly consist of $NaOH$ and $NaNO_3$ are vaporized together by a film evaporator. When the concentration of $NaOH$ reached 85%, the concentrated liquor is recycled into the reactors using high temperature air as the carrier gas as shown in Fig. 2.

3. Experiments

3.1. Chromite ore and reagents

Vietnamese chromite ore was used in the experiment. The chemical composition is listed in Table 1 and mineralogical analysis is shown in Fig. 3. The ore consists mainly of magnesiochromite and quartz.

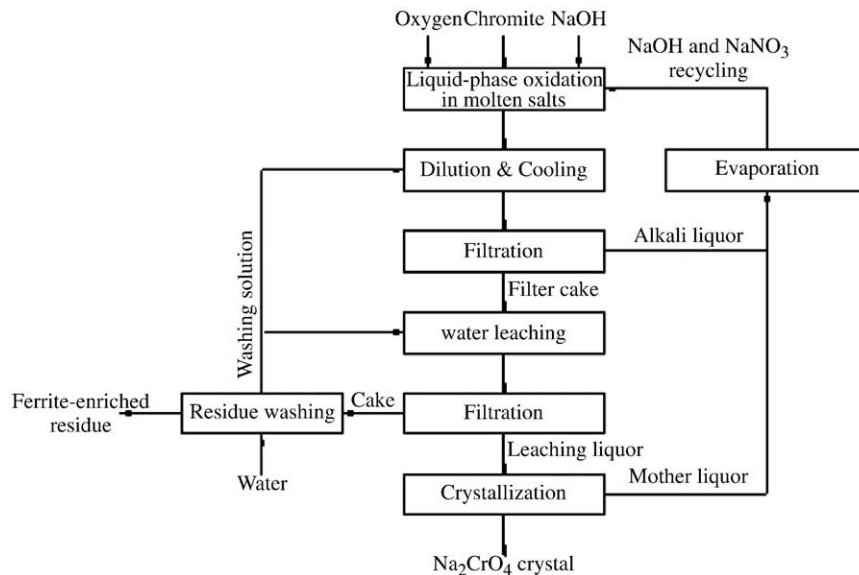


Fig. 2. Principle flow sheet of chromate production.

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