Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 33(2023) 2497−2510
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Effect of sodium aluminate on chromium spinels oxidation in chromite lime-free roasting process

Tian-gui QI, Yao-min LI, Peng WANG, Xiao-bin LI, Zhi-hong PENG, Gui-hua LIU, Qiu-sheng ZHOU

School of Metallurgy and Environment, Central South University, Changsha 410083, China

Received 7 March 2022; accepted 1 September 2022

Abstract: The reaction between $Na_2O\cdot Al_2O_3$ and chromium spinels or chromite in the roasting process was systemically investigated to reveal the effects of $Na_2O\cdot Al_2O_3$ on chromium oxidation. The results of $Na_2O\cdot Al_2O_3$ roasted with $MgO\cdot Cr_2O_3$ illustrate that only about 50% of the chromium in $MgO\cdot Cr_2O_3$ can convert into Na_2CrO_4, while the remaining chromium converts into an Al-bearing spinel $Mg(CrAl)O_4$. $Mg(CrAl)O_4$ is found to be difficult to further react with $Na_2O\cdot Al_2O_3$. The oxidative roasting of $Na_2O\cdot Al_2O_3$ with chromite further confirms that $Na_2O\cdot Al_2O_3$ cannot fully react with some chromium spinels, which reveals the cause of the low chromium oxidation rate in the traditional chromite lime-free roasting process. Based on the experiment results, a strategy for eliminating the impacts of $Na_2O\cdot Al_2O_3$ in the lime-free roasting process was proposed, in which adding more Na_2CO_3 for forming $Na_2O\cdot Al_2O_3$ is considered. The chromium oxidation rate can rise close to 100% with the new strategy. This study contributes to better understanding the chromite lime-free roasting process and provides a new idea for developing the chromate salts manufacturing process more efficiently and cleanly.

Key words: chromate; sodium aluminate; chromite; chromium spinel; oxidative roasting

1 Introduction

Chromium salts play an important role in the national economy and are widely used in metallurgy, chemical industry, military, and machinery [1,2]. The traditional route for manufacturing chromium salts is based on the extraction of chromium oxide as sodium chromate via an oxidative alkali decomposition of the chromite ore in air or oxygen [3−5]. The commercial chromite alkali decomposition processes including lime-based roasting process, lime-free roasting process, and liquid-phase oxidation process are widely used in industry [6,7]. The traditional lime-based roasting process has been obsoleted in many developed and developing countries due to the large amount of carcinogenic chromite ore processing residue (COPR) and serious pollution [8,9]. The liquid-phase oxidation process should be operated in the molten or sub-molten system, its large-scale industrial application problems have yet to be solved [10,11]. Consequently, the lime-free roasting process becomes the dominant and most widely used technology for chromium salts production in the world [4,5].

In the typical lime-free roasting process, the chromite is decomposed by soda-ash at 1000−1200 °C, and the insoluble chromium in chromite is converted into water-soluble sodium chromate (Na_2CrO_4) [12−14]. Sodium chromate is then leached from the roasted clinker by water, and the leaching residue is recycled as recycling slag for subsequent roasting or detoxified for landfill [12]. Obviously, the chromite oxidation reaction in the oxidative roasting process is crucial for chromate extraction efficiency. Unfortunately, the chromium oxidation rate in the industrial lime-free roasting

---

Corresponding author: Tian-gui QI, Tel: +86-731-88836041, E-mail: qitiangui@csu.edu.cn

DOI: 10.1016/S1003-6326(23)66276-4

process is less than 75% [15,16]. Although some unreacted chromium oxides can be re-roasted when they are sent back to the roasting process as recycling slag, the total chromium conversion rate remains below 90% [4,15]. The low chromium conversion rate severely restricts the production efficiency of the lime-free roasting process.

The low chromium oxidation rate was related to the oxidative reaction mechanism [14,17]. The overall chromium oxidation reaction of the spinel in the lime-free roasting process can be represented as follows [14]:

$$FeCr_2O_4+2Na_2CO_3+1.75O_2= 2Na_2CrO_4+0.5Fe_2O_3+2CO_2 \quad (1)$$

$$MgCr_2O_4+2Na_2CO_3+1.5O_2= 2Na_2CrO_4+MgO+2CO_2 \quad (2)$$

According to the reactions, ample Na_2CO_3 and O_2 are the basic condition for chromium spinel decomposition and oxidation. However, an excessive Na_2CO_3 will compose with Na_2CrO_4 to form the Na_2CO_3−Na_2CrO_4 binary liquid phase which may cover the chromite grains retarding the oxygen diffusion or cause serious rotary kiln-ring [18,19]. So, the Na_2CO_3 dosage in the lime-free roasting process is strictly limited to the stoichiometric ratio according to the chromium oxidation Reactions (1) and (2). However, $MgAl_2O_4$, $MgFe_2O_4$, and $MgSiO_3$ in chromite will inevitably react with Na_2CO_3 to form $Na_2O\cdot Al_2O_3$, $Na_2O\cdot Fe_2O_3$, and Na_2SiO_3 under the high-temperature conditions [19,20]. These secondary reactions of Na_2CO_3 would cause the lack of Na_2CO_3 for the chromium oxidation reaction, and thus may influence the chromium oxidization rate.

The traditional view believes that the formation of $Na_2O\cdot Al_2O_3$, $Na_2O\cdot Fe_2O_3$, and $Na_2O\cdot SiO_2$ have little effect on the chromium oxidation reactions, because they suppose that $Na_2O\cdot Al_2O_3$, $Na_2O\cdot Fe_2O_3$, and Na_2SiO_3 are all less thermodynamically stable than Na_2CrO_4, and they can act as alkali to further react with the chromium oxides to form Na_2CrO_4 in the oxidizing roasting process [15,20,21]. Based on this traditional view, as a strategy for mitigating the impacts of the Na_2CO_3−Na_2CrO_4 liquid phase in the industrial lime-free roasting process, some Na_2CO_3 is intentionally controlled to convert into $Na_2O\cdot Al_2O_3$ and $Na_2O\cdot Fe_2O_3$ firstly [22]. However, the previous studies just prove that the intermediate compounds $Na_2O\cdot Al_2O_3$, $Na_2O\cdot Fe_2O_3$, and $Na_2O\cdot SiO_2$ can transform the simple chromium compound Cr_2O_3 into Na_2CrO_4, whether these intermediate compounds could further react with the complex chromium spinels in chromite ore is rarely studied.

Our previous studies suggest that $Na_2O\cdot Fe_2O_3$ and $Na_2O\cdot Al_2O_3$ are readily formed in the chromite lime-free roasting process, $Na_2O\cdot Fe_2O_3$ can further react with chromite to produce Na_2CrO_4, but $Na_2O\cdot Al_2O_3$ seems difficult to fully react with some chromium spinel [20,23]. Furthermore, we have noticed the fact that the chromium oxidation rate is only 70%−85% in the rotary kiln for industrial lime-free roasting process, but $Na_2O\cdot Al_2O_3$ is often simultaneously present in the roasted clinkers and an aluminum removal process is invariably practiced after the clinker leaching in factory [24]. This phenomenon also indicates that the reactions between $Na_2O\cdot Al_2O_3$ and chromium spinel in the roasting process are much more complicated, but they are scarcely studied.

In this study, the reaction behaviors between $Na_2O\cdot Al_2O_3$ and synthesized chromium spinel $MgO\cdot Cr_2O_3$, $Mg(CrAl)O_4$ as well as chromite ore were systematically studied under the lime-free roasting conditions. The influence of the impurity components MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$ on the oxidative roasting reactions between $Na_2O\cdot Al_2O_3$ and chromium spinel was also investigated. The reaction mechanism and the fact that some chromium spinel is difficult to react with $Na_2O\cdot Al_2O_3$ causing the low chromium oxidation in the lime-free roasting process were confirmed. The results correct the traditional views on the effects of sodium aluminate on the chromite ore oxidizing roasting process, and the proposed strategy for eliminating the impact of sodium aluminate provides a new idea for developing the chromate salts manufacturing process more efficiently and cleanly.

2 Experimental

2.1 Materials

The chemicals used in this work were all analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd., China, including Na_2CO_3, Al_2O_3, MgO, Cr_2O_3, and Fe_2O_3. The chemicals were dried at 383 K for 8 h to remove any moisture before being used. $Na_2O\cdot Al_2O_3$ was synthesized by mixing Na_2CO_3 and Al_2O_3 (molar ratio of 1.05:1) and sintering at 1373 K for 4 h in muffle furnace. $MgO·Cr_2O_3$ was prepared by sintering the mixture of MgO and Cr_2O_3 (molar ratio of 1:1) at 1773 K for 6 h. The synthesized $Na_2O·Al_2O_3$ and $MgO·Cr_2O_3$ were ground into powders and passed through a sieve with pore size of 45 μm respectively before they were used. The X-ray diffraction (XRD) patterns of the obtained $Na_2O·Al_2O_3$ and $MgO·Cr_2O_3$ are shown in Fig. 1.

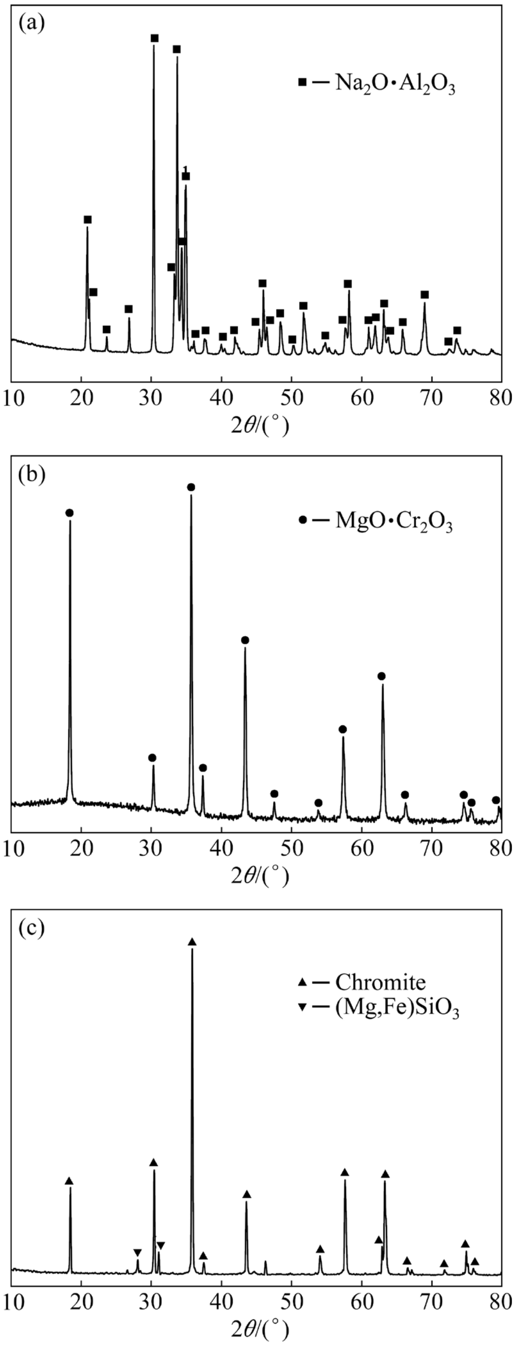


Fig. 1 XRD patterns of synthesized sodium aluminate (a), synthesized magnesium chromium spinel (b), and chromite ore (c)

The chromite ore used in this study was provided by Gansu Jinshi Chemical Industry Co., Ltd., China. It was first dried at 383 K for 6 h in an oven, and then milled in a vibrating mill and sieved by a sieve with pore size of 74 μm. The chemical composition and mineralogical analysis of the chromite ore are shown in Table 1 and Fig. 1, respectively.

Table 1 Chemical composition of chromite ore (wt.%)

Cr_2O_3	Al_2O_3	Fe_2O_3	SiO_2	MgO
41.42	22.95	22.29	4.24	8.63

2.2 Experimental procedure

2.2.1 Oxidizing roasting

To obtain well-mixed raw meal for the oxidizing roasting, the raw meals were prepared by the following two steps: (1) Mixing, the ground chromium-bearing raw material and sodium aluminate (or sodium carbonate) were mixed in certain proportions by a mineral mixer (Changsha Suotuo Scientific Instrument and Equipment Co., Ltd.) for 2 h; (2) Milling, the pre-mixed raw meal obtained in Step (1) was milled in a vibrating mill for 9 min to obtain the well-mixed raw meal.

The oxidizing roasting experiment was carried out in a muffle furnace (Changsha Changcheng Electric Furnace Factory). 10 g of raw meal was put into a corundum crucible and then roasted in the muffle furnace at preset temperatures for certain time, and the resultant clinker was subsequently taken out from the furnace and cooled in air to room temperature. During the roasting, the air was continuously blasted into the muffle furnace through a ventilation device to maintain the oxidizing atmosphere. The cooled clinker was ground to particle size less than 74 μm for further analysis.

2.2.2 Clinker leaching

The leaching experiments were performed in a 150 mL three-neck round-bottom flask, which was immersed in a thermostatic water bath with an electronic temperature controller. 5.00 g of roasted clinker was leached in 100 mL boiling water for 20 min and filtered, and the residue was washed with hot water several times to leach out sodium chromate completely. The filtered solution was diluted to 250 mL in volumetric flask and the residue was dried at 383 K for further analysis.

2.3 Analytical methods

The oxidation rate of the chromium in the roasting process was calculated by Eq. (3), in which the contents of hexavalent chromium (i.e., sodium chromate) and total chromium in the clinker should be obtained. In this work, both the hexavalent chromium and the total chromium were determined by the ferrous ammonium sulfate titration method. The hexavalent chromium in clinkers can be completely leached into the leaching solution in the clinker leaching process, so it can be determined directly by the titration method. For the total chromium content, a caustic molten oxidation procedure was set to ensure that all the chromium in the clinker was oxidized into hexavalent chromium, and then it was determined by titration method.

$$\eta=\frac{w(\mathrm{Cr}^{6+})}{w(\mathrm{Cr_T})}\times 100\% \tag{3}$$

where η is the chromium oxidation rate; $w(\mathrm{Cr}^{6+})$ is the content of water leachable hexavalent chromium in clinkers, expressed in terms of Cr_2O_3 (wt.%); $w(\mathrm{Cr_T})$ is the content of total chromium in the clinkers, also expressed in terms of Cr_2O_3 (wt.%).

The content of $Na_2O\cdot Al_2O_3$ in the raw meal and the clinker was determined by an acid−base titration method. In the titration procedure, the ground raw meal or clinker was mixed with a certain amount water to make the alkali of $Na_2O\cdot Al_2O_3$ leach into the water, adding 3 drops of phenolphthalein indicator, and then conducting the titration process with the aqueous standard solution of hydrochloric acid as titrant. The $Na_2O\cdot Al_2O_3$ reaction rate (v) can be calculated by the following equation:

$$v=\left(1-\frac{w(\mathrm{NA_c})}{w(\mathrm{NA_r})}\times R_{\mathrm{c/r}}\right)\times 100\% \tag{4}$$

where $w(\mathrm{NA_c})$ is the mass fraction of $Na_2O\cdot Al_2O_3$ in the roasted clinker; $w(\mathrm{NA_r})$ is the mass fraction of $Na_2O\cdot Al_2O_3$ in the corresponding raw meal; $R_{\mathrm{c/r}}$ is the mass ratio of the roasted clinker to the corresponding raw meal.

Phase analysis of the clinkers and their leaching residues was performed on a Bruker X-ray diffractometer (D8-Advance, Bruker Corporation) with Cu K_α monochromatic X-rays. The diffraction data were recorded for 2θ from 5° to 75° with a scan rate of 1 (°)/min. Microscopic morphology and microscale composition analyses were conducted by scanning electron microscopy (JSM 6360 LV, Japan Electronics Co., Ltd.) and energy-dispersive X-ray spectroscopy (GENSIS60S; EDAX, USA).

3 Results and discussion

3.1 Effects of $Na_2O\cdot Al_2O_3$ on chromium oxidation of $MgO\cdot Cr_2O_3$

$MgO\cdot Cr_2O_3$ and $FeO\cdot Cr_2O_3$ are considered to be the main chromium-bearing spinel in nature. $FeO\cdot Cr_2O_3$ is readily oxidized and decomposed into Fe_2O_3 and Cr_2O_3 in the oxidizing roasting process [20,25], while the reaction behavior between Cr_2O_3 and $Na_2O\cdot Al_2O_3$ has been identified by some previous researches [26]. So, this work focuses on the oxidization and conversion reaction of $MgO\cdot Cr_2O_3$ with $Na_2O\cdot Al_2O_3$ under high-temperature roasting conditions.

3.1.1 Effects of roasting temperature and time

To identify the oxidizing reaction principle of $MgO\cdot Cr_2O_3$ roasted with $Na_2O\cdot Al_2O_3$, the oxidizing roasting experiments of $MgO\cdot Cr_2O_3$ and $Na_2O\cdot Al_2O_3$ were carried out at various temperatures. The molar ratio of $MgO\cdot Cr_2O_3$ to $Na_2O\cdot Al_2O_3$ in the raw meal was set to be 1:2 in the roasting experiment process, as the theoretical molar ratio of chromium to sodium in the expected reaction product of Na_2CrO_4 is 1:2. Figure 2 shows the variation of chromium oxidization rate with the oxidizing roasting temperature and time.

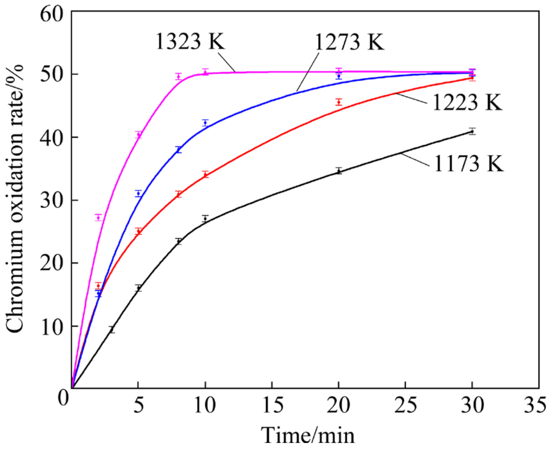


Fig. 2 Variation of chromium oxidation rate in roasting process of $MgO\cdot Cr_2O_3$ and $Na_2O\cdot Al_2O_3$

Figure 2 illustrates that $MgO\cdot Cr_2O_3$ can react with $Na_2O\cdot Al_2O_3$, making the chromium in the spinel oxidized and converted into water-soluble chromium-containing compounds at high temperatures with air. The results show that part of chromium is oxidized in the roasting experiment, and the chromium oxidization rate increases with increasing the roasting temperature and time. The result is consistent with the assumption that $Na_2O·Al_2O_3$ can play as an alkali to convert the chromium spinel into Na_2CrO_4 in the oxidizing roasting process. However, the highest chromium oxidization rate is less than 50% in Fig. 2, which indicates that the chromium oxidization reaction is blocked by some factors or the roasting reaction between $MgO·Cr_2O_3$ and $Na_2O·Al_2O_3$ is more complex than Reaction (5).

$$MgO·Cr_2O_3+2Na_2O·Al_2O_3+1.5O_2= 2Na_2CrO_4+MgO·Al_2O_3+Al_2O_3 \quad (\Delta G^{\ominus}_{1373K}=-74.75\ \text{kJ/mol}) \tag{5}$$

3.1.2 Effects of higher roasting temperature and excessive $Na_2O·Al_2O_3$

The roasting temperature, roasting time, and alkali dosage are the main factors that influence the chromium oxidation reactions in the lime-free roasting process [3,12]. To understand the oxidation and conversion reactions between $MgO·Cr_2O_3$ and $Na_2O·Al_2O_3$ better, the oxidizing roasting experiments with higher roasting temperature, longer roasting time, and excessive $Na_2O·Al_2O_3$ were performed, and the results are presented in Table 2 and Table 3.

As shown in Table 2, the chromium oxidation rates are still maintained at about 50% and are not raised even at a high temperature of 1423 K for 10 h. This finding infers that the roasting temperature and time may not be the limiting factors for chromium oxidation in the roasting process. Table 3 shows that the chromium oxidation rate increases slightly with the increase of the molar ratio of $Na_2O·Al_2O_3$ to $MgO·Cr_2O_3$ (MR) in the raw meal, but the chromium oxidation rate is also maintained at about 50% even raising MR to 3:1. This means that the chromium oxidation rate cannot be significantly raised by adding more $Na_2O·Al_2O_3$ in the roasting system.

The clinkers with various MR in Table 3 were leached by water and a titration test was set for the leaching solution to determine the amount of reacted $Na_2O·Al_2O_3$ in the roasting process. The results in Table 3 show that the reaction rate of $Na_2O·Al_2O_3$ in the roasting process decreases rapidly with the increase of MR, while the chromium oxidation rate is maintained from 47.5% to 50.2%. The further calculations based on the obtained data reveal that the molar ratio of reacted $Na_2O·Al_2O_3$ to $MgO·Cr_2O_3$ in the roasting process may be maintained at a constant value of about 1:1. This finding indicates that the stoichiometric ratio of $Na_2O·Al_2O_3$ to $MgO·Cr_2O_3$ for the chromium oxidation reaction in the roasting process is about 1:1 rather than the traditionally believed ratio 2:1. Furthermore, with this reaction, only about half chromium in $MgO·Cr_2O_3$ could be oxidized and converted into Na_2CrO_4. So, it is confirmed that the oxidation reaction of $MgO·Cr_2O_3$ with $Na_2O·Al_2O_3$ may not follow the traditionally believed reaction as Reaction (5).

Table 2 Chromium oxidation rate of roasting $MgO·Cr_2O_3$ and $Na_2O·Al_2O_3$ at higher temperatures

Temperature/K	Time/h	Chromium oxidation rate/%
1273	2	49.20
	10	49.34
1373	2	49.70
	10	49.92
1423	2	50.34
	10	50.29

Table 3 Effect of MR on chromium oxidation rate and $Na_2O·Al_2O_3$ reaction rate

MR	Chromium oxidation rate/%	$Na_2O·Al_2O_3$ reaction rate/%	$MR_{reacted}$
1:1	47.50	98.78	0.99:1
1.5:1	47.97	65.10	0.98:1
2:1	49.70	50.35	1.01:1
3:1	50.20	33.57	1.06:1

$MR_{reacted}$ is molar ratio of reacted $Na_2O·Al_2O_3$ to $MgO·Cr_2O_3$ in roasting process; roasting experiments were carried out at 1373 K for 1.5 h in air

3.1.3 Mineralogy analysis and reaction mechanism

To better understand the chemical reaction process of $MgO·Cr_2O_3$ and $Na_2O·Al_2O_3$ in the oxidizing roasting process, the phase analyses of the clinker obtained by roasting $MgO·Cr_2O_3$ and $Na_2O·Al_2O_3$ with molar ratio of 1:2 at 1373 K for 10 h and its water leaching residue were characterized by XRD (Fig. 3).

Figure 3 shows that the main phases in the clinker are Na_2CrO_4, $Na_2O·Al_2O_3$, and $Mg(CrAl)O_4$,

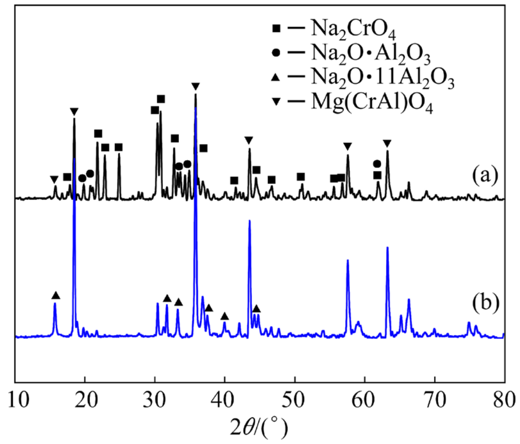
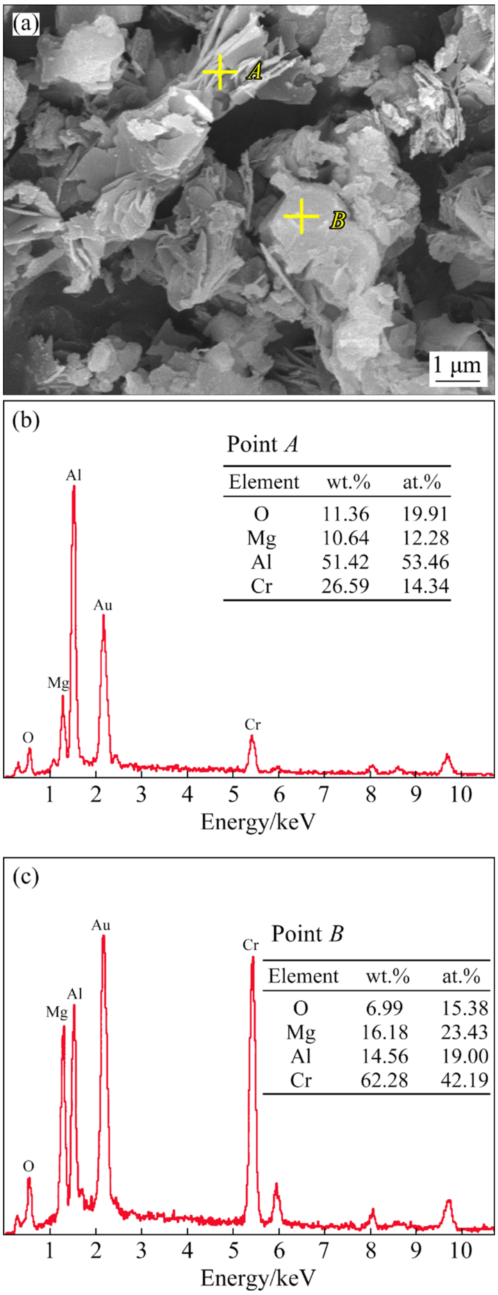


Fig. 3 XRD patterns of clinker (a) and its leaching residue (b) for roasting $Na_2O·Al_2O_3$ and $MgO·Cr_2O_3$ at 1373 K for 10 h

while the main phases in the leaching residue are $Mg(CrAl)O_4$ and $Na_2O·11Al_2O_3$. The diffraction peaks of $MgO·Cr_2O_3$ are not detected both in the clinker and the leaching residue, suggesting that $MgO·Cr_2O_3$ has been decomposed by $Na_2O·Al_2O_3$ and converted into Na_2CrO_4 and $Mg(CrAl)O_4$ in the roasting process. $Na_2O·Al_2O_3$ and $Mg(CrAl)O_4$ are detected simultaneously in the clinker, revealing that $Na_2O·Al_2O_3$ overdoses in the roasting experiment and the excessive $Na_2O·Al_2O_3$ is hard to further react with $Mg(CrAl)O_4$. The results demonstrate that only a part of chromium in $MgO·Cr_2O_3$ can be oxidized and converted into water leachable Na_2CrO_4 by the oxidizing reaction with $Na_2O·Al_2O_3$ in air, while the other part of chromium was transformed into non-leachable spinel compound of $Mg(CrAl)O_4$. This may be the cause of the low chromium oxidization rate in the roasting experiments.

Some researchers consider $Mg(CrAl)O_4$ as a group spinel whose chemical composition and structural formula may vary as $MgCr_{(2-x)}Al_xO_4$ ($0 \le x \le 2$) depending on the formation conditions [27,28]. According to the XRD analysis, chromium oxidation rate and the molar ratio of reacted $Na_2O·Al_2O_3$ to $MgO·Cr_2O_3$ in the previous experiments, $Mg(CrAl)O_4$ (i.e. x=1.0 in the formula of $MgCr_{(2-x)}Al_xO_4$) is confirmed to form in the oxidization roasting process. The EDX analysis of the leaching residue shown in Fig. 4 also supports the formation of $MgCrAlO_4$ in the roasting process. Consequently, the oxidizing reaction between $Na_2O·Al_2O_3$ and $MgO·Cr_2O_3$ under the oxidizing atmosphere might be described as



Point *A*

Element	wt.%	at.%
O	11.36	19.91
Mg	10.64	12.28
Al	51.42	53.46
Cr	26.59	14.34

Point *B*

Element	wt.%	at.%
O	6.99	15.38
Mg	16.18	23.43
Al	14.56	19.00
Cr	62.28	42.19

Fig. 4 SEM image (a) and EDX results (b, c) of clinker leaching residue (clinker obtained by roasting $Na_2O·Al_2O_3$ and $MgO·Cr_2O_3$ at 1373 K for 10 h)

$$MgO·Cr_2O_3+Na_2O·Al_2O_3+0.75O_2= \\ Na_2CrO_4+Mg(CrAl)O_4+0.5Al_2O_3 \\ (\Delta G^{\ominus}_{1373\ K}=-37.37\ \text{kJ/mol}) \tag{6}$$

With this reaction, only 50% of the chromium in $MgO·Cr_2O_3$ could be oxidized and converted into Na_2CrO_4 when $Na_2O·Al_2O_3$ is the alkali donator reacting with the spinel $MgO·Cr_2O_3$ in the oxidizing roasting process. It is entirely consistent with our experiment results of this work. These results change the conventional conception that $Na_2O\cdot Al_2O_3$ could completely react and convert the chromium spinel into Na_2CrO_4 in the lime-free roasting process. The results also suggest that some new strategies should be developed to further improve the chromium oxidation rate in the lime-free roasting process for chromate salts manufacturing.

3.2 Effects of $Na_2O\cdot Al_2O_3$ on chromium oxidation of $Mg(CrAl)O_4$

3.2.1 Oxidizing behaviors of $Mg(CrAl)O_4$ with $Na_2O\cdot Al_2O_3$

$Mg(CrAl)O_4$ seems difficult to react with $Na_2O\cdot Al_2O_3$ during the oxidation roasting process. To confirm the reaction behavior of $Mg(CrAl)O_4$ in the roasting process, $Mg(CrAl)O_4$ was synthesized in the laboratory and the oxidation roasting experiment was conducted.

The $Mg(CrAl)O_4$ was synthesized by roasting the uniform mixture of MgO, Al_2O_3, and Cr_2O_3 with the stoichiometric ratio of 2:1:1 at 1773 K for 6 h. The starting materials MgO, Al_2O_3, and Cr_2O_3 were analytically pure and preroasted at 1273 K for 2 h to release any absorbed water and hydroxide. Figure 5 shows the XRD, SEM and EDX analysis of the synthesized $Mg(CrAl)O_4$. The characterizations confirm that the synthesized compound is indeed the spinel of $Mg(CrAl)O_4$ (PDF#23-1221) with homogeneous particle size and chemical composition.

The chromium oxidation rates of roasting $Mg(CrAl)O_4$ and $Na_2O\cdot Al_2O_3$ with a molar ratio of 1:1 at various temperatures are listed in Table 4. It is shown that all the chromium oxidation rates are less than 2% in the roasting experiment, raising the roasting temperature and increasing the roasting time seem to have little effect on the chromium oxidation rate.

The results in Table 4 further confirm that $Na_2O\cdot Al_2O_3$ is hard to react with $Mg(CrAl)O_4$ under the oxidation roasting conditions. This may be attributed to the more stable spinel structure of $Mg(CrAl)O_4$ thermodynamically and kinetically. The study [14] on the chromite oxidation kinetics shows that the chemical potential (or the partial molar Gibbs energy) of Cr_2O_3 in chromite depends on the composition of the chromium spinel in chromite, which determines the diffusion capacity of Cr^{3+} and Fe^{3+} in the spinel phase. While the

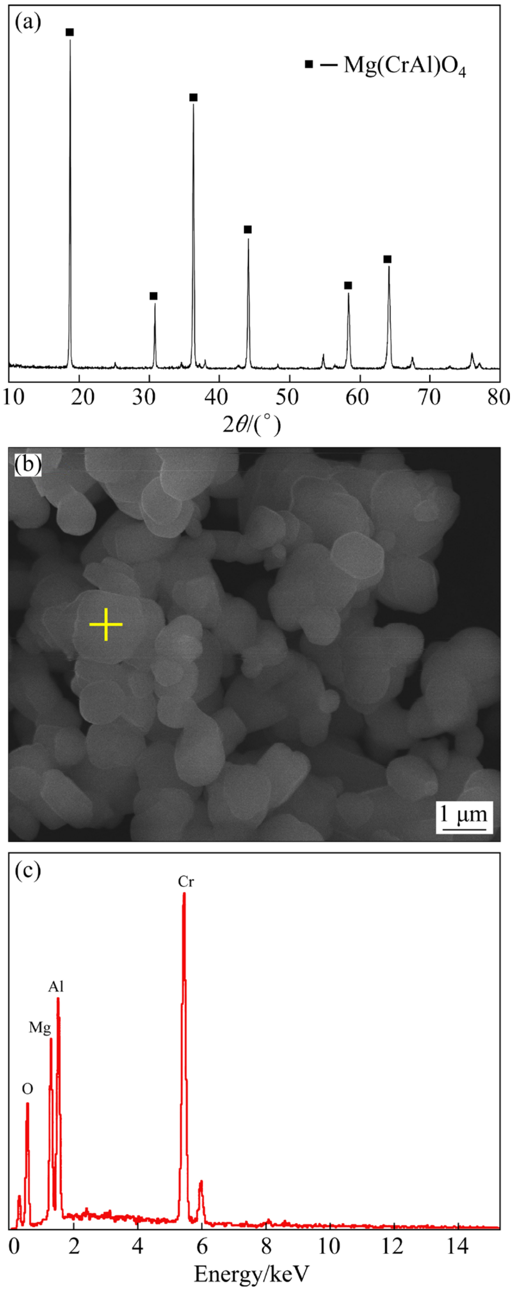


Fig. 5 XRD pattern (a), SEM image (b), and EDX result (c) of synthesized $Mg(CrAl)O_4$ spinel

Table 4 Chromium oxidation rate for oxidative roasting $Mg(CrAl)O_4$ with $Na_2O\cdot Al_2O_3$

Temperature/ K	Time/ min	Chromium oxidation rate/%
1323	60	1.89
	150	1.92
1373	60	1.95
	150	1.80
1423	60	1.85
	150	1.96

kinetics of the oxidization reaction between alkali and chromium spinel is believed to be controlled by the diffusion of M^{3+} cations in the spinel lattice. The studies [15] on the alkali roasting process of various chromite ore suggest that, the higher the Al content in the ore, the lower the chromium oxidation rate in the oxidative roasting process, and correspondingly the smaller the lattice constant of the chromium spinel in the ore. Our previous studies on the thermodynamical analysis of the chromium oxidation reactions show that the change of Gibbs free energy of the reaction between $Na_2O\cdot Al_2O_3$ and $Mg(CrAl)O_4$ is negative in the lime-free roasting temperature range [23], which also supports the view that the kinetics factors may be the key points for the low chromium oxidization rate of $Mg(CrAl)O_4$ roasted with $Na_2O\cdot Al_2O_3$.

3.2.2 Oxidizing behaviors of $Mg(CrAl)O_4$ with Na_2CO_3

The mineralogical structure of $Mg(CrAl)O_4$ is very similar to chromite. It is an ideal raw material for investigating the formation principle of $Na_2O\cdot Al_2O_3$ and its influence on the chromium oxidation reactions in the lime-free roasting process since the interaction effect of Fe/Si-containing components on the oxidation reaction is avoided. In this regard, the reactions between $Mg(CrAl)O_4$ and Na_2CO_3 under lime-free roasting condition were studied experimentally.

Considering the fact that the Na_2CO_3 dosage in the industrial lime-free roasting process is usually limited to just enough for forming Na_2CrO_4 (i.e. molar ratio of Na_2CO_3 to Cr in the raw meal is about 1:1), the oxidative roasting experiments were conducted firstly by roasting Na_2CO_3, $Mg(CrAl)O_4$ and MgO with a molar ration of 1:1:1. The addition of MgO in the raw meal is to simulate the inert filler material in the industrial roasting process to dilute the liquid phase [15]. The roasting temperature is 1273−1323 K, which is the commonly used temperature range for chromite oxidative roasting in industry. The chromium oxidation rates in the experiments are shown in Fig. 6, and the XRD patterns of the obtained clinkers and their leaching residues are shown in Fig. 7.

The results in Fig. 6 illustrate that increasing the roasting temperature and time are conducive to chromium oxidation, the chromium oxidation rate rises rapidly within 10 min and then remains nearly constant at 65%−67%, but the chromium could not be oxidized completely under the roasting conditions.

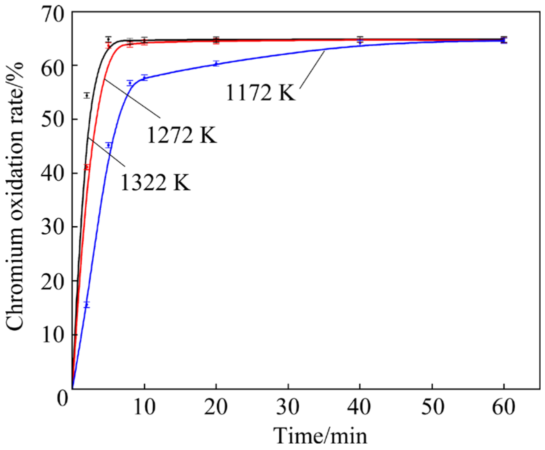


Fig. 6 Chromium oxidation rate for oxidative roasting of $Mg(CrAl)O_4$ with Na_2CO_3 at different roasting temperatures and time

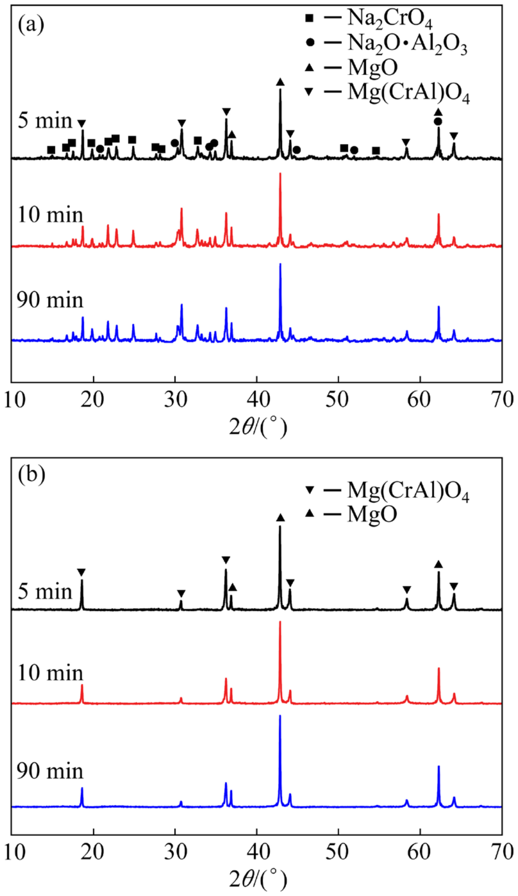


Fig. 7 XRD patterns of clinkers (a) and leaching residues (b) for oxidative roasting $Mg(CrAl)O_4$ and Na_2CO_3 at 1323 K

Figure 7 shows that the unoxidized chromium still exists in the form of $Mg(CrAl)O_4$ because the obvious diffraction peaks of $Mg(CrAl)O_4$ are detected both in the clinkers and leaching residues. Moreover, Fig. 7 also illustrates that Na_2CO_3 is quickly exhausted in the initial stage of the roasting experiment, simultaneously generating $Na_2O\cdot Al_2O_3$ and Na_2CrO_4. When Na_2CO_3 is exhausted, the chromium oxidation reactions seem to stop. These results verify the following facts: (1) chromium-bearing spinel $Mg(CrAl)O_4$ is readily decomposed by Na_2CO_3 in the oxidative roasting process; (2) $Na_2O\cdot Al_2O_3$ is formed rapidly by the reaction of Na_2CO_3 and Al-bearing components; (3) $Na_2O\cdot Al_2O_3$ is difficult to further react with $Mg(CrAl)O_4$ to generate Na_2CrO_4 under the oxidative roasting conditions.

Combined the above results and facts, the oxidative roasting reaction between Na_2CO_3 and $Mg(CrAl)O_4$ with air may be expressed as

$$2Mg(CrAl)O_4+3Na_2CO_3+1.5O_2= 2Na_2CrO_4+Na_2O\cdot Al_2O_3+2MgO+3CO_2 \quad (\Delta G^{\ominus}_{1373\ \mathrm{K}}=-180.17\ \mathrm{kJ/mol}) \tag{7}$$

In Reaction (7), 1.5 mol Na_2CO_3 is required for 1 mol $Mg(CrAl)O_4$, in which two-thirds of the Na_2CO_3 will compound with chromium for forming Na_2CrO_4 and another one third will be consumed for generating $Na_2O\cdot Al_2O_3$. In this regard, the low chromium oxidation rate in Fig. 6 may be attributed to the lack of Na_2CO_3, as the dosage of Na_2CO_3 in the experiments was calculated without any consideration for the generation of $Na_2O\cdot Al_2O_3$.

Considering the fact that $Na_2O\cdot Al_2O_3$ is very difficult to further react with $Mg(CrAl)O_4$, a sufficient amount of Na_2CO_3 is required for the chromium to be oxidized completely. As shown in Table 5, the chromium oxidation rate can reach 98.20% and 99.11% respectively, when raising the Na_2CO_3 amount to make the molar ratio of Na_2CO_3 to $Mg(CrAl)O_4$ up to 1.5:1 and 2:1.

Table 5 Effects of Na_2CO_3 dosage on chromium oxidation rate of $Mg(CrAl)O_4$ in roasting process

MR	Temperature/K	Time/min	Chromium oxidation rate/%
1:1	1373	90	64.13
1.5:1	1373	90	98.20
2:1	1373	90	99.11

In conclusion, $Mg(CrAl)O_4$ was difficult to react with $Na_2O\cdot Al_2O_3$ under the lime-free roasting conditions, and thus the formation of $Na_2O\cdot Al_2O_3$ may cause incomplete chromium oxidation in the traditional lime-free roasting process. This finding has broken the conventional understanding of the reactions between $Na_2O\cdot Al_2O_3$ and chromium spinels, which is well agreement with the facts (e.g. the low chromium oxidation rate and the coexisting of $Na_2O\cdot Al_2O_3$ in clinkers) in the industrial lime-free roasting process. This finding also suggests that an additional amount of Na_2CO_3 for forming $Na_2O\cdot Al_2O_3$ should be taken into account in the lime-free roasting process of chromite.

3.3 Effects of impurity on reaction of $Na_2O\cdot Al_2O_3$ and chromium spinel

The natural chromite ore usually contains a variety of elemental components, mostly locked in a spinel structure [14,19]. When the chromite is decomposed in the oxidative roasting process, the spinel structure will be destroyed and the impurity components such as MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$, will be released. To verify whether these impurity components have any effect on the reactions between $Na_2O\cdot Al_2O_3$ and chromium spinels, some comparative roasting experiments were conducted by mixing the impurity components into the original raw meals, as shown in Table 6.

Table 6 Effect of impurity component on chromium oxidation reaction of chromium spinel with $Na_2O\cdot Al_2O_3$

Original raw meal	Added impurity component	Molar ratio of final raw meal	Chromium oxidation rate/%
$Na_2O\cdot Al_2O_3$: $MgO\cdot Cr_2O_3$ (Molar ratio 2:1)	Blank	2:1:0	49.90
	MgO	2:1:1.2	98.30
	Fe_2O_3	2:1:1.5	84.14
	$MgO\cdot Fe_2O_3$	2:1:1.5	70.05
$Na_2O\cdot Al_2O_3$: $Mg(CrAl)O_4$ (Molar ratio 2:1)	Blank	2:1:0	2.08
	MgO	2:1:1.2	1.98
	Fe_2O_3	2:1:1.5	1.92
	$MgO\cdot Fe_2O_3$	2:1:1	1.89

Roasting temperature 1323 K, and time 2 h

Table 6 demonstrates that the impurity components of MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$ have a significant influence on the oxidative roasting reactions of $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$. The chromium oxidation rate increased from 49.90% in the bank experiment to 98.30%, 84.14%, and 70.05% when MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$ were added, respectively. But for the reactions between $Na_2O\cdot Al_2O_3$ and $Mg(CrAl)O_4$, no visible change in the chromium oxidation rate was observed. This indicates that the influences of these impurity components on chromium oxidation are related to the chromium spinel structure. Once the spinel $Mg(CrAl)O_4$ forms in the roasting system, the chromium seems hard to further react with $Na_2O\cdot Al_2O_3$ even with the assistance of MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$.

Figure 8 shows the XRD patterns of the leaching residues of the clinkers prepared by roasting the raw meal of $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$ with and without adding impurity. It is shown that the main phase in the clinker leaching residue is $Mg(CrAl)O_4$ when the clinker is roasted without MgO, while that changes into $MgO\cdot Al_2O_3$ when the clinker is roasted with MgO. This infers that MgO may involve the oxidation reaction process of $MgO\cdot Cr_2O_3$ and $Na_2O\cdot Al_2O_3$, which changes the composition and structure of the reaction products and inhibits the formation of inert chromium spinel $Mg(CrAl)O_4$, and thus making the chromium oxidation rate increase. Similar to the results of adding MgO, the formation of $Mg(CrAl)O_4$ can be avoided when Fe_2O_3 and $MgO\cdot Fe_2O_3$ were added in the roasting process of $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$, correspondingly the chromium oxidation rate increased significantly as listed in Table 6.

Figure 9 shows the SEM images and EDX results of the leaching residues from the clinkers prepared by roasting the raw meal of $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$ with various impurity components. Combined the result in Fig. 4, it can be seen that the morphology and constituent of the leaching residue

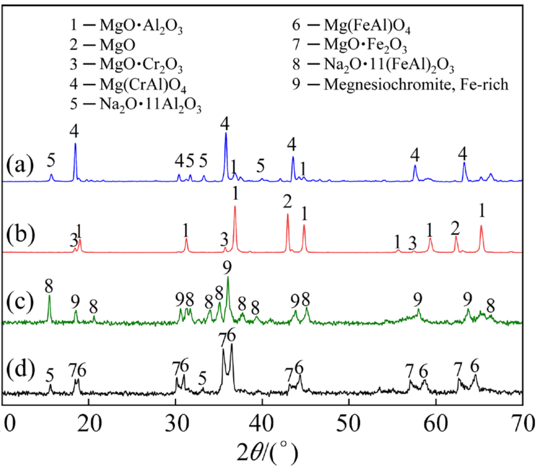


Fig. 8 XRD patterns of leaching residues from clinkers obtained by roasting $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$ with impurity: (a) Blank; (b) With MgO; (c) With Fe_2O_3; (d) With $MgO\cdot Fe_2O_3$

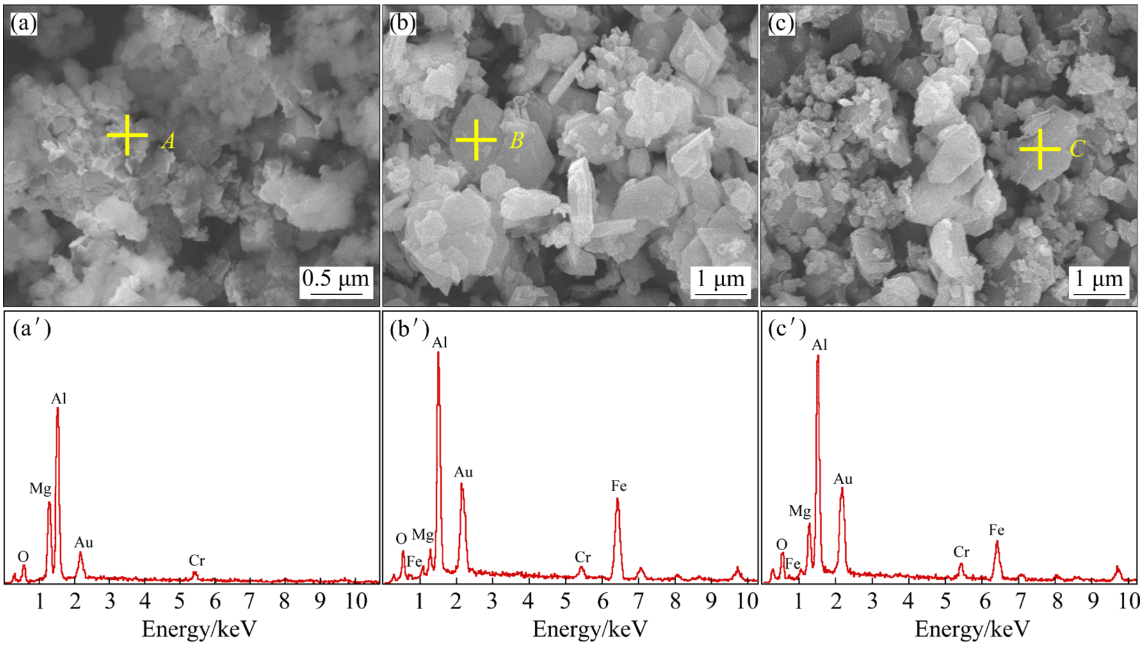


Fig. 9 SEM images (a, b, c) and EDX results (a′, b′, c′) of leaching residues from clinkers obtained by roasting $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$ with impurity: (a, a′) With MgO; (b, b′) With Fe_2O_3; (c, c′) With $MgO\cdot Fe_2O_3$

changed significantly when the impurity components were added in the roasting process, which further supports the view that the adding of the impurity components can affect the structure and composition of the reaction products in the reaction of $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$.

Combinded the chromium oxidation rate, phase and composition changes during the roasting process of $MgCr_2O_4$ and $Na_2O\cdot Al_2O_3$, the effects of the impurity components on the chromium spinel oxidation can be summarized as follows: the impurity components may be involved in the reaction between $MgCr_2O_4$ and $Na_2O\cdot Al_2O_3$ in the oxidaition roasting process, which causes the change of the phase and composition of the reaction products. While the changes in the phase and composition, especially in the chromium-containing phase, inevitably affect the oxidation of chromium, since the stability and diffusion capacity of Cr^{3+} in chromium spinel vary with the structure and composition as mentioned preciously [14,29]. Consequently, the composition and the structure of the components may significantly affect the chromium oxidation process of the reaction between $Na_2O\cdot Al_2O_3$ and chromium spinel.

3.4 Effect of $Na_2O\cdot Al_2O_3$ on oxidizing reactions of chromite

3.4.1 Oxidizing behaviors of chromite with $Na_2O\cdot Al_2O_3$

The natural chromite ore has a more complex chemical component and mineral structure than the synthesized spinels. To study the effects of $Na_2O\cdot Al_2O_3$ on chromium oxidation in the lime-free roasting process, the synthesized $Na_2O\cdot Al_2O_3$ was directly mixed with chromite ore and then roasted at 1273 and 1323 K, respectively. The molar ratio of $Na_2O\cdot Al_2O_3$ to Cr_2O_3 in chromite was also set at 2:1, to make the molar ratio of Na_2O in $Na_2O\cdot Al_2O_3$ to Cr_2O_3 in chromite consistent with that in the expected reaction product of Na_2CrO_4. The results of chromium oxidation rate in the roasting experiments are presented in Fig. 10.

Figure 10 shows that the chromium oxidation rate increases with roasting time in the initial stage, and then maintains at a constant value. Rising roasting temperature is beneficial to accelerating the oxidation reactions, but the final chromium oxidation rates at 1273 and 1323 K are maintained at almost the same value of about 86%. The chromium oxidation principle in these experiments is similar to that of the reaction between chromite and Na_2CO_3 [12]. So, it seems that $Na_2O\cdot Al_2O_3$ could indeed act as an alkali to react with most of the chromium in chromite and form Na_2CrO_4. But, another fact also illustrates that the chromium is not completely oxidized and converted in the experiments of roasting $Na_2O\cdot Al_2O_3$ and chromite in air.

The XRD patterns of the clinkers in Fig. 10 show that obvious $Na_2O\cdot Al_2O_3$ is detected in the clinkers roasted at 1323 K for 20 and 80 min. This indicates that the $Na_2O\cdot Al_2O_3$ is not exhausted in the roasting experiments, and thus the incomplete oxidation of chromium could not be caused by the short of $Na_2O\cdot Al_2O_3$. Correspondingly, in the leaching residues, as shown in Fig. 11, the spinel

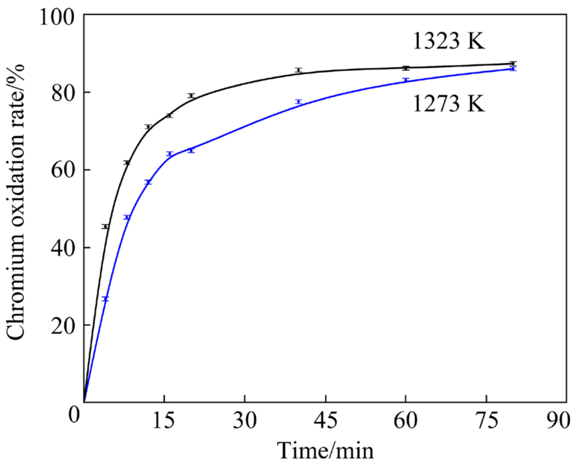


Fig. 10 Variation of chromium oxidation rate for oxidative roasting of chromite with $Na_2O\cdot Al_2O_3$

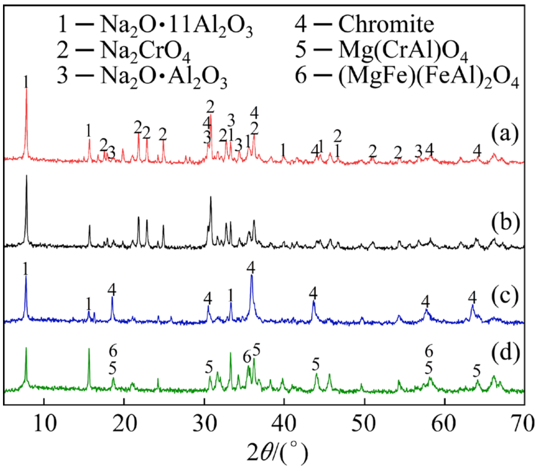


Fig. 11 XRD patterns of clinkers (a, b) and leaching residues (c, d) for roasting chromite with $Na_2O\cdot Al_2O_3$ (a, c) 20 min; (b, d) 80 min (Roasting temperature: 1323 K)

$Mg(CrAl)O_4$, and some unreacted chromite, are detected. Considering these stable chromium spinels are difficult to further react with $Na_2O\cdot Al_2O_3$ under the oxidative roasting conditions, it is reasonable to believe that the low chromium oxidation rate may be caused by the low reactive chromium-bearing spinels formed in the roasting process.

The results further confirm that $Na_2O\cdot Al_2O_3$ could not completely react with some stable chromium spinels. This may be one of the key reasons for the low chromium oxidation rate in the lime-free roasting process, especially when the dosage of Na_2CO_3 in furnace burden is limited to a low level.

3.4.2 Strategy of eliminating impact of $Na_2O\cdot Al_2O_3$ on chromite oxidation

In summary, the conventional views supposed that $Na_2O\cdot Al_2O_3$ can fully react with chromium spinel and convert into $Na_2O\cdot CrO_4$, and thus the amount of Na_2CO_3 consumed by the Al-bearing components is not taken into account in the raw meal for the traditional lime-free roasting process. But, this work clearly confirms that Na_2CO_3 is readily reacted with Al-bearing components to form $Na_2O\cdot Al_2O_3$ under the lime-free roasting conditions, while the formed $Na_2O\cdot Al_2O_3$ hardly further reacts with some refractory chromium-containing spinels, such as $Mg(CrAl)O_4$. Consequently, the formation of $Na_2O\cdot Al_2O_3$ will inevitably cause the low chromium oxidation rate in the oxidative roasting process, due to the lack of Na_2CO_3 for the oxidation reaction of the refractory chromium-containing spinels.

Based on the formation and reaction behavior of $Na_2O\cdot Al_2O_3$ in the lime-free roasting process, a new strategy to make the chromium in chromite oxidized more completely can be proposed. The additional amount of Na_2CO_3 consumed by the impurities (at least including Al-bearing components) must be accounted for and added into the raw meal for the chromite lime-free roasting process. That is, the amount of Na_2CO_3 in raw meal should satisfy the $n(Na_2CO_3)\geq[2n(Cr_2O_3)+n(Al_2O_3)]$ for simultaneously forming Na_2CrO_4 and $Na_2O\cdot Al_2O_3$ in the roasting process. Practically, as shown in Fig. 12, $n(Na_2CO_3)\geq[2n(Cr_2O_3)+n(Al_2O_3)+n(SiO_2)]$ is necessary for guaranteeing the complete oxidation of chromium in chromite, due to the fact that the impurities of Si-bearing components may also consume Na_2CO_3 prior to the formation Na_2CrO_4 [17,19].

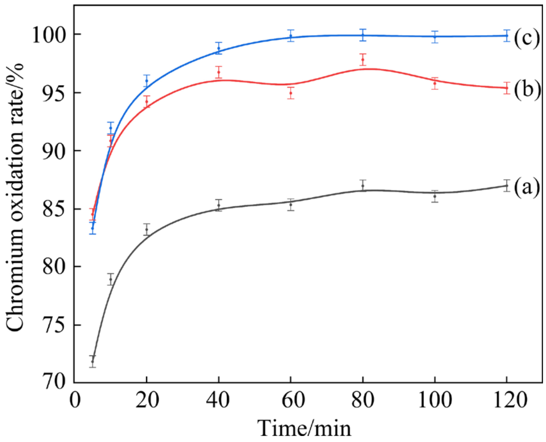


Fig. 12 Chromium oxidation rate of chromite in comparative oxidative roasting experiments with different Na_2CO_3 strategies: (a) Taditional strategy $n(Na_2CO_3)=[2n(Cr_2O_3)]$; (b) New strategy $n(Na_2CO_3)=[2n(Cr_2O_3)+n(Al_2O_3)]$; (c) New strategy $n(Na_2CO_3)=[2n(Cr_2O_3)+n(Al_2O_3)+n(SiO_2)]$ (Roasting temperature: 1373 K; Roasting time: 2 h)

The comparative experiment results in Fig. 12 verify the validity of the new strategies for the chromite lime-free roasting process. With the new Na_2CO_3 adding strategy, the chromium oxidation rates can be close to 100% in the clinkers, meaning that a high chromium extraction yield and low chromium content of the COPR can be achieved. In addition, all the Al-bearing components are expected to be converted into leachable $Na_2O\cdot Al_2O_3$, which can be leached in the following clinker leaching process, and then can be efficiently recovered as aluminum hydroxide by an aluminum utilization method [30]. The leaching separation of Al-bearing components from the clinkers together with the high chromium recovery not only makes the COPR discharge amount reduce remarkably but also simplifies the composition of the COPR, which allow the new COPR to dispose or to utilize more efficiently [15,18].

The essence of the new strategy is increasing the dosage of Na_2CO_3 in the chromite roasting process. The main drawback of this strategy is the risk of more molten liquid phase to form in the roasting process. The excessive liquid phase may hinder the oxygen diffusion and lead to rotary kiln ringing, which may affect the chromium extraction efficiency and cause difficulties for the roasting in the rotary kiln [31]. But, this drawback can be overcome by adjusting the proportion of the recycling slag in the roasting process. Returning part of leaching residue as recycling slag back to the rotary kiln is an established and efficient technique for control of molten liquid phase in the industrial lime-free roasting process [18]. Moreover, almost all the factories with the chromite lime-free roasting process have the recycling slag adding system, so it is easy to eliminate the drawback mentioned above by adjusting the process parameters (the proportion of the recycling slag) on the existing production system. With the new roasting strategy developed in this work, the contents of chromium and aluminum in the new leaching residues are much lower than those in traditional residues, so the new leaching residue as recycling slag may have better efficiency for eliminating the impacts of the molten liquid phase in the roasting process.

4 Conclusions

(1) $Na_2O\cdot Al_2O_3$ can react with chromium spinel $MgO\cdot Cr_2O_3$ simultaneously generating Na_2CrO_4 and $Mg(CrAl)O_4$ in the oxidative roasting process. $Mg(CrAl)O_4$ is difficult further to react with $Na_2O\cdot Al_2O_3$, which makes only about 50% of the chromium in $MgO\cdot Cr_2O_3$ oxidized and converted into Na_2CrO_4 when roasting $MgO\cdot Cr_2O_3$ with $Na_2O\cdot Al_2O_3$ in oxidizing atmosphere.

(2) The components of MgO, Fe_2O_3 and $MgO\cdot Fe_2O_3$ can improve the chromium oxidation rate of the reaction between $Na_2O\cdot Al_2O_3$ and $MgO\cdot Cr_2O_3$, but they have little effect on the chromium oxidation reaction between $Na_2O\cdot Al_2O_3$ and $Mg(CrAl)O_4$. The formation of $Na_2O\cdot Al_2O_3$ and $Mg(CrAl)O_4$ together with the difficult reaction between $Mg(CrAl)O_4$ and $Na_2O\cdot Al_2O_3$ is the main cause of the incomplete oxidation of chromium in the traditional chromite lime-free roasting experiments.

(3) To make the chromium oxidized completely in chromite lime-free roasting process, the additional consumption of Na_2CO_3 for forming $Na_2O\cdot Al_2O_3$ must be taken into account and the corresponding amount of Na_2CO_3 should be added in the raw meal. With the new Na_2CO_3 addition strategy, the chromium oxidation rate is close to 100% in chromite lime-free roasting process.

Acknowledgment

The authors are grateful for the financial support from the National Natural Science Foundation of China (No. 51874372).

References

[1] QI Jian-tao, ŚWIATOWSKA J, SKELDON P, MARCUS P. Chromium valence change in trivalent chromium conversion coatings on aluminium deposited under applied potentials [J]. Corrosion Science, 2020, 167: 108482.

[2] YANG Ming-e, YANG Hao-xiang, TIAN Sheng-hui, WANG Ming-yu, WANG Xue-wen. Cyclic metallurgical process for extracting V and Cr from vanadium slag: Part II. Separation and recovery of Cr from vanadium precipitated solution [J]. Transactions of Nonferrous Metals Society of China, 2021, 31(9): 2852−2860.

[3] PRASAD S, KUMAR M, RANDHAWA N S. Processing of chromite overburden by soda roasting to recover chromium as sodium chromate [J]. Transactions of the Indian Institute of Metals, 2021, 74(9): 2221−2230.

[4] PENG Hao, GUO Jing, LV Li-ping, HUANG Hui-sheng, LI Bing. Recovery of chromium by calcium-roasting, sodium-roasting, acidic leaching, alkaline leaching and sub-molten technology: A review [J]. Environmental Chemistry Letters, 2021, 19(2): 1383−1393.

[5] ESCUDERO-CASTEJÓN L, TAYLOR J, SÁNCHEZ-SEGADO S, JHA A. A novel reductive alkali roasting of chromite ores for carcinogen-free Cr^{6+}-ion extraction of chromium oxide (Cr_2O_3)—A clean route to chromium product manufacturing [J]. Journal of Hazardous Materials, 2021, 403: 123589.

[6] CHEN Gang, WANG Xiao-hui, DU Hao, ZHANG Ying, WANG Jia-jun, ZHENG Shi-li, ZHANG Yi. A clean and efficient leaching process for chromite ore [J]. Minerals Engineering, 2014, 60: 60−68.

[7] TANG Xiao-yu, WU Hai-feng, QUAN Xue-jun, FENG Cheng-fei, LI Gang, QIU Fa-cheng. Separation of sodium chromate from the high alkaline media based on precipitation transformation using barium hydroxide [J]. New Journal of Chemistry, 2020, 44(5): 12048−12057.

[8] DU Y G, CHRYSOCHOOU M. Microstructural analyses of Cr(VI) speciation in chromite ore processing residue from the soda ash process [J]. Journal of Hazardous Materials, 2020, 393: 122385.

[9] LI Bo, HAN Ping, ZHANG Bo, FENG Hai-yao, LI Wu, DONG Ya-ping. A concise and mild green synthetic route of sodium chromate through ferrochrome electrochemical oxidation and in-situ purification [J]. Journal of Hazardous Materials, 2020, 387: 121699.

[10] WANG Zhong-hang, DU Hao, WANG Shao-na, ZHENG Shi-li, ZHANG Yi, HWANG S, KIM N S, JEONG T E. Electrochemical enhanced oxidative decomposition of chromite ore in highly concentrated KOH solution [J]. Minerals Engineering, 2014, 57: 16−24.

[11] ZHENG Shi-li, ZHANG Yi, LI Zheng-yu, QI Tao, LI Hui-quan, XU Hong-bin. Green metallurgical processing of chromite [J]. Hydrometallurgy, 2006, 82(3/4): 157−163.

[12] ANTONY M P, JHA A, TATHAVADKAR V D. Alkali roasting of Indian chromite ores: thermodynamic and kinetic considerations [J]. Mineral Processing and Extractive

Metallurgy, 2006, 115(2): 71−79.

[13] BRUEN C P, LOW W W, SMALLEY E W. Process for the production of sodium chromate from chromite ore: US 3852059 [P]. 1974−12−03.

[14] TATHAVADKAR V D, JHA A, ANTONY M P. The soda-ash roasting of chromite minerals: Kinetics considerations [J]. Metallurgical and Materials Transactions B, 2001, 32(4): 593−602.

[15] DING Yi, JI Zhu. Production and application of chromium compounds [M]. Beijing: Chemical Industry Press, 2003. (in Chinese)

[16] QI Quan, LI Liang, WEI Liang-yu, HU Bao-ming, LIU Zheng, LIU Xu-qing. Study on leaching kinetics of hexavalent chromium from aged calcium-free chromium slag [J]. Main Group Chemistry, 2021, 20(3): 317−329.

[17] CHEN Yong-an, WANG Wu-yu, LI Ping, ZHENG Shi-li, ZHANG Xiang-dong, CHE Xiao-kui, ZHANG Yi. Re-oxidation mechanism of chromite roasting in late stages [J]. The Chinese Journal of Nonferrous Metals, 2015, 25(1): 203−210. (in Chinese)

[18] ANTONY M P, TATHAVADKAR V D, CALVERT C C, JHA A. The soda-ash roasting of chromite ore processing residue for the reclamation of chromium [J]. Metallurgical & Materials Transactions B, 2001, 32(6): 987−995.

[19] TATHAVADKAR V D, JHA A, ANTONY M P. The effect of salt-phase composition on the rate of soda-ash roasting of chromite ores [J]. Metallurgical and Materials Transactions B, 2003, 34(5): 555−563.

[20] QI Tian-gui, LIU Nan, LI Xiao-bin, PENG Zhi-hong, LIU Gui-hua, ZHOU Qiu-sheng. Thermodynamics of chromite ore oxidative roasting process [J]. Journal of Central South University of Technology, 2011, 18(1): 83−88.

[21] BROWN D H, FERGUSON D A. Thermal analysis of chromium(III) and chromium(VI) systems with silica and sodium silicate [J]. Journal of Thermal Analysis, 1976, 9(1): 79−82.

[22] SUBBANNA S N, MORGAN T R, FRICK D G. Method for production of alkali metal chromates from chrome ores: US 4244925 [P]. 1981−01−13.

[23] ZHOU Qiu-sheng, NIU Fei, WANG Jun-e, QI Tian-gui, LI Xiao-bin. Influences of impurities of ferrous oxide and aluminum oxide on oxidation rate of trivalent chromium and its mechanism [J]. The Chinese Journal of Nonferrous Metals, 2012, 22(5): 1503−1508. (in Chinese)

[24] WEI Guang-ye, QU Jing-kui, QI Tao, ZHENG Yu-dong, GUO Qiang. Research development of aluminum removal in chromium compound production [J]. The Chinese Journal of Nonferrous Metals, 2013, 23(6): 1712−1722. (in Chinese)

[25] LI Xiao-bin, QI Tian-gui, PENG Zhi-hong, LIU Gui-hua, ZHOU Qiu-sheng. Kinetics of chromite ore in oxidation roasting process [J]. The Chinese Journal of Nonferrous Metals, 2010, 20(9): 1822−1828. (in Chinese)

[26] GARBERS A M, van VUUREN C P J. A thermoanalytical study of the solid state reactions in the Cr_2O_3−Na_2CO_3−O_2 system [J]. Thermochimica Acta, 1987, 120: 9−17.

[27] SOKOLOV V A, MALYSHEVA T Y. The structure of fusion-cast high-chrome oxide refractories in the Cr_2O_3−MgO−Al_2O_3 system [J]. Refractories and Industrial Ceramics, 2005, 46(2): 127−131.

[28] KLEMME S, STC O'NEILL H. The effect of Cr on the solubility of Al in orthopyroxene: Experiments and thermodynamic modelling [J]. Contributions to Mineralogy and Petrology, 2000, (140): 84−98.

[29] MURTHY K S R C, GHOSE J, NAGESWARA RAO E. Reactivity in the spinel formation reaction in CuO/Al_2O_3, Fe_2O_3, Cr_2O_3 systems [J]. Journal of Materials Science Letters, 1983, 2(8): 393−394.

[30] ZHANG Pei-yu, WEI Guang-ye, GUO Qiang, QU Jing-kui, QI Tao. Crystallization of gibbsite from synthetic chromate leaching solution in sub-molten salt process [J]. Transactions of Nonferrous Metals Society of China, 2015, 25(8): 2734−2743.

[31] ESCUDERO-CASTEJON L, SANCHEZ-SEGADO S, PARIRENYATWA S, JHA A. Formation of chromium-containing molten salt phase during roasting of chromite ore with sodium and potassium hydroxides [J]. Journal for Manufacturing Science and Production, 2016, 16(4): 215−225.

铝酸钠对铬铁矿无钙焙烧过程中铬氧化的影响

齐天贵，李耀民，王 鹏，李小斌，彭志宏，刘桂华，周秋生

中南大学 冶金与环境学院，长沙 410083

摘 要：研究 $Na_2O\cdot Al_2O_3$ 与铬尖晶石及铬铁矿的氧化焙烧反应行为，揭示 $Na_2O\cdot Al_2O_3$ 对铬氧化的影响。结果表明：$Na_2O\cdot Al_2O_3$ 与 $MgO\cdot Cr_2O_3$ 的氧化焙烧过程中，$MgO\cdot Cr_2O_3$ 中仅有约 50%的铬被氧化转化为 Na_2CrO_4，其余的铬转化为含铝尖晶石 $Mg(CrAl)O_4$。$Mg(CrAl)O_4$ 在铬铁矿氧化焙烧条件下很难与 $Na_2O\cdot Al_2O_3$ 进一步反应。$Na_2O\cdot Al_2O_3$ 与铬铁矿氧化焙烧进一步证实了 $Na_2O\cdot Al_2O_3$ 不能与部分铬尖晶石充分反应，从而揭示了传统铬铁矿无钙焙烧生产铬盐过程中铬氧化转化率低的原因。根据实验结果，提出了一种消除 $Na_2O\cdot Al_2O_3$ 对无钙焙烧过程影响的新策略，即在炉料中增加 Na_2CO_3 的配量以满足形成 $Na_2O\cdot Al_2O_3$ 的需要，新策略可使铬氧化率提高至近 100%。本研究更新了人们对铝酸钠在铬铁矿无钙焙烧过程作用机理的认识，为开发高效清洁的铬盐生产技术提出了新思路。

关键词：铬盐；铝酸钠；铬铁矿；铬尖晶石；氧化焙烧

(Edited by Xiang-qun LI)