

# A new method for the treatment of chromite ore processing residues

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Received 15 December 2006; received in revised form 26 March 2007; accepted 2 April 2007

Available online 6 April 2007

## Abstract

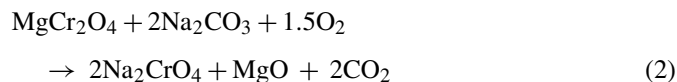
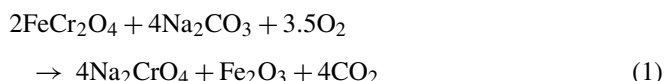
Chromite ore processing residue (COPR), derived from the so-called high-lime processing of chromite ore, contains a significant fraction of a leachable Cr(VI) which is harmful to human being and other organisms. In recent years, the concern over environmental pollution from the waste residue containing Cr(VI) has become a major problem for the chromium chemical industry. The main purpose of this investigation is to evaluate a new method for remediation of Cr(VI) in COPR. COPR was mixed with reductants, sucrose, starch or flour, and was calcinated at elevated temperatures in inertial gas. Effects of temperature, dosages of reductants and time on Cr(VI) reduction were investigated. Above 500 °C, Cr(VI) can be completely reduced to Cr(III).

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*Keywords:* Chromite; Residue; Chromate; Calcination; Reduction

## 1. Introduction

Chemicals containing chromium are widely used in many fields, such as metallurgy, leather tanning, electroplating, lumber and other industries. Sodium chromate is the basic intermediate product from which all other chromium compounds are produced. The old standard sodium chromate production process [1,2], the so-called high-lime process, is based on calcination of the mixture of chromite ore, soda ash and dolomite in rotary kilns at about 1100 °C, in an oxidizing atmosphere. The chromite components are oxidized according to the following reaction:



The use of dolomite as a filler results in a large quantity of waste—chromite ore processing residues (COPR), sometimes as much as 4 tonnes per ton of product [3,4], and that COPR contains up to 2% of Cr(VI) [2]. Because Cr(VI) is carcinogenic, mutagenic, and toxic through dermal and oral exposure, COPR

is considered as highly toxic waste. In Europe and the USA, the high-lime process is no longer used, but some 40% of world chromate production is still reliant on this process in the former Soviet Union, China, India and Pakistan [5,6].

Millions of tonnes of COPR produced by the high-lime process have, in the past, been disposed of in urban environments around the world [7–9]. Hundreds of tonnes of COPR are still coming out each year. For example, more than 6 million tonnes of COPR have been stored in heaps and about 1 million tonnes are produced each year in China [10]. Many approaches to decrease the Cr(VI) release of COPR have been experimented [11–14]. More than 200 pieces of papers which involve in the treatment and utilization of COPR can be found in VIP INFORMATION-Database of Chinese Scientific Journal. All of them may be included in two categories: (1) converting Cr(VI) in COPR to Cr(III), which is in general strongly retained in the solid phase and is an essential dietary micronutrient [15,16]; (2) recovering Cr(VI) from COPR and reusing. However, because the COPR is a very complex multicomponent system, with a variable quantitative composition in each mineral phase [7,17] and has a high pH, full reduction of Cr(VI) to Cr(III) is very difficult. Solid reductants, such as coal, cannot intimately contact with Cr(VI). Gaseous reductants are controlled by diffusion. Some reductants usually used in aqueous alkaline solution have been tried, too. However, almost all of them tried to reduce Cr(VI) in the leaching solution of COPR or contaminated materials, not in COPR itself [8,18]. Farmer et al. [19,20] and Geelhoed et al.

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[15] reported the reduction results of Cr(VI) in COPR by Fe(II) which has been most intensively studied in solution. They concluded that Fe(II) is ineffective in reducing Cr(VI) to Cr(III) because precipitation occurred when it contacted with COPR due to the high pH of COPR. Ferrous sulfate even substantially

was removed and cooled to the ambient temperature without stopping aeration of carbon dioxide. Leachable Cr(VI) of the treated COPR was measured according to Chinese Government Standard GB/T15555.4-1995 and GB 5086.2-1997. The reduced fraction of Cr(VI) was defined as

$$\frac{\text{Leachable Cr(VI) of COPR before reduction} - \text{Leachable Cr(VI) of COPR after reduction}}{\text{Leachable Cr(VI) of COPR before reduction}}$$

increased the Cr(VI) release of COPR due to anion exchange of sulfate for chromate in the layered double hydroxide mineral hydrocalumite. Su and Ludwig [21] studied the treatment of Cr(VI) in a solid waste which was derived from the production of ferrochrome alloy and had quite similar properties with COPR, using a mixed reductant solution of  $\text{FeSO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_4$ . Ferrous sulfate in combination with  $\text{Na}_2\text{S}_2\text{O}_4$ , which inhibits precipitation of Fe(II) and allows for its effective dissemination within the surface, indicated effective reduction of Cr(VI), while  $\text{Na}_2\text{S}_2\text{O}_4$  alone was ineffective. Considering the fact that Cr(VI) content is lower than 2%, usually 1% in COPR, it is not cost effective for recovering Cr(VI). This work presents the results of our research on the reduction of Cr(VI) in COPR by sucrose, starch and flour at elevated temperatures, based on our previous study [22].

## 2. Materials and methods

### 2.1. Materials and reagents

The COPR used in this study was taken from Zhenxing Chemical Plant (Henan, China), which is still producing sodium dichromate by the high-lime process. The soluble Cr(VI) content of the COPR is 1.07% and was determined by ferrous ammonium sulfate titration [23]. The composition of the COPR supplied by the plant was listed in Table 1.

Other chemicals, including sucrose and soluble starch, were purchased from Erqi Chemicals Co., Ltd. (Zhengzhou, China). The flour was purchased from a local supermarket.

### 2.2. Methods

COPR was ground to fine powders with an agate mortar and pestle. The samples were mixed with the reductants mentioned above in crucibles that were then put into a tube furnace. In order to ensure full and uniform contact of reductants with Cr(VI), the reductants were prepared to an aqueous solution or slurry of given concentrations. Carbon dioxide was introduced into the tube furnace to displace the air in it, ensuring the reduction reaction to be carried out under an oxygen-free atmosphere. The furnace was heated to a predetermined temperature and maintained for a preset period. After that the tube

## 3. Results and discussion

Figs. 1–4 show the reduction results of Cr(VI) by sucrose at 200, 300, 400, 500 °C. It can be seen that higher temperatures favor the reduction of Cr(VI). At temperatures of or above 500 °C, the reduction can be expected to end in about 10–20 min. However, it did not finish in up to 2 h at 200 °C. Moreover, it can be also found that the reduction rate and extent increase

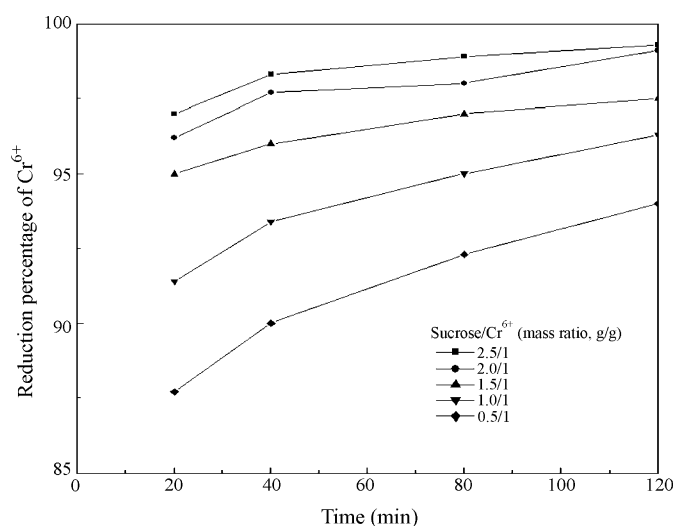


Fig. 1. Reduction percentage of  $\text{Cr}^{6+}$  at 200 °C with sucrose as reductant. (Initial  $\text{Cr}^{6+}$  content = 1.07%.)

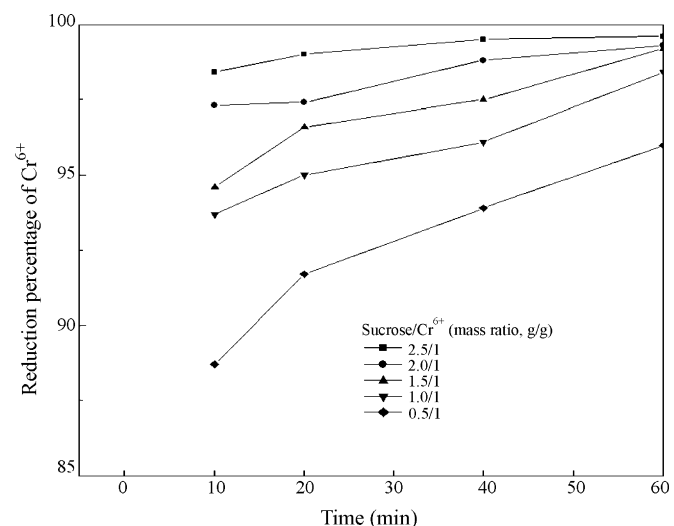


Fig. 2. Reduction percentage of  $\text{Cr}^{6+}$  at 300 °C with sucrose as reductant. (Initial  $\text{Cr}^{6+}$  content = 1.07%.)

Table 1  
Composition of the COPR

Species	$\text{Cr}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	MgO	$\text{SiO}_2$	CaO	$\text{Al}_2\text{O}_3$	Others	Total
wt%	5.83	14.30	19.95	12.58	33.75	6.43	7.16	100

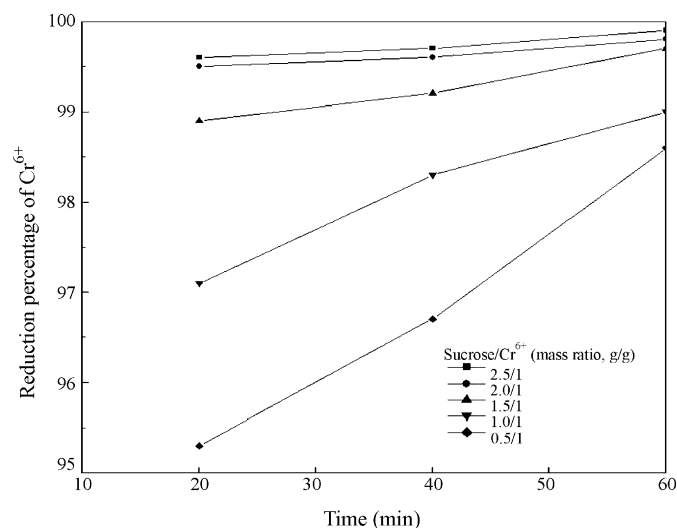
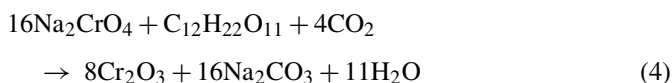
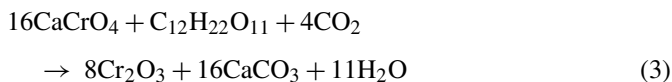


Fig. 3. Reduction percentage of  $\text{Cr}^{6+}$  at  $400\text{ }^\circ\text{C}$  with sucrose as reductant. (Initial  $\text{Cr}^{6+}$  content = 1.07%.)

with increasing sucrose addition at all temperatures investigated. The reduction of Cr(VI) by sucrose can be represented by the following equations:



According to the equations, 1 mol of sucrose would reduce 16 mol of Cr(VI), that is, 1 g of Cr(VI) need 0.41 g of sucrose. Actually, the reaction mechanism might vary with the increase of temperature and reaction time. More sucrose is necessary because sucrose changes with temperature and time. Ahmed [24] found that mono- and disaccharides are not quantitatively

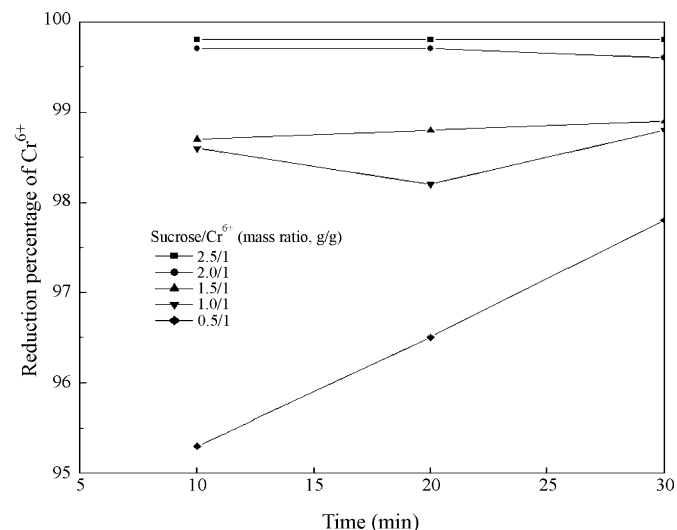
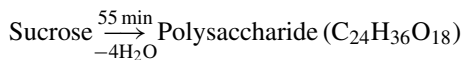
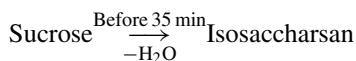


Fig. 4. Reduction percentage of  $\text{Cr}^{6+}$  at  $500\text{ }^\circ\text{C}$  with sucrose as reductant. (Initial  $\text{Cr}^{6+}$  content = 1.07%.)

oxidized with Cr(VI). It is known that sucrose changes to glucose and levan at  $160\text{ }^\circ\text{C}$ , and at  $200\text{ }^\circ\text{C}$ , caramelization takes place, sucrose is pyrolyzed as follows [25]:



The reactions are catalyzed in alkaline media. Pyrolysis extent increases with the increase of temperature. The pyrolysis products consist of aldehyde, ketone, carboxylic acid, ester, and so on, which might have higher reductivity. Therefore, the reduction of Cr(VI) by sucrose might be a very complex process. In the early stage of reduction and at a relative low temperature, sucrose reacted with Cr(VI) and degrades simultaneously. In the late stage of reduction and at a relative high temperature, sucrose decomposed completely and it was pyrolysis products that reacted with Cr(VI). Obviously, although more sucrose benefits the reduction of Cr(VI), it is temperature that controls the reactions. At  $200\text{ }^\circ\text{C}$ , pyrolysis products of sucrose were only water and condensed constituents which might have low reactivity, sucrose itself should play a main role in the reduction of Cr(VI). At a higher temperature, more high-reactive pyrolysis products came forth so that the reduction of Cr(VI) was easier. Gaseous reductants from the pyrolysis may also break down the aggregates in the COPR and make the Cr(VI) encapsulated expose to reduction. Liang and Meng [26] studied the reduction of Cr(VI) in COPR by aqueous molasses solution and the effluent from the production process of monosodium glutamate in steam, and the results showed that temperature was a key factor.

The reduction extent of Cr(VI) is related to reaction time. Generally, reduction percentage of Cr(VI) increases with the increase of time. At  $500\text{ }^\circ\text{C}$ , reduction finished in about 12 min (Fig. 5).

Reduction of Cr(VI) by soluble starch and wheat flour were also studied. The results were shown in Table 2. It can be found that the three kinds of reductants almost have the same efficacy. It is known that thermal treatment of dry starch usually

Table 2  
Reduction percentage of Cr(VI) at  $600\text{ }^\circ\text{C}$

Time (min)	Reductants	Mass ratio of reductants to Cr(VI)				
		2.5:1	2.0:1	1.5:1	1.0:1	0.5:1
10	Sucrose	100.0	100.0	100.0	99.5	98.1
	Starch	100.0	100.0	99.2	98.5	97.7
	Flour	100.0	100.0	100.0	99.8	98.4
20	Sucrose	100.0	100.0	100.0	100.0	99.7
	Starch	100.0	100.0	100.0	100.0	99.9
	Flour	100.0	100.0	100.0	99.0	99.5

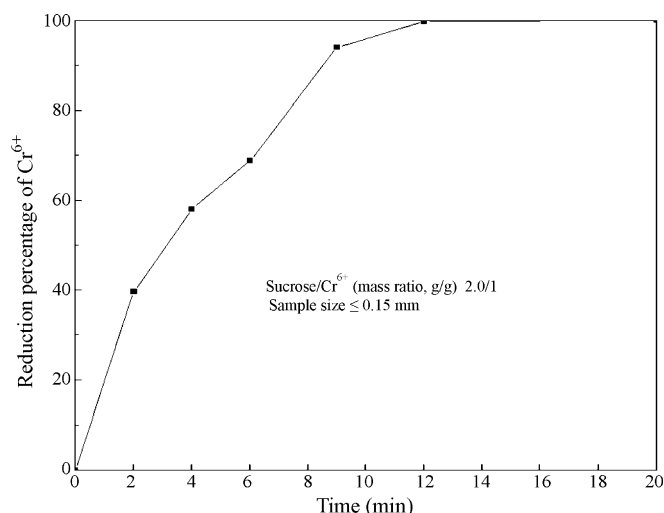


Fig. 5. Reduction percentage of Cr<sup>6+</sup> at different time with sucrose as reductant. (Initial Cr<sup>6+</sup> content = 1.07%, 600 °C.)

leads exclusively to its depolymerization, unless the temperature applied exceeds 300 °C. The starch undergoes a series of irreversible changes. The initial phase causes modification of the polymer structure to form pyrodextrins. At higher temperatures, depolymerization of the macromolecules takes place with the formation of β-(1,6)anhydro D-glucopyranose (levoglucosan), 2-furaldehyde (furfural) and a range of lower molecular-weight volatile and gaseous fragmentation products. A carbonaceous residue remains after all the volatile products have been driven off [27,28]. These processes are similar to those of sucrose pyrolysis. Wheat flour consists of starch (~80%), protein (~13%), pentosan (~2%), fat (~2%), cellulose and ash [29,30]. Therefore, it is no surprise that flour has the same efficacy as sucrose and starch. It can be deduced that similar cheaper materials such as potato flour, corn flour, even some wastes containing soluble carbohydrates, might also be used to treat COPR.

#### 4. Conclusion

A new method for the treatment of COPR was investigated. By mixing COPR with the solution of sucrose, starch or flour slurry and calcinating the mixers at 500–600 °C under inertial gas CO<sub>2</sub> protection, Cr(VI) in COPR can be reduced completely into Cr(III). Only if reductants are enough, which should be twice the stoichiometric ratio, reduction of Cr(VI) finishes in a few minutes. This provides another choice for the abatement of chromium pollution from a potentially hazardous material. Cheaper reductants such as the wastes or byproducts from processing agricultural produces, and the feasibility of the commercial exploitation of this method will be investigated.

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