# A CLEAN PRODUCTION PROCESS OF CHROMIC OXIDE

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## Introduction

Chromic oxide is an important basic chemical and finds many applications including metallurgical materials, green pigments, construction materials, refractory materials and catalysts. Presently, the industrial production of chromic oxide generally employs two processes (Ding, 2003): one is the reduction of sodium dichromate with ammonia sulfate; the other is the thermal decomposition of chromic anhydride. Both of the processes employ hexavalent chromium as the raw materials. However, the industrial production of hexavalent chromium compounds, including sodium dichromate and chromic anhydride, leads to serious environmental problem and low resource utilization.

Fig. 1 illustrated the traditional production process for hexavalent chromium compounds, as well as chromic oxide. It produces useful products of sodium dichromate and chromium anhydride, as well as several kinds of toxic residues, including chromium-containing residue, aluminum-enriched residue and chromium-containing Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) and sodium bisulfate.

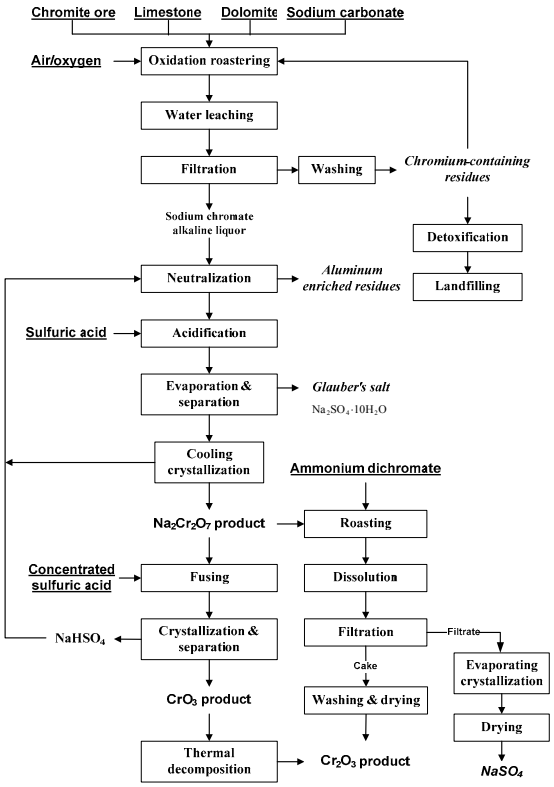


**Fig. 1.** Illustrative Flow Sheet of the Traditional Production Process for Chromium Compounds

In the traditional process, there are three main problems. The first is the environmental pollution. During production of one ton of chromium anhydride product, the chromate production plant discharges

approximately 2.0 to 2.5 tons of toxic chromium-containing residues that are difficult to be detoxified and comprehensively used because of high content of hexavalent chromium. Also, the produced calcium chromate is highly toxic and carcinogenic. Furthermore, the discharge of large amount of chromium-containing gases and dusts creates serious pollution. The second problem is that the conversion efficiency of chromium is only 76%, which means that a considerable amount of chromium is discharged into the residue. The third problem with the process is the production of by-products that are not valuable. The chromium-containing Glauber's salt and sodium bisulfate produced are of little use and constitute a pollution source. Consequently, the total atom utilization efficiency of the traditional process is quite low.

In this paper, a clean production process, which was recently developed by the Institute of Process Engineering, Chinese Academy of Sciences, will be described in details (Zhang, 2005). With the design objective of eliminating pollution at the source, the clean process greatly improves the resource utilization efficiency and successfully achieves the zero emission of chromium-containing residues.

## Overall Description of the Clean Process

### *Illustrative Flow Sheet*

As shown in Fig. 2, the clean production process of chromic oxide mainly includes the liquid-phase oxidation in Sub-Molten Salt (SMS) medium, the multi-phase separation and evaporative crystallization, the hydrogen reduction of potassium chromate, and the activated sintering of the intermediate product (Li, 2008a).

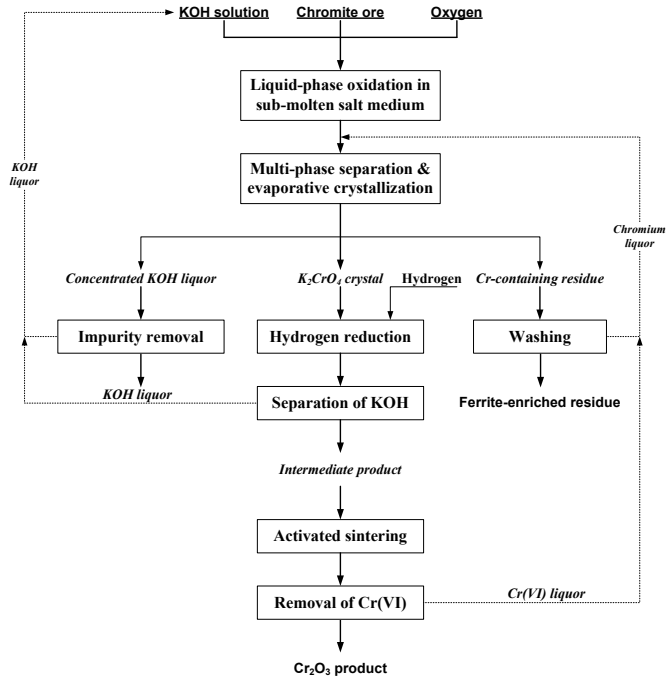


**Fig. 2.** Illustrative Flow Sheet of the Clean Production Process of Chromic Oxide

### *Main Reactions in the Clean Process*

For the trivalent chromium in the chromite ore, it is firstly converted into hexavalent chromium as potassium chromate during the liquid-phase oxidation process.

$$Cr_2O_3 + 4KOH + 1.5O_2 \rightarrow 2K_2CrO_4 + 2H_2O \quad (1)$$

Then it is converted back into trivalent chromium as chromic oxide in the hydrogen reduction process.

$$2K_2CrO_4 + 3H_2 \rightarrow 4KOH + Cr_2O_3 + H_2O \quad (2)$$

Since the final product, chromic oxide, bears no potassium, the KOH consumed in the liquid-phase oxidation process can be actually recovered and recycled inside the process. Therefore, no more raw materials than chromite ore, oxygen, and hydrogen are consumed in the clean process theoretically.

$$Cr_2O_3(\text{chromite ore}) + 3H_2 + 1.5O_2 \rightarrow Cr_2O_3(\text{final product}) + 3H_2O \quad (3)$$

For the associate components in the chromite ore, including Al, Mg, Si, and Fe, they mainly enter the ferrite-enriched residue and are converted into the byproduct desulfurization agent.

***Comparison of the Clean Process with the Traditional Process***

Fig. 3 showed the comparison of the clean process with the traditional process for producing chromic oxide and four features of the clean process were also stated.

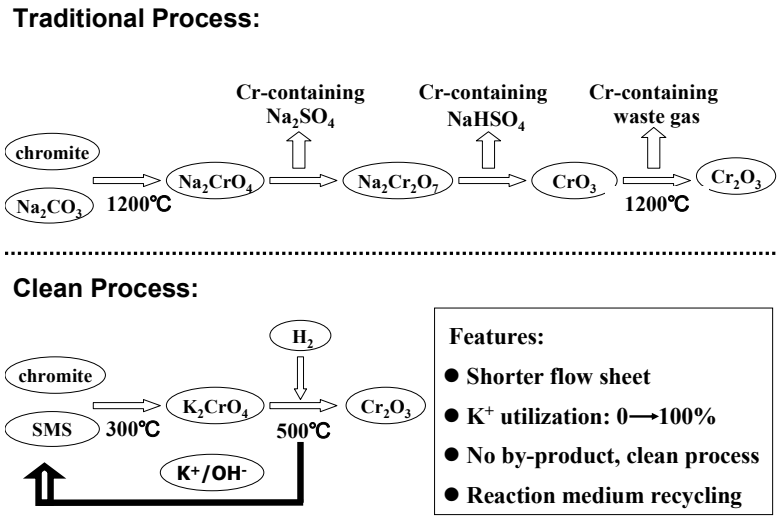


**Fig. 3.** Comparison of the Clean Process with the Traditional Process

From the raw material, chromite ore, to the final product, chromic oxide, only the intermediate product, potassium chromate is produced, the clean process achieves a shorter flow sheet than the traditional process. Since no potassium-bearing byproduct or waste is produced, the utilization of potassium can be as high as 100%. The reaction media, KOH in SMS, can be completely recovered in the hydrogen reduction unit. Moreover, since no chromium-containing byproduct or waste is produced, a clean process is thus achieved.

## Lab Scale Test Results and Discussion

***Typical Composition of the Chromite ore (Xu, 2005)***

Table 1 listed the chemical analysis of the chromite ore (originating from Vietnam). Fig. 4 illustrated the X-ray diffraction and phase identification results.

**Table 1**. Chemical Analysis of the Chromite Ore Used in the Lab Scale Test

| Component | $Cr_2O_3$ | FeO | MgO | $SiO_2$ | $Al_2O_3$ | $MnO_2$ |
|---|---|---|---|---|---|---|
| Content, %wt | 41.40 | 22.31 | 8.88 | 12.73 | 11.94 | 0.08 |

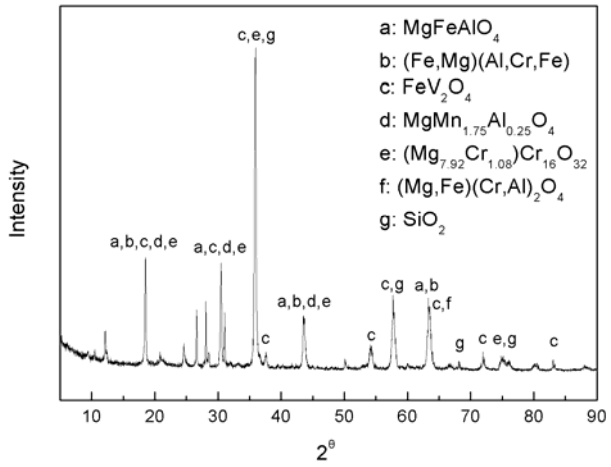


**Fig. 4.** The X-ray Diffraction and Phase Identification Results of the Chromite Ore Used in Lab Scale Test

***Liquid-phase Oxidation (Xu, 2005)***

In the liquid-oxidation process, the following reactions, besides Reaction (1), mainly occur:

$$2FeO \cdot Cr_2O_3 + 8KOH + 7/2\,O_2 \rightarrow Fe_2O_3 + 4H_2O + 4K_2CrO_4 \quad (4)$$

$$2MgO \cdot Cr_2O_3 + 8KOH + 3O_2 \rightarrow 2MgO + 4H_2O + 4K_2CrO_4 \quad (5)$$

$$Al_2O_3 + 2KOH \rightarrow 2KAlO_2 + H_2O \quad (6)$$

$$SiO_2 + 2KOH \rightarrow 2K_2SiO_3 + H_2O \quad (7)$$

The extraction sequence of the main components in the chromite ore, Cr, Al, and Si, was given in Fig. 5. And the X-ray diffraction and phase identification results of the chromite ore process residue was given in Fig. 6. It can be seen that the aluminum in the chromite ore is almost steadily leached into the liquor according to Reaction (6). However, the silicon in the chromite ore might firstly be leached into the liquor according to Reaction (7) and then react with aluminum and potassium hydroxide and produce potassium aluminosilicate ($KAlSiO_4$).

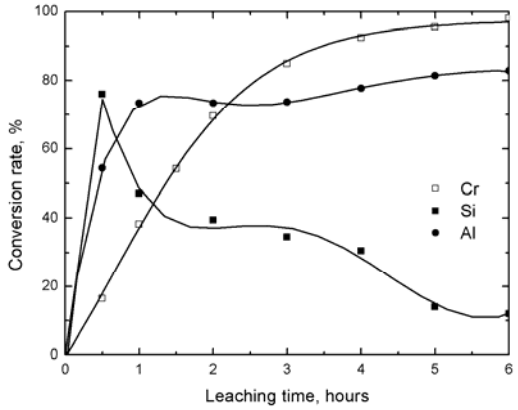


**Fig. 5.** The Extraction Sequence of Cr, Al, and Si during the Liquid-phase Oxidation Process

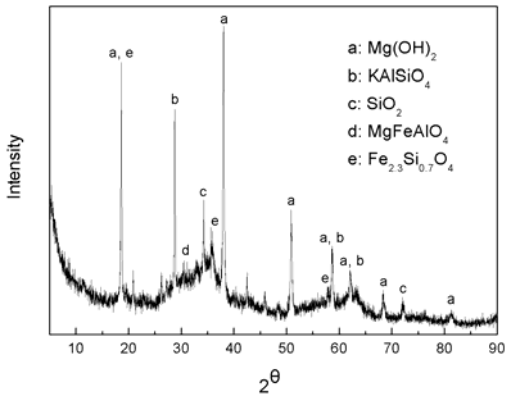


**Fig. 6.** The X-ray Diffraction and Phase Identification Results of the Chromite Ore Processing Residue

Fig. 7 illustrated the effect of reaction temperatures on the conversion of chromium for the combination of Reactions (1), (4), and (5). It can be found that, at a temperature higher than 320℃, the conversion of chromium can be achieved as high as 98%.

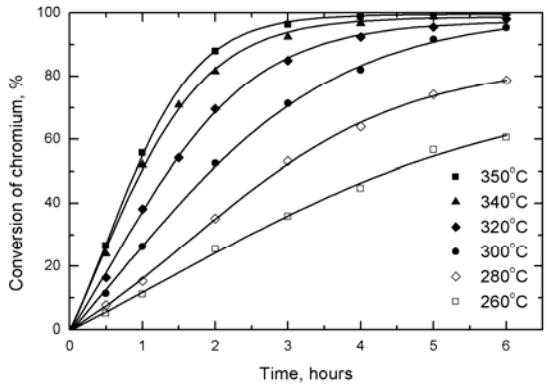


**Fig. 7.** Effect of Reaction Temperature on the Conversion of Chromium

***Hydrogen Reduction*** (Bai, 2006b)

In the hydrogen reduction and activate sintering process, the following reactions actually occur. For the hydrogen reduction:

$$2K_2CrO_4 + 3H_2 \rightarrow 2KCrO_2 + 2KOH + H_2O \quad (8)$$

For the hydrolysis and separation of KOH process:

$$KCrO_2 + H_2O \rightarrow CrOOH + KOH \quad (9)$$

Therefore, the main composition of the intermediate product is CrOOH, as can be seen in Fig. 8. For the activated sintering process:

$$2CrOOH \rightarrow Cr_2O_3 + H_2O \quad (10)$$

$$2KCrO_2 + 1.5O_2 \rightarrow K_2Cr_2O_7 \quad (11)$$

Through Reaction (11), the deep removal of potassium from the finally product, chromic oxide, is made possible, as can be seen in Fig. 9. Fig. 10 showed the SEM pattern of the $Cr_2O_3$ final product (Li, 2008b).

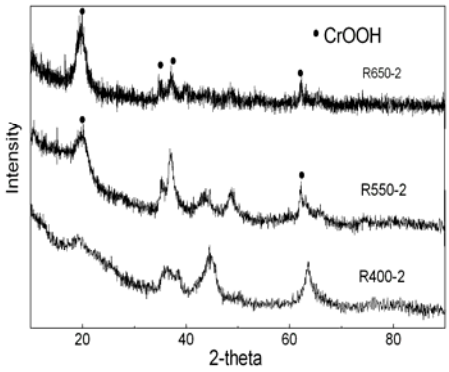


**Fig. 8.** XRD Pattern of the Intermediate at Different Reduction Temperatures

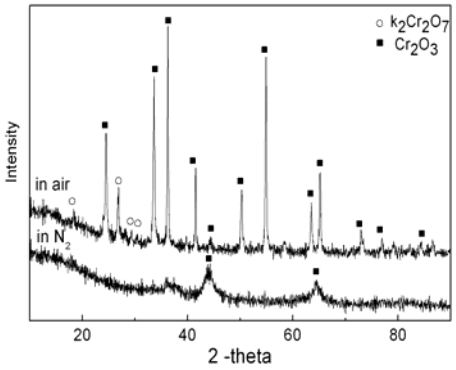


**Fig. 9.** XRD Pattern of the Activated Sintering Product in Different Atmospheres


**Fig. 10.** The SEM Pattern of the $Cr_2O_3$ Final Product

Table 2 listed the hydrogen reduction conversion under different reduction temperatures (Bai, 2006a). It can be seen that, at a temperature higher than 500℃, the conversion of hexavalent chromium can be achieved as high as 98% in a reaction time period of 90 min.

**Table 2.** Effect of Reducing Temperature on the Conversion of Hexavalent Chromium in 90 min

| Temperature, ℃ | 350 | 400 | 450 | 500 | 600 | 700 |
|---|---|---|---|---|---|---|
| Conversion, % | 3.2 | 12.9 | 95.1 | 98.2 | 99.3 | 99.8 |

## Industrial Demonstration

By use of the clean production described above, a demonstration plant with an annual production capability of 2,000 tons of chromic oxide has been built in China. The comparison of the industrial operation results of the clean process with those of the tradition process was given in Table 3 (Zhang, 2005). The clean process has exhibited promising results for the industrial production of chromic oxide.

**Table 3.** Comparison of the Industrial Results of the Clean Process with those of the Traditional Process

| Item | Traditional process | Clean process |
|---|---|---|
| Chromium conversion, % | 75 | 98 |
| Reaction temperature, ℃ | 1200 | 300 ~ 350 |
| Resource utilization, % | 15 | 90 |
| Chromium-containing residue amount, t/t | 2.0 | 0.5 → 0 (final zero emission) |
| Energy consumption | -- | Decreased by 20% |
| Production cost | -- | Decreased by 17% |

## Conclusion

With the design objective of eliminating pollution at the source, the clean production process greatly decreases the reaction temperature, remarkably improves the resource utilization efficiency and successfully achieves the zero emission of chromium-containing residues. The industrial demonstration results have shown a promising prospect for the industrial production of chromic oxide.

## Acknowledgements

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