

## Cleaning of Chromate Manufacture Process

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(Received 1999-12-29)

**Abstract:** Sodium chromate solubility is determined in the range of NaOH concentrations from 450 to 810 g/L and solution temperatures from 30 to 110 °C. The optimized conditions to separate sodium chromate from NaOH in leached solution are resolved. It is first found the method to efficiently separate sodium chromate from NaOH and sodium aluminate in crude sodium chromate. Bench-scale studies on the separating are performed. Finally, good separation results are achieved.

**Key words:** chromate; separation; clean process

Chromate is a vital raw material in chemical engineering industry. Presently, it is produced by soda roasting. Some disadvantages of the production method contain poor chromium extraction yield (about 76%), great amounts of residues with hypertoxic hexavalence chromium ion, and high consumption of energy, which hinder seriously development of chromate industry. Consequently, a series of investigations to improve chromium extraction yield and reduce amounts of toxic residues have been done in the world. The extraction of chromium through melting sodium hydroxide liquid-phase oxidation is a very significant method with high rate of its chromium extraction (about 99%), less consumption of energy and less amount of residue discharge. The method was ever performed by Denver Research Institute, University of Denver, America [1,2], as well as Nippon Chemical Institute Co., Ltd., Tokyo, Japan [3,4]. But no applications have been found in industry, because of difficulties in separating chromate from impurities. The scope of the project is to develop a new and more efficient method to separate chromate from all kinds of impurities in the process of chromium extraction from chromite and finally the clean production of chromate is achieved.

### 1 Experimental

The solution after water-leaching of the product from oxidization of chromite by melting sodium hydroxide liquid-phase is subjected to cooling crystallization in the temperature range of 40–110°C to separate chromate and aluminate from sodium hydroxide. The crude chromate crystal obtained after cooling crystallization

is subjected to countercurrent washing to remove aluminate and sodium hydroxide at 80°C. The crude sodium aluminate solution obtained after washing is hydrolyzed to get pure Al(OH)<sub>3</sub> and the solution containing chromate and NaOH at the room temperature. All kinds of raffinates are recycled into original step after concentration.

### 2 Results and Discussion

#### 2.1 Separation of sodium chromate from sodium hydroxide

The chromite mixed with melting sodium hydroxide reacts with sodium hydroxide and oxygen to form sodium chromate in the temperature range of 510–550°C. Generally, 5–6 times theoretical amounts of sodium hydroxide are added to the decomposed chromite completely during melting sodium hydroxide liquid phase oxidation. **Figure 1** show that sodium chromate solubility in NaOH solution is dependent of the mass concentration of NaOH as well as solution temperature. It is also found from the figure that sodium chromate solubility decreases rapidly with increasing in NaOH concentration in the range of less than 600 g/L NaOH solution, decreases very slowly with increasing in NaOH concentration in the range of more than 600 g/L NaOH, and increases rapidly with increasing in solution temperature in the range of more than 600 g/L NaOH.

The relation of sodium chromate solubility with NaOH concentration is shown as **figure 2**, from which it is observed that the differences in sodium chromate solubilities between 45 and 110°C have a nearly linear

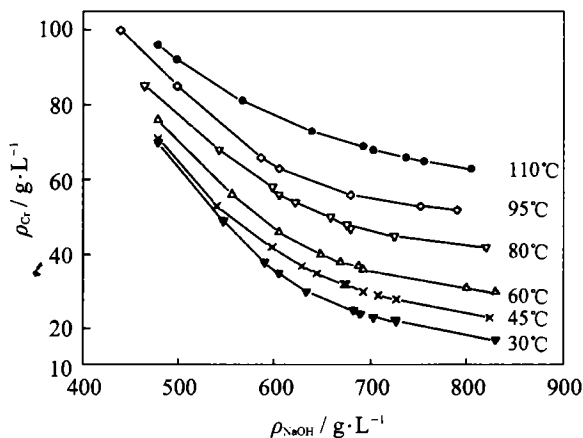


Figure 1 Sodium chromate solubility in relation with the mass concentrations of NaOH and solution temperatures.

relation with NaOH concentration in the range of less than 665 g/L NaOH solution as well as increase obviously with increasing in NaOH concentrations. However, the differences keep almost constant in NaOH solution in excess of 665 g/L.

In general, the NaOH solution concentration obtained by water-leaching oxidization product is proximately in the range of 650–700 g/L. By comparing the results in figure 2, it is practical that sodium chromate is separated from sodium hydroxide by cooling crystallization. The satisfying conclusion is reached that sodium chromate of 65%–70% is crystallized out as crude  $\text{Na}_2\text{CrO}_4$  crystal and NaOH of 80%–85% remains in raffinate. Crude  $\text{Na}_2\text{CrO}_4$  contains a certain amount of sodium aluminate and NaOH. Crude  $\text{Na}_2\text{CrO}_4$  is further purified by a new special method, pure  $\text{Na}_2\text{CrO}_4$  is obtained as a final product, and the raffinate containing mainly NaOH is concentrated and recycled into original oxidization step.

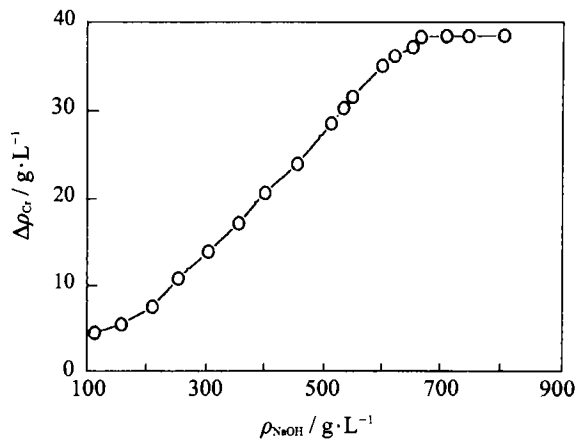


Figure 2 Differences in sodium chromate solubility between 45–110°C in relation with the mass concentration of NaOH.

## 2.2 Purification of crude sodium chromate

The crude sodium chromate crystal obtained above contains proximately 27%–30% NaOH, 50%–56%  $\text{Na}_2\text{CrO}_4$  (evaluated as Cr, 16%–18%Cr), 11%–14%  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ , and 3%–6% other impurities. The NaOH/Al ratio in crystal is about 7:1. It is difficult that  $\text{Na}_2\text{CrO}_4$  is separated from impurities only with the help of countercurrent washing, because it is necessary that NaOH concentration in excess of 550 g/L is controlled to reduce dissolving loss from  $\text{Na}_2\text{CrO}_4$  in NaOH solution to the lowest degree. However, in that case where the sodium aluminate solubility is 24 g/L (evaluated as Al), corresponding the NaOH/Al ratio is about 23:1 (556/24, seen in table 1), the value is much greater than 7:1. It can be calculated that sodium aluminate in part still remains in solid mixture as crystal after countercurrent wash. Therefore, it is impractical that sodium chromate is separated from sodium hydroxide and sodium aluminate only by using the difference between

Table 1 solubility about sodium aluminate in NaOH solution coexisting with saturated sodium chromate at 80°C.

$\rho_{\text{NaOH}} / \text{g} \cdot \text{L}^{-1}$	418	440	467	497	502	556	604	629	642	678	704
$\rho_{\text{Al}} / \text{g} \cdot \text{L}^{-1}$	42.5	39.0	35.4	32.1	28.9	24.0	21.6	20.7	19.8	16.4	15.0

their solubilities.

To solve the problem, preliminary studies involving efficient separation of sodium chromate from sodium hydroxide and sodium aluminate yield very good results. It is found that sodium aluminate and sodium chromate can be crystallized out from leached solution and form a special structure matter by adding a little amount of additive into leached solution and cooling crystallization. The kind of matter is called as ultrastructure crystal, and the reason why it forms will be further investigated. When the ultrastructure matter is washed through countercurrent constant temperature washing at 80°C, it easy to form supersaturated sodium

aluminate solution. The results from bench-scale washing are shown in table 2, from which it can be seen that sodium aluminate in ultrastructure crystal dissolves to form supersaturated solution, supersaturated concentration of sodium aluminate in solution are only dependent of ultrastructure crystal compositions and like-

Table 2 Supersaturated solution mass concentration of sodium aluminate at 80°C.

Ultrastructure crystal composition			Solution composition	
$w_{\text{Cr}} / \%$	$w_{\text{NaOH}} / \%$	$w_{\text{Al}} / \%$	$\rho_{\text{NaOH}} / \text{g} \cdot \text{L}^{-1}$	$\rho_{\text{Al}} / \text{g} \cdot \text{L}^{-1}$
15.2	29.0	3.9	580	77.5
16.7	27.0	3.3	545	66.9

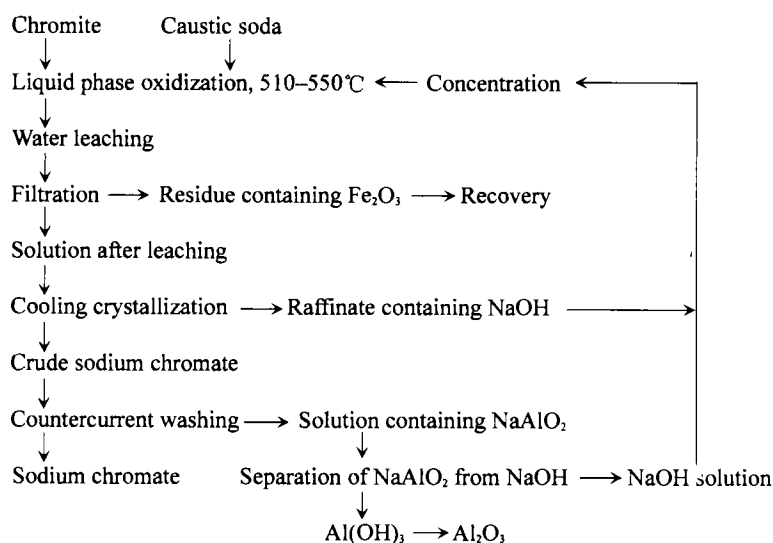
ly independent of NaOH concentration.

It actually becomes possible to efficiently separate sodium chromate from sodium aluminate and sodium hydroxide by utilizing the sodium aluminate characters mentioned above and countercurrent washing at 80°C. The results from countercurrent washing (seen in table 3) show that sodium aluminate and sodium hydroxide have been removed basically out of crude sodium chromate, the dissolving loss of sodium chromate is about 18% during washing. The solution obtained after washing crude sodium chromate mainly contains NaOH and sodium aluminate. It is subjected to further separation and the final product is  $\text{Al}(\text{OH})_3$  or  $\text{Al}_2\text{O}_3$  and solution

containing NaOH. NaOH solution is concentrated and also comes back to original step. Figure 3 is schematic flow chart. From the chart, it is known that clean technological production of  $\text{Na}_2\text{CrO}_4$  has come true.

**Table 3** Countercurrent washing results in mass fraction for ultrastructure crystal at 80°C. %

No.	Case	$w_{\text{Cr}}$	$w_{\text{NaOH}}$	$w_{\text{Al}}$
1	Before washing	15.2	29.0	3.9
	After washing	28.1	0.73	0.38
2	Before washing	16.7	27.0	3.3
	After washing	28.7	0.51	0.20



**Figure 3** Schematic flow diagram of clean production of chromate [5,6].

### 3 Conclusions

(1) The satisfying results reached that sodium chromate of 65–70% is crystallized out as crude  $\text{Na}_2\text{CrO}_4$  crystal and NaOH of 80–85% remains in raffinate by cooling crystallization of leaching solution.

(2) Pure  $\text{Na}_2\text{CrO}_4$  and solution containing  $\text{NaAlO}_2$  are obtained by countercurrent washing of crude  $\text{Na}_2\text{CrO}_4$  crystal containing a certain amount of sodium aluminate and NaOH.

(3) Pure  $\text{Al}(\text{OH})_3$  is obtained by hydrolyzing the solution containing  $\text{NaAlO}_2$  from countercurrent washing.

### Acknowledgements

The special project is financed by Chinese Academy

of Sciences (No.KZ95T-05).

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