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Fabrication of Cr_2O_3 powder from waste MgO-Cr refractory

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The possibility of producing Cr_2O_3 powder from waste magnesia-chromium refractory was investigated by sulfuric acid reaction, alkali fusion, water leaching & purification and heat treatment. The effects of temperature, the amount of NaOH added and the flow rate of air on chromium extraction efficiency in an alkali fusion step were investigated.
The fusion product was leached with methanol to solve free-NaOH, and then leached with water to produce a Na_2CrO_4 solution. The purity of chrome(VI) oxides, prepared both from monochromate with an impurity content and monochromate purified with CO_2 were also examined. The purified monochromate solution was reduced from Cr(VI) to Cr(III) with $NaHSO_3$ solution. The reduced solution was neutralized with NaOH to produce $Cr(OH)_3$. Water washing was treated to eliminate Na_2SO_4 from neutralized $Cr(OH)_3$ slurry. The washed $Cr(OH)_3$ was dried and thermally treated to produce Cr_2O_3 powder. The properties like lightness and hue of Cr_2O_3 fabricated in this study were L = 47.47, a= -14.40 and b = 17.21.

Keywords : MgO-Cr Refractory, Utilization, Pigment, Leaching, Chromium Oxide.

1. Introduction

Chromium oxide(Cr_2O_3) is heavily used in inorganic pigment, grinding material industries, in addition to its important role in refractory industry. In this work, the possibility of producing Cr_2O_3 from magnesia chromium refractory was investigated. A simplied process flow sheet, followed in this study for treatment of magnesia-chromium refractory is shown in Fig. 1. Briefly, it consists of four major steps ; sulfuric acid reaction, alkali fusion, water leach & purification and heat treatment.
The chemical reactions that takes place during the sulfuric acid reaction step are :

Free-MgO + $H_2SO_4 \rightarrow MgSO_4 + H_2O$ ----- (1)
Metal-Fe + $H_2SO_4 \rightarrow FeSO_4 + H_2$ ----- (2)
$H_2Cr_2O_7 + 6FeSO_4 + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$ -------------- (3)
$Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 12Mg(OH)_2 \rightarrow 12MgSO_4 + 2Cr(OH)_3 + 6Fe(OH)_3$ ---------- (4)

By sulfuric acid reaction, free MgO and metal-Fe are dissolved from waste magnesia chromium refractory and Cr(VI) is reduced without adding of reducing agent. The residue, after sulfuric acid reaction, was fused with NaOH with air bubbling. The chemical reaction that takes place during the alkali fusion step is :
$2(Mg, Fe)(Al,Cr)_2O_4 + 10NaOH + O_2 \rightarrow 4Na_2CrO_4 + 2NaAlO_2 + 4H_2O$ ------------ (5)

The product of alkali fusion reaction is then solidified and sparging to precipitate Al and Si compounds :

$4Na_2CrO_4 + 2NaAlO_2 + CO_2 \rightarrow 4Na_2CrO_4 + Na_2CO_3 + 2Al(OH)_3$ ----------- (6)

$Na_2OSiO_2 + CO_2 \rightarrow Na_2CO_3 + SiO_2$ ----------- (7)

Sodium monochromate is then treated with sulfuric acid to give sodium dichromate :

$4Na_2CrO_4 + 4H_2SO_4 \rightarrow 2H_2Cr_2O_7 + 4Na_2SO_4 + 2H_2O$ --- (8)

Sodium dichromate is treated with $NaHSO_3$ solution to reduce Cr(VI) to Cr(III). The reduced chromium sulfate($Cr_2(SO_4)_3$) is treated with sodium hydroxide to neutralize Cr(III) solution.

$2Cr_2(SO_4)_3 + 12NaOH \rightarrow 4Cr(OH)_3 + 6Na_2SO_4$ ------- (9)

The final $Cr(OH)_3$ is treated with fresh water to eliminate sodium sulfate and then treated with heat to produce Cr_2O_3 powder :

$4Cr(OH)_3 \rightarrow 2Cr_2O_3 + H_2O$ ------------ (10)

2. Experiment

2.1 Sulfuric acid reaction

Sulfuric acid reaction was used to eliminate free-MgO element contained in waste magnesia-chromium refractory . To do this reaction the waste refractory was crushed, screened as follow sizes (–0.075mm, 0.075～0.5mm, 0.5～2.36mm and +2.36mm) and then reacted with sulfuric acid. Through this reaction the solution rate of free-MgO was examined with the variation of reaction time. Also the relationship between the pH of reacted solution by the sulfuric acid and its purity was tested.

2.2 Alkali fusion

A residue of chromite concentrate filtered after sulfuric acid reaction was used in alkali fusion experiments. These experiments were conducted in a temperature-controlled furnace into which the stainless steel reactor containing the charge was placed. Air was bubbled through the charge and the charge was stirred from the top by a stirrer. Amount of NaOH additions and reaction temperature were the main parameters under investigation.

Several experiments were conducted by adding 2, 4 and 6 times the amounts of NaOH to residue under flow rate of air (2ℓ/min) at different temperatures (500, 600 and 700℃) and for 1 to 4hr of reaction periods. Stirring speed was kept

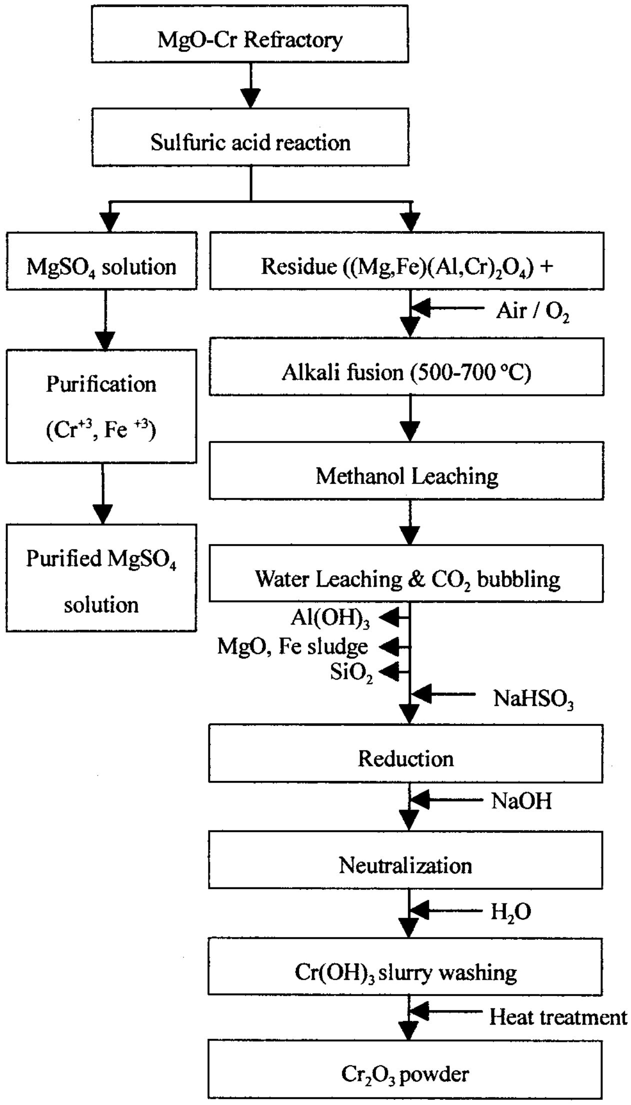

Fig. 1. Simplified process flow sheet for treatment of chromite concentrates.

constant at 300 rpm for all fusion experiments.

Investigated parameter of the leaching experiments was ; Solid/Liquid = 1/ 10, temperature 25℃ and leaching period 2hr. CO_2 was sparged into the monochromate solution with a flow rate 1 ~ 4.2ℓ/h to precipitate Al and Si compounds.

2.3 Heat treatment

Purified dichromate solution was reduced with $NaHSO_3$, neutralized with NaOH to precipitate $Cr(OH)_3$ and then washed several times to eliminate Na_2SO_4. After that the washed $Cr(OH)_3$ was heat treated at various temperatures. The heat treated powders were examined by XRD and spectrophotometer (MINOLTA : CM-3500d) to examine their crystal structures and their hues, respectively.

3. Results and discussion

3.1 Sulfuric acid reaction

The chemical compositions of crushed waste magnesia chromium refractory were shown in table 1.

Table 1. Chemical Compositions of waste MgO-Cr refractory used in this study. (wt%)

Size(mm)	+2.36	0.5-2.36	0.075-0.5	-0.075
T-Fe	5.6	5.28	5.05	5.10
M-Fe	0.48	0.35	0.28	0.20
CaO	0.72	0.64	0.68	0.80
SiO_2	0.95	1.12	1.10	1.19
Al_2O_3	5.48	5.15	4.25	3.73
MgO	53.31	57.42	59.90	65.71
Cr_2O_3	27.29	27.70	23.79	19.62

These crushed refractories were reacted with dilute sulfuric acid(H_2SO_4 : H_2O = 1:5, 1L). The variations of solution's pH during the addition of refractory to dilute sulfuric acid were represented in figure 2. And figure 3 shows that the impurities included in $MgSO_4$ solution, like Al, Si, Cr^{3+} and Fe^{3+}, could be eliminated by increasing the reacted solution's pH.

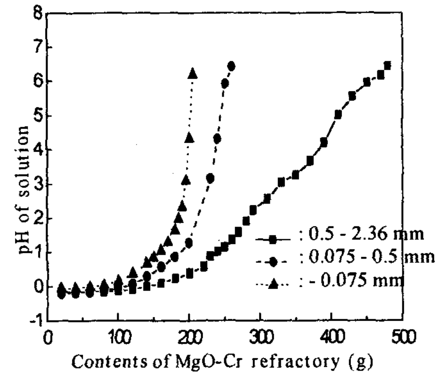

Fig. 2. pH of $MgSO_4$ solution in sulfuric acid reaction

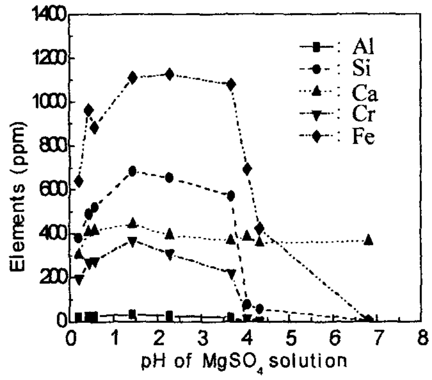

Fig. 3. Contents of elements to the pH of $MgSO_4$ solution

3.2 Alkali fusion

Table 2. shows the chemical compositions of residue used in this study.

Table 2. The chemical compositions of residue. (wt%)

CaO	MgO	Al_2O_3	Fe_2O_3	Cr_2O_3	SiO_2
0.56	22.22	7.33	11.25	43.90	1.44

A chromium recovery over 95% was reached with NaOH addition of 4 times of residue, at 600℃ fusion temperature for 4h and 6 times of residue, at 700℃ fusion temperature for 2h, with 2ℓ/min air flow rate and 300rpm stirring of reaction period. Fig.4 displays the results of fusion experiment and shows that as more addition of NaOH and fusion temperature are increased, the chromium extraction ratio increased.

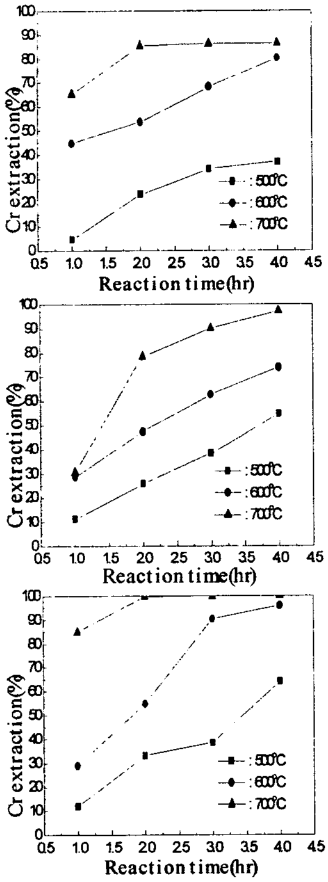

Fig. 4. Variation of Cr extraction to alkali fusion temperature and reaction time.

3.3 Purification of monochromate solution

To increase the purity of Cr_2O_3, purification of monochromate solution was operated with CO_2 sparging. CO_2 was sparged with flow rate of 3ℓ/h through a 1ℓ monochromate solution to eliminate major impurity elements, Al ans Si. Table 3 shows the chemical compositions of monochromate.

Table 3. Chemical composition of monochromate

(ppm)

Cr	Na	Mg	Al	Si	K	Ca	Fe
7.57 (mg/ml)	13.93 (mg/ml)	0.87	1107	33.1	13.8	1.70	0.14

Fig 5 shows that at the end of 120min purification process Al (< 1ppm) and Si (<0.01ppm) levels are accomplished.

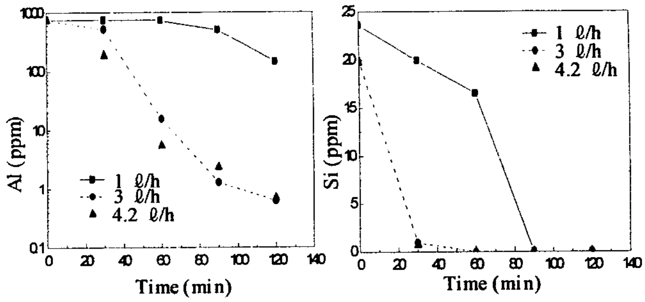

Fig. 5. The effect of CO_2 sparging on impurity content of monochromate solution.

3.4 Heat treatment

H_2SO_4 is added to control the pH of monochromate solution and convert it to dichromate solution. And this dichromate solution is reduced with $NaHSO_3$ and neutralized with NaOH. Neutralized $Cr(OH)_3$ sludge is filtered and washed several times to eliminate Na_2SO_4 attached to the surface of $Cr(OH)_3$. And then this $Cr(OH)_3$ is heat treated from 400℃ to 1200℃, for 1h, respectively. The hue of Cr_2O_3 powder is transformed from blue to green with the increase of heat treatment temperature. Fig.6 shows the XRD pattern of heat treated Cr_2O_3 powder at various temperature. The hue of Cr_2O_3 powder, heat treated at 1200℃ for 1h, showed L= 47.47, a = -14.40 and b = 17.21.

4. Conclusion

It was shown in this study that waste magnesia chromium refractory, generally landfilled, was treated by the sulfuric acid reaction and 'alkali fusion + water leach + heat treatment' to obtain $MgSO_4$ solution and Cr_2O_3 powder, respectively. Most free MgO of magnesia chromium refractory were eliminated by sulfuric acid reaction. As more particle size of magnesia chromium refractory was decreased, the sulfuric acid reaction rate increased. In this study, the most satisfactory alkali fusion conditions (Cr extraction ratio > 95%) were found to be ; 4 times of the residue amount of NaOH addition, 700℃, 4h or 6 times of the residue amount of NaOH addition, 600℃, 2h, 2ℓ/min air flow rate and 300rpm stirring speed. Leached Cr solution was purified, reduced, neutralized, washed and heat treated to produce Cr_2O_3 powder. The hue of it showed L= 47.47, a = -14.40 and b = 17.21.

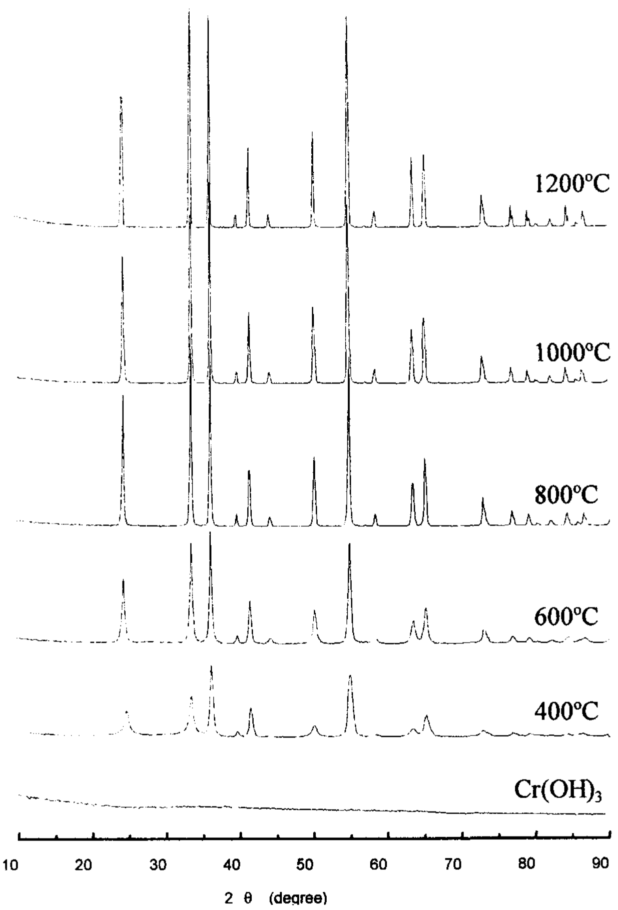

Fig. 6. XRD patterns of heat-treated Cr_2O_3 powders.

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