Eurasian ChemTech Journal 9 (2007) 97-103

The Study of the Formation of Sodium Chromate from El-Baramiya High-Silica Chromite Ore Concentrate Using Hydrated Lime

F.M.S. El-Dars[1]*, M.E.H. Shalabi[2], H.A.M. Abuzeid[3], M.G. Khalifa[4] and A.B. Farag[1]

[1]Chemistry Department, Faculty of Science, Helwan University, Helwan, Egypt

[2]Central Metallurgy Research and Development Institute, Cairo Egypt

[3]National Research Center, Cairo, Egypt

[4]El-Tabbin Metallurgical Institute, Cairo, Egypt

Abstract

The formation of sodium chromate from a mixture of high-silica chromite ore concentrate (48.8%), soda ash and hydrated lime was investigated. Hydrated lime was added to an optimal mixture of Cr_2O_3:Na_2CO_3 (mole ratio 1:2.5) (mole ratio of CaO 0-3) and the materials were roasted at 1000°C for 60 min and P_{O2} 0.21 atm. Results revealed a significant decrease in sodium chromate yield (from 42% to 25%) as the (CaO/Cr_2O_3) mole ratio increased from 0-0.5. Increasing the (CaO/Cr_2O_3) mole ratio above 1.0, an optimal chromate yield of 70% was achieved at the mole ratio of 2.5. In addition, roasting of optimal mixtures of soda ash, chromite ore and hydrated lime (CaO) (mole ratio 2.5:1:2.5) within the temperature range of (900-1000°C) provided a maximum chromate yield of 92% at 1000°C after 2 hours. Overall, the data revealed that while the hydrated lime addition significantly increased the reaction product yield, it also increased the process energy of activation from 112 kJ/mole for the Na_2CO_3:Cr_2O_3 (mole ratio 2.5:1) mixture to 171.6 kJ/mole during roasting time (40-100 minutes).

Introduction

The economics of chromite ore recovery depends upon the occurrence of the mineral and its chemical composition [1]. In Egypt, sufficient reserves of chromite ore are present at El-Baramiya region in the Eastern Desert [2]. Nevertheless, this ore requires more dressing to increase Cr percentage for large-scale production of chrome chemicals – such as sodium chromate and chromium metal – the essential materials for local industries. However, in order to promote the production of these chemicals within Egypt, local options must be examined so as not to increase the economic burden incurred by the importing of these chemicals.

Technically, for the production of chromate salts, a mixture of dried, crushed and ground chromite ore with soda ash (as a source of sodium carbonate) is charged for roasting within a rotary kiln furnace [3,4]. In order to obtain an optimal yield, an oxidizing atmosphere is maintained during this process and the temperature in the firing zone is controlled between 1100-1150°C.

Generally, the rate of the chromate formation reaction was reported to be influenced by a number of variables, namely: the reaction temperature, the partial pressure of gas, size of materials and the composition of the reaction mixture [5-13]. Higher chromate yields were obtained after roasting the ore within the temperature range of 750-1200°C [6,7,9,13-15]. As well, it was reported that the yield of sodium chromate obtained was dependent upon the partial pressure of oxygen maintained during roasting [8]. Concerning the materials size, previous studies have shown that maintaining the particle size less than 0.074 mm increased the rate of ore oxidation [3]. Moreover, it was reported that the agglomeration of the feed mix and the use of palletized raw materials [7] or briquettes [13] controlled losses during the roasting procedure as well as provided for higher chromate salt yields.

---

*corresponding author. E-mail: fkledars@hotmail.com

Printed in Kazakhstan

Regarding the composition of the roasted mixture, earlier work indicated that roasting of mixtures of chromite ore with soda ash and lime, calcium oxide and/or dolomite increased the rate of chromate formation [13]. El-Tawil *et al.* [7] found that adding CaO accelerated the rate of ore roasting in the presence of soda ash. As well, the data revealed that the energy of activation for the reaction was reduced to 201 kJ/mole and it was concluded that the rate-controlling step was a solid diffusion mechanism. From another perspective, Ozer *et al.* [16] showed that the kinetics of the chromite conversion into sodium chromate in the presence of soda ash and limestone at 750-900°C and at 8% O_2 was 2-nd order with respect to Cr_2O_3 and the reaction had energy of activation of 157 kJ/mole. More recently, Shalabi *et al.* [13] reported that the rate controlling was solid-solid mechanism at the end of reaction when dolomite was added to a mixture of chromate ore concentrate and soda ash.

However, while production of chromate salts is not undertaken in Egypt on an industrial scale, this study aimed to examine the reaction of the formation of sodium chromate using local ore concentrated, soda ash and available raw materials. In this context, the kinetics of the reaction of formation of sodium chromate from an optimal mixture of Cr_2O_3 ore concentrate and Na_2CO_3 (1:2.5 mole ratio) [12,13] by the addition of hydrated lime (based on CaO content) as a catalyst. The study was conducted in a tube furnace at P_{O_2} 0.21 atm (open air system) to attest the influence of temperature and change in CaO/Cr_2O_3 mole ratio within the reaction mixture.

Experimental

Materials

Representative samples of El-Baramiya region chromite concentrate for these investigations were provided by the Beneficiation Unit of the CMRDI. Soda ash (90% Na_2CO_3) was obtained from Misr Chemical Co. (El-Max, Alexandria) and hydrated lime from the Egyptian Iron and Steel Co. in Helwan. Table 1 illustrates that the chromite ore concentrate used had a Cr_2O_3 of 48.8% as well as oxides of Mg, Al and Fe. Hydrated Lime material contained mainly 63.15% CaO and 0.5% MgO with over 34% of ignition loses. Table 2 revealed that the raw materials used (chromite ore concentrate, lime and soda ash) had a particle size over 0.074 mm and, thus, were ground in the mill until ~100% of the material passed through the 0.074 mm screen.

Briquetting/Roasting Procedures

The materials were mixed thoroughly together then charged to a special mold (3 cm long and 1 cm inner diameter) and shaped using a manual hydrau-

Table 1

Chemical analysis of chromite ore concentrates and hydrated lime (wt.%)

Raw materials	FeO	Cr_2O_3	SiO_2	CaO	Al_2O_3	MgO	$Na_2O + K_2O + Cl$	L.O.I.
Chromite ore concentrate	10.2	48.8	6.5	1.2	15.2	16.8	–	0.65
Hydrated lime	–	–	0.80	63.15	–	0.5	–	34.7

L.O.I: Ignition Loses

Table 2

Particle size distribution for raw materials used

Particle size, mm	Chromite ore concentrate	Soda ash	Lime
+ 0.316	5.01	4	6
+ 0.2-0316	20.51	5	22
+ 0.1-0.2	36.1	29	38
+ 0.074-0.1	18.5	10	20
- 0.074	19.88	52	14

lic pressing machine. The study was conducted in a vertical tube open (open air system) to allow for the introduction of air into the furnace during roasting (from up downwards) and maintaining the reaction P_{O_2} at 0.21 atm accordingly. The roasting reactor used consisted of a heavy-duty temperature controlled tube furnace inside which a nickel-chrome wire basket of a diameter 5 cm hung vertically on a balance. A Ni-Ni/Cr thermocouple was set in the middle of the tube furnace and the temperature inside the furnace was held constant at 900-1000°C (±1°C) using a voltage regulator. A typical roasting procedure conducted was as follows:

- The system was checked for operation efficiency and corrective measures, if required, were taken accordingly;
- The required weight of agglomerated materials was charged into the basket and then into the reactor assembly when the furnace temperature reached the experimental predestined value (900, 925°C, *etc.*);
- After a predetermined period, roasting was stopped, the basket with the roasted products was removed, and briquettes were cooled in a desiccator;
- Chemical analysis of the samples was conducted after each individual run was performed [12].

Chemical determination of sodium chromate [12]

Procedure

1 g of the roasted briquette or pellet (green color) was dissolved in 400 ml distilled water and the solution was heated at 95-98°C and stirred for 15 min. After filtration, 25 ml of the filtrate (yellow color) was drawn out into a 500-ml conical flask and acidified with 10-15 ml 2N H_2SO_4. From a burette, 40-50 ml of 0.02 N solution of Mohr's salt was precisely delivered into the flask. The solution was diluted with 100 ml distilled water and the excess Mohr's salt was back-titrated with standard permanganate solution to a grayish color (combination of the green color of Cr^{3+} with the pink color of MnO_4^- ions). After the end – point was reached, 1-2 extra drops of permanganate were added to ensure a distinct pink color was obtained, indication of over-titration. The procedure was repeated three or more times and an average was calculated. For the blank, 25 ml the Mohr's salt solution was titrated in presence of 10-15 ml of sulfuric acid.

The percentage of sodium chromate obtained was calculated according to the following equation [7]:

Chromate recovery (*expressed as chromic oxide*) = (*Chromic oxide as sodium chromate/ chromic oxide in the sample*)×100%

Results and Discussion

The Effect of Hydrated Lime Addition on the Chromic Oxide Recovery

El-Dars *et al.* [12] indicated that an optimum amount of Cr_2O_3 recovery for the same ore concentrate was obtained with a Cr_2O_3:Na_2CO_3 mole ratio = 1:2.5 roasted at ~1000°C and for 40 min. During this work, the CaO mole ratio of hydrated lime was varied from 0-3.0 relative to the mixture Cr_2O_3 mole ratio = 1. Briquetting conditions (briquette pressure ~75 kg/cm^2 and briquette height 1.5 cm) were maintained. Figure 1 shows that the Cr_2O_3 recovery in solution decreased to a minimum of 24.9% at CaO/Cr_2O_3 mole ratio = 0.5:1, while it reached a maximum of 70% at 2.5:1 mole ratio. The former result may be attributed to the dissociation of lime hydroxide $Ca(OH)_2$ to CaO leading to an increase in the briquette porosity and, subsequently, decreasing the contact between mixture particles. The increased chromate yield at CaO/ Cr_2O_3 mole ratio = 2.5:1 may be attributed to the reaction between calcium oxide after dissociation with SiO_2, Fe_2O_3 and Al_2O_3 to form calcium silicate, calcium ferrite, and calcium magnesium aluminate and, thus, increasing the free sodium carbonate reacting within the mixture. Above this mole ratio, the increase in hydrated lime leads to an increase in melt formation and subsequently, a decrease in the briquette porosity leading to a decrease in Cr_2O_3 % recovery.

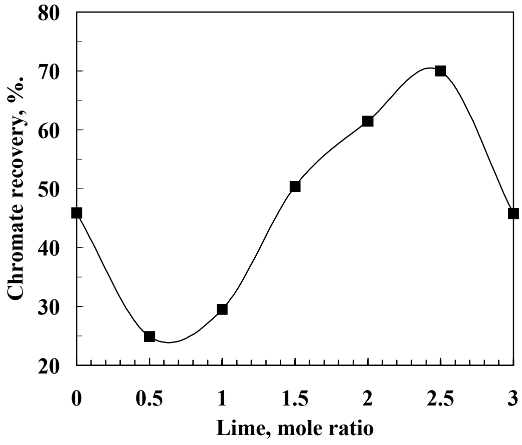

Fig. 1. The effect of varying lime mole ratio on chromate recovery % (as chromic oxide).

Kinetics of the Formation of Sodium Chromate in the Presence of Hydrated Lime

The kinetics of roasting of a briquette composed of a mixture of chromite ore concentrate; soda ash and CaO (mole ratio 1:2.5:2.5) were studied within the temperature range of 900-1000°C (Fig. 2). Figure 2 shows that as the temperature and time increased, the chromic recovery (R%) increased providing a maximum of 91.8% at 1000°C and after 120 min.

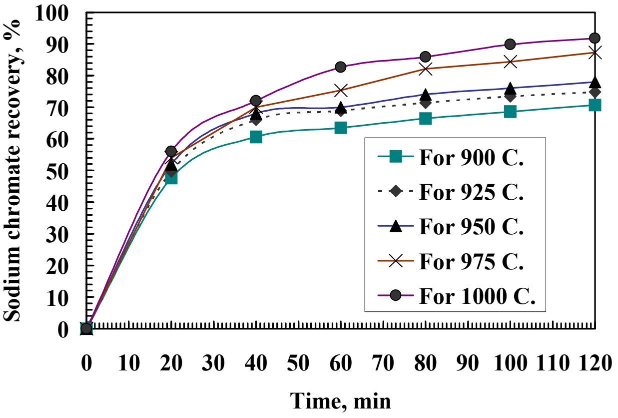

Fig. 2. The effect of varying the roasting time and temperature on sodium chromate recovery from briquettes of chromite ore concentrate, soda ash and lime (1:2.5:2.5).

To determine the rate controlling step or mechanism for these isotherms, different models were tried and the following model was found to be the most acceptable [17]:

$$k_2 t = [1 - (1 - R)^{1/3}]^2 = f(R) \qquad (1)$$

where R is the decimal fraction of chromic oxide recovery, t is the time of reaction (min), k is the rate constant (min^{-1}).

The plot between $[1 - (1 - R)^{1/3}]^2$ and ln$t$ is illustrated in Fig. 3 indicated a linear relationship. To determine the energy of activation, the Arrhenius equation for ln$k$ where plotted versus the inverse of the reaction temperature (Fig. 4). From this figure, the activation energy was found to be around 171.635 kJ/mole that corresponds to a solid diffusion controlled mechanism [9]. Ansari *et al.* [18] concluded that if the energy increased to between 121-158 kJ/mole, the reaction mechanism was solid-state diffusion controlled. As well, El-Tawil *et al.* [7] found that the chromite ore and sodium carbonate reaction with CaO had an E_a reduction from 261 to 201 kJ/mole (reflecting a solid diffusion control mechanism). Also, roasting of chromite ore concentrate with soda ash and lime in air (P_{O_2} = 0.21 atm) at 60% chromate recovery (expressed as chromic oxide) was a solid diffusion mechanism with E_a = 106 kJ/mole [11].

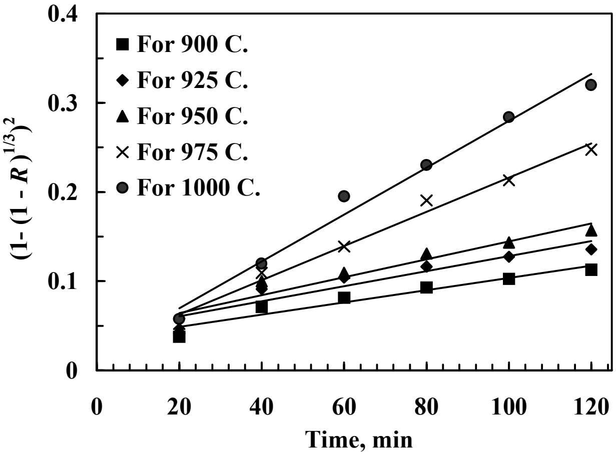

Fig. 3. Plot of $(1 - (1 - R)^{1/3})^2$ and time for the final reaction period (20-120 min) at different temperatures.

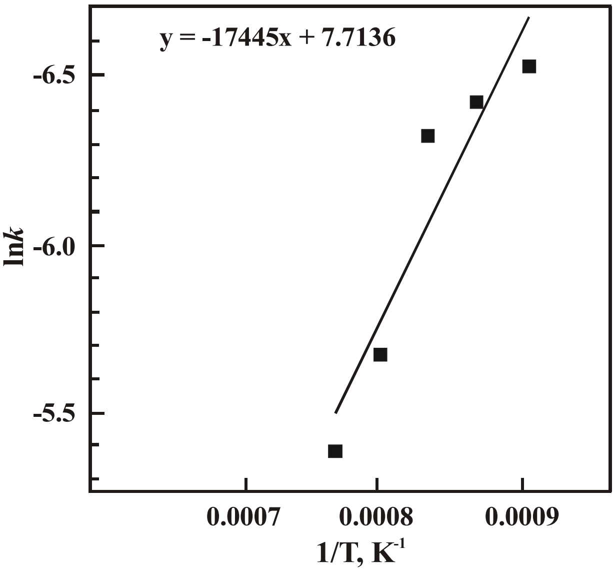

Fig. 4. Arrhenius plot for ln$k$ versus $1/T$ (K^{-1}) for the final reaction period at different temperatures (20-120 min).

Factors Affecting the Extraction of Sodium Chromate in Distilled Water

Briquettes of the reaction mixture of chromite ore concentrate, soda ash and CaO (1:2.5:2.5) roasted at 1000°C for 2 hrs were subjected to a set of experimental investigations to determine the optimum sodium chromate extraction conditions in solution. Factors studied were: stirring time in solution, solution temperature and solid-liquid ratio.

The Effect of Solution Stirring Time

1 g of the roasted mixture was dissolved in distilled water where an optimal solid/liquid ratio = 1:400 and water temperature of 100°C were maintained and the stirring time was varied from 5 to 15 min. Figure 5 shows that the recovery increased with the increase in stirring time, which may be attributed to fact that increasing the stirring time increased the chance of complete liberation of sodium chromate and, subsequently, enhanced its dissolution efficiency [12,13]. The optimum stirring time that gave approximately 91.8% chromic oxide recovery was 12 min.

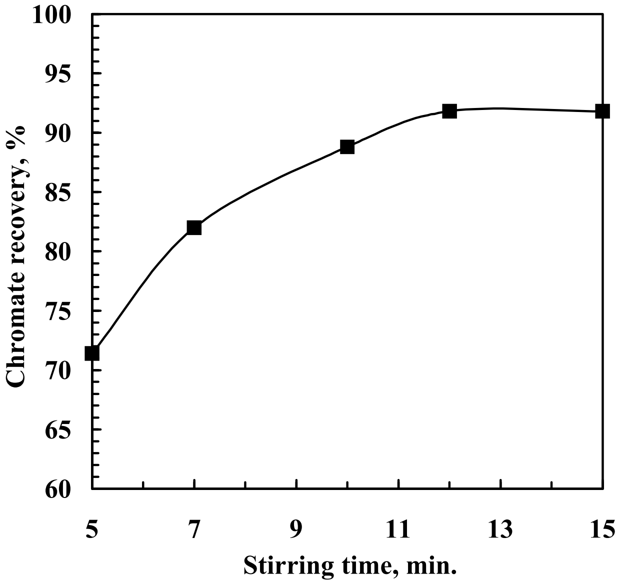

Fig. 5. The effect of varying the stirring time on chromate recovery % in solution.

The Effect of Solution Temperature

The effect of varying the extraction solution temperature from 40°C to 100°C was investigated at the optimum conditions (solid/liquid ratio = 1:400) and 12 min stirring time. The results indicated that as the temperature of the water increased the chromic oxide recovery % increased (Fig. 6), which may be attributed to the increase in chromate dissolution [12,13].

The Effect of Varying the Liquid/Solid Ratio

The effect of varying the liquid/solid ratio upon the chromic oxide recovery was investigated at the optimum conditions 100°C water temperature and 12 min stirring time. The results indicated that as the liquid/solid ratio increased the dissolution efficiency increased (Fig. 7), reflecting the increased dissolution of sodium chromate molecules in water.

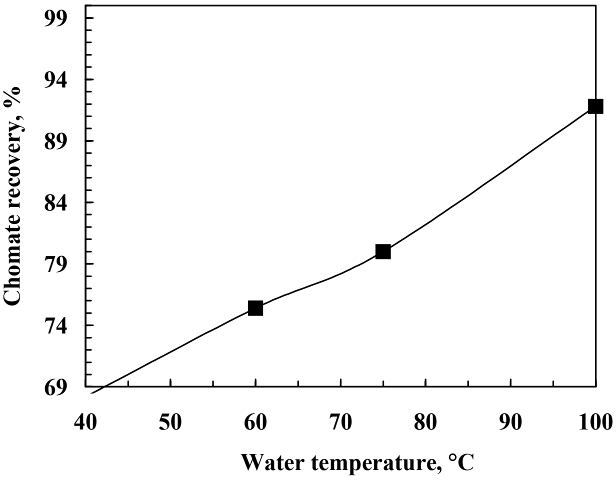

Fig. 6. The effect of varying solution temperature on chromate recovery %.

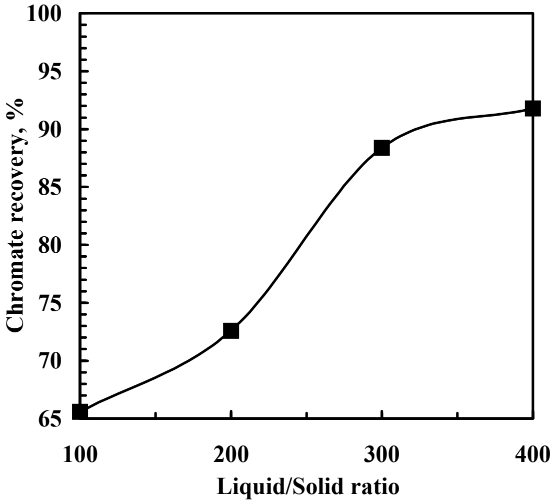

Fig. 7. The effect of varying the liquid/solid ratio on chromate recovery % in solution.

X-ray Diffraction of the Reaction Products of Chromite Ore Concentrate, Soda Ash and Lime

X-ray diffraction of the final product of roasting chromite ore concentrate, soda ash and lime (CaO) (mole ratio= 1:2.5:2.5) at 1000°C for 2 hrs is illustrated in Fig. 8.

From this diagram, it was clear that the major compounds formed during roasting were Na_2CrO_4 and $Na_2CrO_4 \cdot 4H_2O$. Other compounds detected were $CaCrO_4$, β-Ca_2SiO_4, $Ca_3Al_2O_6$, $Ca_3Al_{10}O_{18}$ and $CaO \cdot Fe_2O_3$. Essentially, 42 reactions may take place during the roasting process of chromite concentrate and

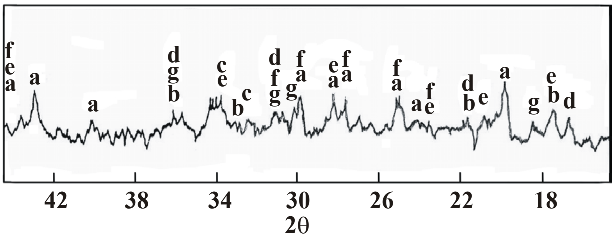

Fig. 8. X-ray diffraction of the final product of roasting chromite ore concentrate, soda ash and hydrated lime (mole ratio 1:2.5:2.5) (temperature 1000°C and for 2 hours).

sodium carbonate [19]. In the case a mixture of chromate concentrate roasted with sodium carbonate and lime was used, this extends to an overall 61 reactions [7,20]. From these reactions, Na_2CrO_4 is formed because of the reaction of $FeCr_2O_4$ and $MgCr_2O_4$ with Na_2CO_3, $NaAlO_2$, $NaFeO_2$, and Na_2SiO_3. This intermediate chromium in the presence of oxygen and excess of reacting compounds leads to the formation of Na_2CrO_4 and other compounds identified by the X-ray diffractogram. Reactions that may be involved in the above product formations are:

a) $CaO{\cdot}Fe_2O_3$:

$$Fe_2O_3 + Na_2CO_3 = 2\ NaFeO_2 + CO_2 \qquad (2)$$

$$2NaFeO_2 + CaO\ (\text{hydrated lime}) = \\ = Na_2O + CaO{\cdot}Fe_2O_3 \qquad (3)$$

b) $\beta\text{-}Ca_2SiO_4$:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2 \qquad (4)$$

$$2CaO + Na_2SiO_3 = Na_2O + \beta\text{-}Ca_2SiO_4 \qquad (5)$$

c) $CaCrO_4$:

$$CaCO_3 = CaO + CO_2 \qquad (6)$$

$$Cr_2O_3 + 2CaO + {}^3\!/_2O_2 = 2CaCrO_4 \qquad (7)$$

d) $Ca_3Al_{10}O_{18}$:

$$Al_2O_3 + Na_2CO_3 = 2NaAlO_2 + CO_2 \qquad (8)$$

$$3CaO + 10NaAlO_2 = 5Na_2O + Ca_3Al_{10}O_{18} \qquad (9)$$

Conclusions

As the CaO in hydrated lime/Cr_2O_3 mole ratio increased from 0-3, the chromic oxide recovery decreased to a minimum at 0.5 (24.5%) and then increased to a maximum (70%) at 2.5 (CaO/Cr_2O_3 mole ratio). The results indicated that roasting of an optimal mixture of chromite ore concentrate, soda ash and hydrated lime CaO (mole ratio = 1:2.5:2.5) during the temperature range of 900-1000°C yielded a 91.8% Cr_2O_3 recovery. The study data concluded that kinetics of the formation of sodium chromate from this optimal mixture was solid diffusion mechanism with the apparent activation energy being 171.63 kJ/mole. As well, it revealed that the optimal and economic conditions for maximum chromate recovery % (expressed as chromic oxide) from this mixture in solution were:

a) stirring time = 12 minutes;
b) solid/liquid ratio = 1:400;
c) water extraction temperature = 100°C.

References

1. Papp, J. Chromium, US Geological Survey, 2000.
2. Morsi, I.M., Shalabi, M.E.H., El-Barawy, K.A. and El-Tawil, S.Z., "Chromium recovery from chromite concentrate by sintering roasting technique", Refectory Materials Extraction, Processing and Applications, K. Nons, C. Liddell, D.R. Sadaway and R.G. Bautista (editors), The Minerals, Metals & Materials Society, 1990, pp. 87-97.
3. Kirk, O., "Encyclopedia of Chemical Technology", 2-nd edition, Vol. 5, 1984.
4. Hosdowich, J.M., Chromium, Vol. 2, Reinhold Publishing Corp., NY, 1965, pp. 65-92.
5. Kireeva, M.A. and Kashirskaya, I.Ya., Deposited Doc., VIN III, 2326-84, 1984, p. 11.
6. Stephen, C. and Lawson, F. "Alkali roasting of chromite", AIMM, Proc. Vol. 28, 1984, pp. 247-251.
7. El-Tawil, Z, Morsi, I. M., Shalabi, M.E.H. and Mohamed, O.A., "Soda ash roasting of chromite ore concentrate pellets", Neue Hutte, 36 (4), 1991, pp. 140-145.
8. Tripathy, A.K., Ray, H.S. and Pattanayak, P.K., "Kinetics reaction between chromium sesquioxide and anhydrous Na_2CO_3 in oxidizing atmospheres", Trans. Inst. Min. Metall. Sect. C (May-Aug), 1994, pp. 147-151.
9. Shalabi, M.E.H., El-Hussiny, N.A., Zaher, F.M.S., El-Ebiary, N.N. and El-Afifi, S.Y., "Kinetic of Formation of sodium chromate from El-Baramiya Chromite Ore Concentrate with soda ash briquetting", Gospadarka Surowcami Mineralnymi, 15, 1999, pp.111-131.
10. Shalabi, M.E.H., El-Hussiny, N.A., Shebl, F.Z., El-Afifi, S.Y., XXI International Mineral Processing Congress, Rome, B, 2000, pp. 16-21.

11. Shalabi, M.E.H., El-Hussiny, N.A., Shebl, F.M.Z., El-Afifi, S.Y., "The role of O_2, N_2 and a mixture of both with varying proportions of N_2 on the formation of sodium chromate", The Transactions of the Egyptian Society of Chemical Engineers, 27(2), 2001, pp. 474- 485.
12. El-Dars, F.M.S., Abuzeid, H.A.M., Khalifa, M.G., Shalabi, M.E.H. and Farag, A.B. "Formation of Sodium Chromate from Chromite Ore Concentrate and Soda Ash Briquetting and factors affecting its recovery", Egyptian Journal of Chemistry, 45 (2), 2002, pp. 299-312.
13. Shalabi, M.E.H, Khalifa, M.G, Abuzeid, H.A.M, El-Dars, F.M.S, and Farag, A. B. The study of the formation of Sodium Chromate from El-Baramiya high-silica Chromite Ore Concentrate using dolomite, The Journal of Ore Dressing, Vol. 8 issue 15, 2006, pp. 11- 20.
14. Vilnyanski, Y. and Pudovkina, O.N. "The Chemistry of the Production of Sodium Chromate", J. Appl. Chem. USSR, 1947, (20):794.
15. Bruen, C.P., Low, W.W. and Smalley, E.W. US Patent: US3816095: Method for recovering Chromium values from chromite ore, Allied Chemical Corporation, N.Y., USA, 1974.
16. Ozer, A., Gulaboglu, S.M., Bayrakeeken, S.G. and Ahmet, K. Kim. Muchendisligi Semp, No. 4, 1992, pp. 31-36.
17. Jander, W. and Anorg, Z., Allg Chem., No. 163, 1927, p. 1.
18. Ansari, O., A. Khier, S. and Singer, J. ARE Iron and Steel Making, 1990, 11:237-246.
19. Jorochova and Ponelckee M, Chemistry and Technology of Chromium Trode (YHUVUM), 1975, pp. 29-38.
20. Kowalski, Z. XXXVIII Seminarium Fizykochemiczne Problemy Mineralurgii, Warsaw, 2001, p. 95.

Received 13 February 2007.