

STUDIES ON INDIGENOUS CHROMITE ORE

Part I. Laboratory Studies on the Manufacture of Sodium Chromate from Low-grade Indigenous Chromite Ore

ABDUL HAMEED SHAIKH and SHABBIR AHMED QURASHI

Pilot Plant Design and Development Division, PCSIR Laboratories, Karachi

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Abstract. Laboratory studies on the manufacture of sodium chromate from indigenous low-grade chromite ore (Cr_2O_3 contents \approx 35-37%) have been presented. The effect of different variables involved namely the proportion of the reactants (i.e. chromite ore, lime and soda-ash), the temperature, time of reaction and the particle size of the ore in terms of overall recovery of chromium from the chromite ore have been studied and optimum reaction conditions determined.

Some introductory work on the purification of sodium chromate is also presented.

Chromates and dichromates of sodium are the basic chromium chemicals. Both these chemicals are used in the manufacture of chromic acid, their potassium and ammonium salts, tanning compounds, chromium pigments, textile chemicals and score of other formulations. The importance of these chemicals can be better understood from the pattern of their end use as given in Table 1.

TABLE 1. PATTERN OF END USE OF CHROMIUM CHEMICALS.¹

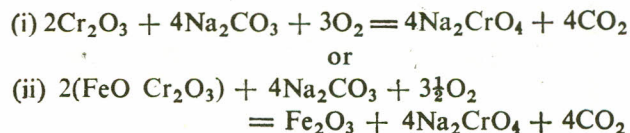
Pigments and allied products.	32-36 %
Leather and textile.	20-30 %
Surface treatment of metal and corrosion control.	20-27 %
Chemicals and allied products.	4-6 %
All other.	6-20 %

Pakistan has large reserves of chromite ore. Almost the whole production of the chromite ore is being exported and there is little utilization of this commodity within the country. Out of the total production of 30,197 tons of chromite ore for the year 1972, 22,004 tons, worth about 40 lakhs was exported.² However, it can more beneficially be used for the production of primary chromium chemicals to meet the needs of the industry. At present the production of chromium chemicals within the country is almost negligible. In order to step up production, work on the adaptation of foreign technology was started in these laboratories sometime in June 1970. The present paper relates to the laboratory studies on the process of manufacture of sodium chromate from indigenous low-grade chromite ore (Cr_2O_3 contents \approx 35-37%).

Although the process for the manufacture of sodium chromate from chromite ore is well established, but the optimum reaction conditions are

dependent on the nature and complexity of the chromite ore that is the extent to which the impurities are present, the degree of the fusion of the calcine, the rate of oxidation (air supply) and finally extraction or leaching out of the chromate salts.

The reaction between chromite and soda ash may be represented by the following equations :



The proportions of the reactants calculated from the above equations are true only, when the components used are pure, but in practice pure components cannot be used for the reasons of high cost. Besides chromite ore in addition to Cr_2O_3 , contain iron, alumina, silica and magnesia in varying proportions (Table 2). Some of these also react with soda ash. Thus the amount of soda ash required is much different from the theoretical and will have to be practically worked out to suit the individual requirements. Moreover, a feed prepared according to the reacting proportions of chromite ore and soda ash alone has a tendency to fuse at a higher temperature. To overcome this, a number of approaches have been suggested.³ One of them is to use a part of soda ash in the primary roast followed by leaching to remove soluble sodium salts and the subsequent treatment of the residue with the balance soda ash in the second roast. Even three roasting stages have been suggested, but this practice has a lesser scope as it enhances the operational difficulties and the cost of production.

The other remedy is to mix lime with the chromite ore and soda ash. Lime can be used either in the form of lime stone, CaCO_3 , CaO or dolomite, magnesite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) etc. It has a number of beneficial effects. Its presence improves the

TABLE 2. COMPOSITION OF RAW MATERIALS.

Raw material	Moisture wt %	Loss on ignition wt %	Chromium as (Cr ₂ O ₃) wt %	Iron as (Fe ₂ O ₃) wt %	Silica (SiO ₂) wt %	Calcium		Magnesium oxide (MgO) wt %	Aluminium oxide (Al ₂ O ₃) wt %	Combined oxides (R ₂ O ₃) wt %	Sod. carbo- nate (Na ₂ CO ₃) wt %
						as CaO wt %	as CaCO ₃ wt %				
Chromite ore	—	1.360	35.476	18.600	6.28	1.600	—	18.870	12.920	—	—
Soda-ash	0.66	—	—	—	—	—	—	—	—	—	98.05
Lime-stone (CaCO ₃)	—	—	—	—	2.20	—	97.23	0.360	0.70	—	—
Lime (CaO)	0.08	—	—	—	0.38	92.56	—	3.330	0.46	—	—

physical character of the calcine (increase in temperature of fusion), accelerates oxidation and reacts chemically with various constituents of the chromite ore. It also improves soda ash efficiency by replacing soda from combination with silica and alumina of the ore. However, the use of the larger amounts of lime produces cementitious qualities and the subsequent leaching of sodium chromate with water becomes difficult. Thus the proportions of lime again has to be determined experimentally, keeping in view the leaching efficiency and the fusibility of the calcine. Results of all these investigations have been presented in related Figures and Tables.

Apparatus and Procedure

The apparatus used for running different experiments was comprised of an electric box furnace with temperature range 0-1200° fitted with a small air-blower, a gas meter (dry type) for the supply of measured quantity of air and a stainless steel dish (10 × 6 × 4 cm) for heating the sample.

The different steps involved in the procedure for the production of sodium chromate consisted of preparation of feed, heating/roasting of the feed, leaching the roasted mass followed by the purification, concentration and drying to obtain anhydrous sodium chromate.

In the preparation of the feed, chromite ore and lime (CaCO₃ or CaO) were crushed and ground separately to pass through —150 mesh BSS sieve. Soda ash and lime were predried at 110° to remove moisture. All the three components were then separately weighed and then thoroughly mixed for about half an hour in a mixer. A known weight of the feed was then transferred to calcining-dish and heated at desired temperature in the presence of a constant supply of air for a period of 1½ hr.

The roasted mass, after cooling removed from the dish, is weighed to determine the loss in weight. The sodium chromate formed was leached with hot water and the filtrate (≈ 1.0–1.5 litres) concentrated on a hot plate or a burner. During concentration certain impurities may separate out with the change in the pH of the solution and the solution was filtered, whenever, required. The evaporation was continued till the volume of the solution was reduced to about 50-100 ml. The supersaturated solution was then slowly and carefully heated till major portion of the water was evaporated. It was then dried in an air-oven at 110°, cooled in a desiccator and weighed to determine the yield of sodium chromate. The same sample was also analysed to determine its purity.

Results and Discussion

The different variables involved in the manufacture of sodium chromate from the chromite ore are the proportion of the reactants, i.e. chromite ore, soda ash and lime, the particle size, temperature and time for roasting. With the type and composition of the chromite ore used (Table 2) these variables and their effect on the overall efficiency of the process (in terms of recovery of chro-

mium from the chromite ore and the yield and purity of sodium chromate obtained), were studied in the manner described below

TABLE 3. EFFECT OF SODA ASH (AIR-RATE, 1 CU FT/MIN ROASTING TEMPERATURE, 950°; ROASTING TIME, 1-1/2 HR).

Composition of the feed ore:soda-ash:limestone	Sodium chromate (percent yield)	Overall recovery of chromium from the ore (percent)	Percentage of Sodium chromate
80 : 30 : NIL	37.20	35.60	95.72
80 : 50 : NIL	76.70	64.30	83.60
80 : 55 : NIL	80.80	67.50	83.60
80 : 60 : NIL	86.60	57.40	66.05
80 : 70 : NIL	79.40	39.60	49.88
80 : 80 : NIL	88.80	33.60	35.05
80 : 20 : 10	32.72	22.50	68.76
80 : 40 : 10	53.33	44.00	82.24
80 : 60 : 10	84.84	65.40	76.85
80 : 80 : 10	80.00	41.60	51.23
80 : 100 : 10	71.51	8.67	12.13
80 : 20 : 20	29.20	25.80	88.89
80 : 30 : 20	44.60	39.20	87.93
80 : 40 : 20	61.50	47.40	85.03
80 : 50 : 20	87.40	68.40	78.19
80 : 60 : 20	86.70	45.70	49.88
80 : 55 : 20	84.60	58.50	69.43

The Proportion of the Reactants

(a) *Effect of Soda Ash (Na_2CO_3)*.—The effect of soda ash has been determined with and without the presence of lime. Three sets of experiments were performed. In the first set of experiments, the feed contained only chromite ore and soda ash, while in the second and third set of experiments, the feed contained 12.5 and 25% limestone of the weight of chromite ore, respectively.

Keeping the weight of the chromite ore constant (80 g) the quantity of soda ash in the feed in all the sets of experiments was gradually increased from 25 to 125% of the weight of chromite ore (20 to 100 g). The results of these experiments have been presented in Fig. 1, where the soda ash contents of the feed have been plotted against the overall recovery of chromium from the chromite ore. The figure contains three curves each representing a set of experiments mentioned above. The curves indicate similarity of behaviour with and without the use of limestone. All the curves show gradual increase in the recovery of chromium and reach a maximum where the soda ash contents of the feed were between 62.5-75% of the weight of chromite ore, thereafter the recovery of chromium gradually falls to about 30-40%. Referring to the Table 3, it is further observed that the yield of sodium chromate increases, but the purity of sodium chromate does not rise with the increase in the soda ash contents in the feed. Maximum purity is obtained when comparatively lesser amounts of soda ash are used. In order to fix the proportion of soda ash, a balance in all the three above mentioned factors has to be taken into account. Thus it will be seen that for 80 g of the chromite ore approximately 62

to 75% of soda ash (50-60 g) will have to be used, which is almost double the amount of the theoretical need.

(b) *Effect of Lime*.—Lime has been used both in the form of limestone and lime. Their effects on the overall recovery of chromium from the chromite ore and the yield and purity of sodium chromate obtained is determined. Referring to Fig. 2, where the limestone contents of the feed have been plotted against the overall recovery of chromium from the chromite ore, it is observed that the increase in limestone upto about 37% of chromite ore have little effect on the recovery of chromium, thereafter the increase in limestone appear to have an adverse effect, i.e. it retards the overall recovery of chromium from the ore. This may possibly be due to the fact that the actual rate of decomposition of limestone around 900° is slow⁴ and thereby making available lesser amount of CaO than the required one. A much higher temperature may thus be required for the reaction to complete.

Calcium Oxide (CaO)

When the limestone in the feed is replaced by commercial grade calcium oxide (for composition see Table 2) marked improvements in all the three factors namely the overall recovery of chromium from the chromite ore and the yield and

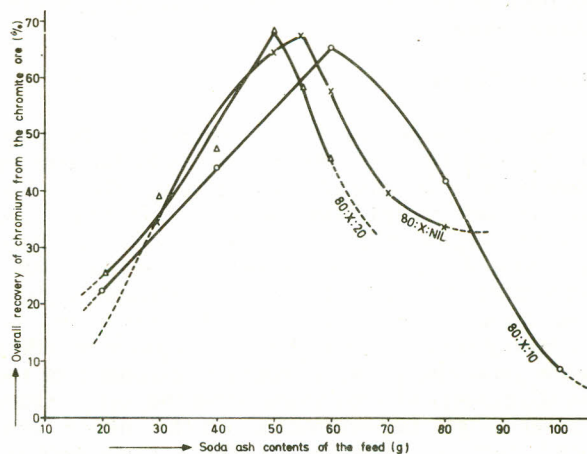


Fig. 1. Soda ash contents of the feed vs overall recovery of chromium from chromite ore.

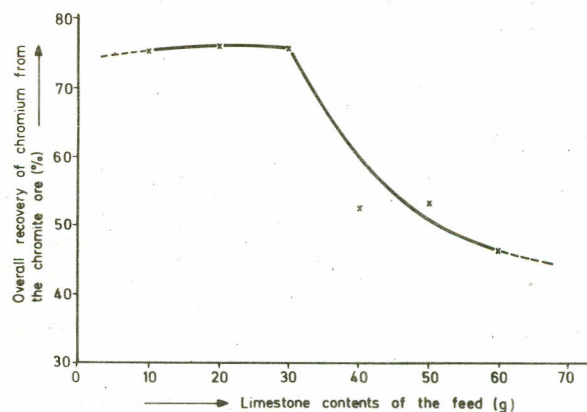


Fig. 2. Limestone contents of the feed vs overall recovery of chromium from the chromite ore.

purity of sodium chromate obtained are noted. The results appear in Fig. 3, where the increase in calcium oxide contents of the feed have been plotted against the overall recovery of chromium from the chromite ore. The figure has three curves, each curve representing a series of experiments with different feed ratios, namely the curve, (a) represents a feed ratio 80 g ore, 40 g soda ash and x g CaO, (b) 80 g ore, 45 g soda ash and x g CaO, and the curve (c) 80 g ore, 50 g soda ash and x g CaO, x represents the amount of calcium oxide and varies from 25 to 125% of the amount of chromite ore in the feed. The curve (a) and (b) are nearly similar that is the recovery of chromium in both the cases after reaching a sharp maximum falls off rapidly. In curve (a) the recovery of chromium reaches a maximum (75%) with feed ratio 80:40:40, i.e. 80 g ore, 50% soda ash and 50% CaO, while in curve (b) the maximum (85.6%) occurs with feed ratio of 80:45:70, i.e. 80 g ore, 56% soda ash and 87.5% of CaO. The pattern of the curve (c) is different from the other two. The curve is almost a parabola and the recovery of chromium from the ore is gradual and reaches a maximum (84.4%) with feed ratio 80:50:60, i.e. 80 g ore, 62.5% soda ash and 75% CaO.

From the standpoint of percent yield and percent purity of sodium chromate as well as that of recovery of chromium from the chromite ore, the best feed ratio is 80 g ore, 62.5% soda ash and 75% calcium oxide.

Time of Roasting

Another important factor which has bearings on the efficiency of the process and the cost of production is the time of roasting of the feed. The roasting time varied from 1 to 4 hr. The results are shown in Fig. 4, where the time of roasting have been plotted against the overall recovery of chromium from the ore. The figure represents a parabolic curve. It is observed that the increase in time of roasting from 1 to 3 hr have no significant effect on the yield and purity of sodium chromate or the overall recovery of chromium from the ore. There is a very slight improvements on the above mentioned factors. However, to ensure a complete reaction, the suitable time of reaction in our case lies between 1 and 1½ hr.

Particle Size of the Ore

Particle size of the ore (feed) also have an effect on the recovery of chromium from the ore, the rate of oxidation and the cost of production. It has been observed that finer the particle size of the ore, better is the rate of oxidation. But fine grinding obviously effects the cost of production. A particle size range from -60 to -300 mesh BSS was investigated and the results are presented in Fig. 5. The curve is again a parabola showing a maximum recovery of chromium between a particle size range of -150 to +200 mesh BSS and thereafter, showing a gradual decline in the recovery of chromium. The yield and purity of sodium chromate obtained is also maximum between these particle sizes.

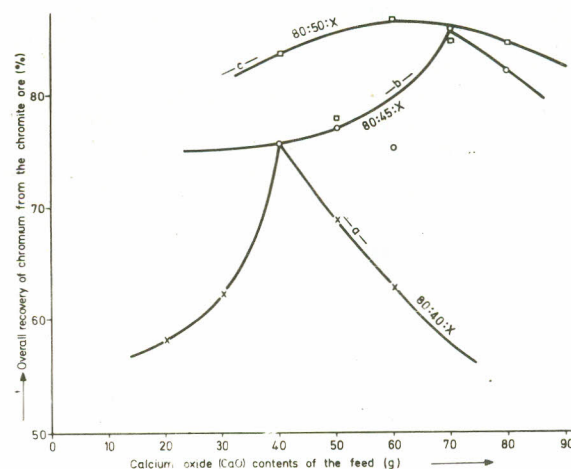


Fig. 3. Calcium oxide contents of the feed vs overall recovery of the chromium from chromite ore.

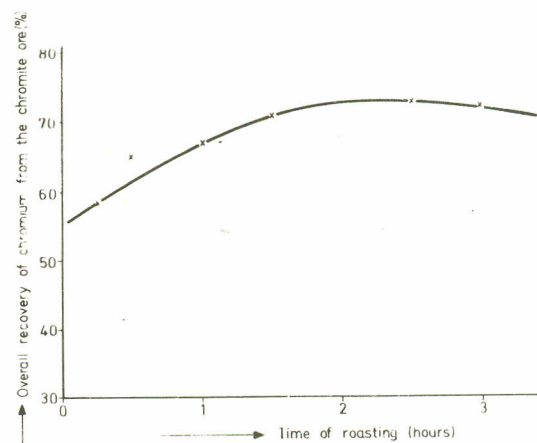


Fig. 4. Time of roasting vs overall recovery of chromium from chromite ore.

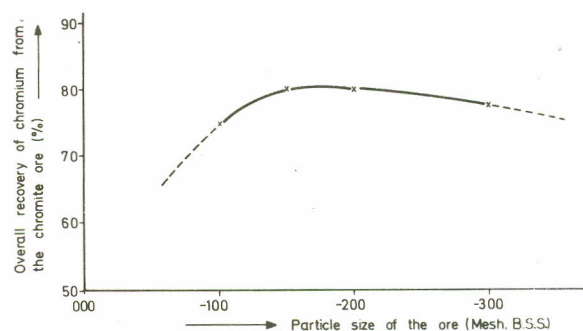


Fig. 5. Particle size of the ore vs overall recovery of chromium from the chromite ore.

Temperature of Roasting

The temperature is another important variable which effects the recovery of chromium as chromate. A temperature range of 850 to 1100° has been employed to study its effect. The results

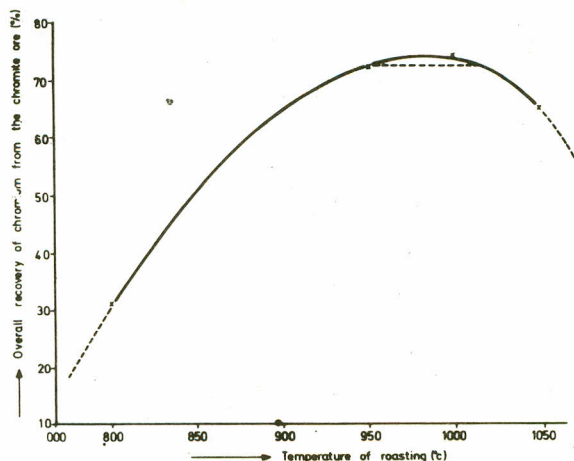


Fig. 6. Temperature of roasting vs overall recovery of chromium from chromite ore.

of these investigations on the roasting temperatures of chromite ore appear in Fig. 6, where the temperature of roasting is plotted against the overall recovery of chromium from the chromite ore. The figure represents a parabola showing maxima over a temperature range of 950–1000°. At this temperature the yield of sodium chromate is about 91% equivalent to an overall recovery of chromium from the ore as 72.2%.

Conclusion

From the foregoing results and discussion, it can be concluded that if 80 g of chromite ore ($\text{Cr}_2\text{O}_3 \approx 35-37\%$) be heated with 50 g soda ash and 60 g calcium oxide (i.e. 62.5 and 75% of the weight of chromite ore respectively) in a furnace to a temperature of 950–1000° for 1½ hr, sodium chromate representing 86.4% recovery of chromium from the chromite ore in a single stage operation is recovered. The purity of sodium chromate thus obtained is 96%.

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