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Recovery of Chromium from stainless steel dust

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Abstract: This investigation deals with the recovery of chromium as sodium chromate of 99.5% purity from stainless steel dust containing 7.72% chromium obtained from stainless steel processing plants. The stainless steel dust mostly contained iron in oxide form along with chromium, nickel (1.71%) and manganese (3.55%). The steel dust was roasted with soda ash followed by water leaching to recover the major constituent chromium. It was found that the roasting at 1073 K in 90 minutes resulted in maximum (95%) chromium recovery. Kinetics of sodium chromate formation followed topochemical model involving chemical reactions at the surface with activation energy of 22 kJmol^{-1}. TG/DTA, XRD phase identification and SEM-EDX confirmed the experimental observation and the mode of reaction.

Keywords: stainless steel dust, roasting, sodium chromate, solid waste.

Introduction

Production and processing industries dealing with chromium based substances are in enormous pressure from environmental protection group to control the waste materials because of the problem associated with carcinogenic and mutagenic Cr^{6+} ion.[1] One such waste containing chromium is produced by stainless steel

processing plant. The stainless steel dust is available during annealing and shot blasting of stainless steel. It contains iron in major amount along with nickel, chromium, silica and manganese. Initially, the main thrust is to recover chromium (7.7%) because nickel and manganese are in low quantities. Chromium chemicals are commercially produced by alkali roasting (soda-ash roasting) of chromite ores. During the soda-ash roasting reaction, sodium carbonate is mixed with chrome ore and heated at a temperature above 1073 K in air. The sodium oxide produced a as result of the decomposition reaction of Na_2CO_3 reacts with the chromium ion (Cr^{3+}) of the chromium spinel in an oxidizing atmosphere and forms water soluble sodium chromate.[2,3] The overall reaction can be described by

$$Cr_2O_3 + Na_2CO_3 = Na_2Cr_2O_4 + CO_2 \qquad (1)$$
$$Na_2Cr_2O_4 + Na_2CO_3 + 3/2\ O_2 = 2Na_2CrO_4 + CO_2 \qquad (2)$$
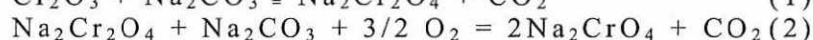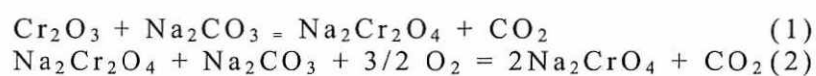
After the reaction, sodium chromate is leached out in water. Unreacted chromium oxide remains with the residue and ends up in the waste stream for land fills.

The main thrust of the previous research on soda ash roasting[4] has been to optimize the process parameters for improving the kiln performance. Various methods such as pellet roasting[5] and duplex pellet technology[6] were also investigated. Techniques such as sodium hydroxide leaching[7,8] and the hydrometallurgical extraction of chromate from lean chromite ores[9] were also reported. The lime based process in which lime is added in the roasting charge was developed for the roasting of MgO and SiO_2 rich chromite ores.[2] The process enhanced the conversion efficiency significantly and also improved the operational conditions of the kiln. The traditional method of sodium chromate production on a commercial scale is based on soda ash roasting of the chromite ore either in a kiln or in a rotary hearth furnace. The objective of the present research is to investigate the formation of sodium chromate from stainless steel dust. The kinetics of extracting chromium from the dust using the soda-ash roasting process under an oxidizing condition are also presented.

Experimental
Physical and chemical characterisation
The stainless steel dust containing chromium used in the present study was obtained from Singhal Industries, at Hisar, Haryana in India. The constituents of the dust were determined by chemical analysis and the results are reported in Table 1.

Table 1 Chemical analyses of stainless steel dust

Metal	%
Cr	7.72
Mn	3.55
Ni	1.71
SiO_2	1.36
Fe	Rest

The physical characterisation included X-ray powder diffraction and scanning electron microscopic observation. The distribution of chromium present in the dust spinel was determined using energy dispersive X-ray (EDX) method.

Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) was carried out with the dust sample to understand the reactions taking place during the soda-ash roasting. A known amount of the sample was mixed with the stoichiometric amounts of sodium carbonate and placed in the chamber of simultaneous TG/DTA, Sieco-320 model. It was then heated to 1273 K at a heating rate of 283 K per minute. The atmosphere chosen for the TGA study was static air. The weight changes were continuously recorded as a function of time and temperature using the *in-situ* data logging device.

Soda-ash roasting of stainless steel dust

Experiments were carried out to optimize the parameters for achieving maximum yield of sodium chromate. The dust was thoroughly mixed with varying quantities of sodium carbonate. The molar ratio of sodium carbonate to chromium oxide was varied from 0.5 to 2.5 of the stoichiometric amount. For the kinetics studies a series of roasting experiments were carried out to examine the effects of time and temperature of roasting for the formation of sodium chromate. The range of temperature chosen in the present investigation was varied between 873 and 1173 K. Sample weighing 10 g each was heated isothermally in static air for a set period of time varying the range 15 to 120 min. The reaction product containing sodium chromate was leached in hot water and the solution was analyzed for chromium content. Based on the results the fraction of chromium extracted was calculated.

Results

Characterisation

From the XRD analysis it was found that the chromium present in the stainless steel dust was in form of chromium oxide (Cr_2O_3) and iron as oxide (Fe_2O_3). The Nickel,

Manganese and SiO_2 were present as the minor amounts along with chromium.

The TG/DTA plots for the soda ash roasting reaction of stainless steel dust in air are shown in Fig.1. The changes in the weight loss of the sample (mixture of stainless steel dust and sodium carbonate) were strongly dependent on the temperature.
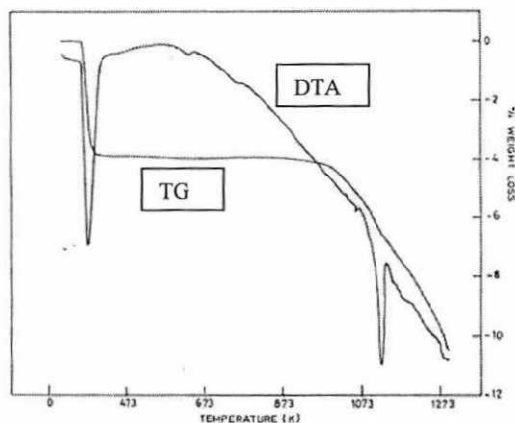

Fig.1. TG / DTA pattern of stainless steel dust with sodium carbonate.

Two endothermic peaks along with weight loss were observed at 373 K and 1123 K. The first stage described the weight loss at 373 K due to the removal of moisture. The second stage of endothermic peak and steady weight loss at 1123 K may account for the decomposition of sodium carbonate to sodium oxide, (Na_2O) and removal of CO_2 gas. At this point the formation of sodium chromate was started with the reaction of Na_2O and Cr_2O_3

Based on the thermo gravimetric analysis the effect of temperature on soda ash roasting for chromium recovery was examined. Stainless steel dust was mixed with two molar ratio of sodium carbonate and the mixture was heated in a muffle furnace; the results are shown in Fig.2. It is apparent from the results that the chromium recovery increased with the rise in temperature at a fixed time (90 min) of roasting. There was no significant improvement in the chromium recovery beyond 1073 K of roasting. The maximum recovery of chromium was to be 95% under this condition.
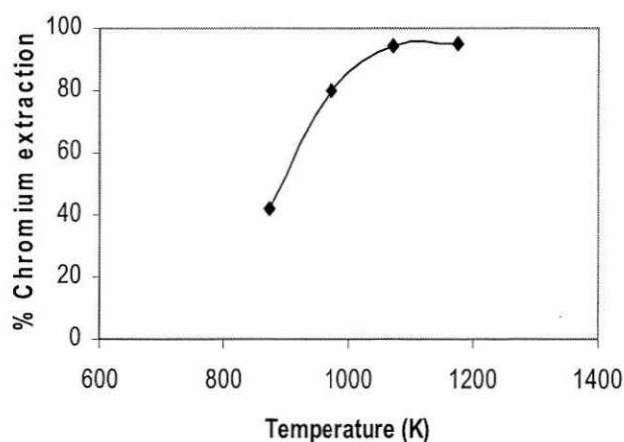
Fig.2. Effect of temperature on extraction of chromium

(Molar ratio of Cr_2O_3/Na_2CO_3: 1:2, t: 90 min)

The amount of sodium carbonate required for roasting of the stainless steel dust was also varied. The results depicted in Figure 3 showed extraction of chromium increases with rise in molar ratio of sodium carbonate with the dust.
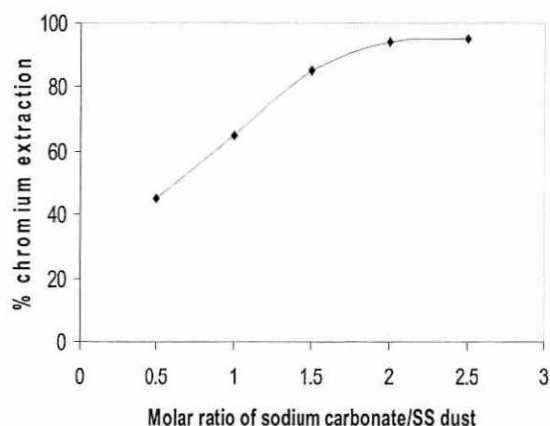

Fig.3. Effect of sodium carbonate addition on the extraction of chromium

(T: 1073 K, t: 90 min)

At 0.5 molar ratios of sodium carbonate and chromium oxide present in the stainless steel, only 45% chromium was extracted. Maximum chromium extraction of 95% at 2.0 molar ratio of $Na_2CO_3:Cr_2O_3$ was achieved at 1073 K and 90 min of retention time. The formation of sodium chromate was further confirmed by XRD and SEM-EDX analysis. Typical XRD pattern of roasted product at 1073 K in 90 min are shown in Fig.4.
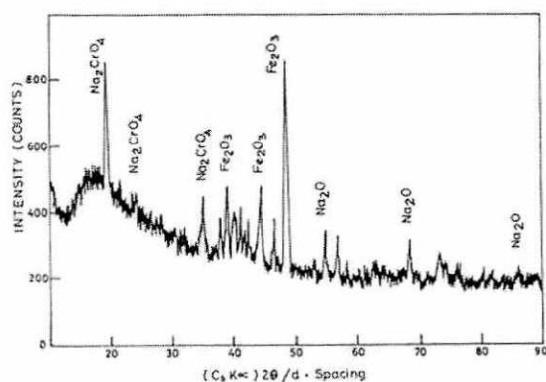
Fig.4. XRD pattern of roasted product at 1073 K in 90 min.

The XRD pattern showed that presence of sodium chromate along with Fe_2O_3 and unreacted Na_2O. The well defined peak of sodium chromate clearly indicated the reaction of sodium carbonate and chromium oxide present in the stainless steel dust. The SEM-EDX analysis of roasted product at 1073 K in 90 min further confirmed the presence of sodium chromate phase (Figure 5).
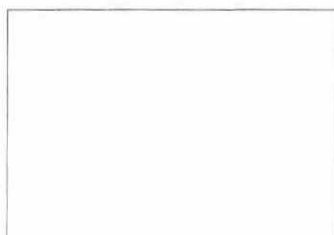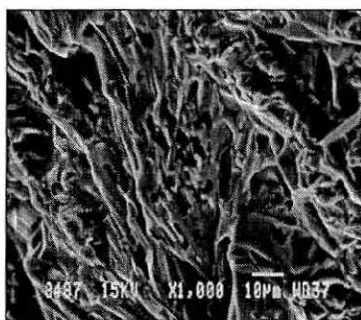

Fig.5. SEM-EDX analysis of roasted product at 1073 K in 90 min.

Well developed whisker type morphology may be seen in SEM photograph for sodium chromate phase. The porosity observed with SEM may be due to the evolution of CO_2 gas during the course of reaction.

Kinetics of soda-ash roasting

The effect of time and temperature on the extent of chromium recovery during the soda ash roasting is presented in Figure 6. The results showed increase in chromium recovery with the rise in both roasting time and temperature. It is also evident that the reaction rate is not much affected after 90 min of reaction.

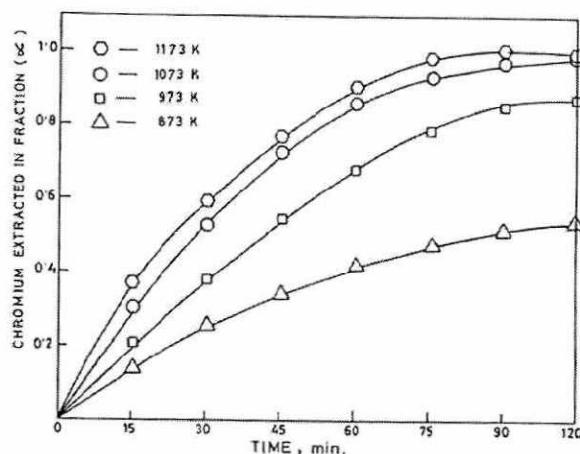At 1073 K temperature and 90 min time, maximum 95% of chromium was extracted.

Fig.6. Effect of time on extraction of chromium at different temperature
Molar ratio of Na_2CO_3/Cr_2O_3: 2/1

From the plot at different temperatures in with time and fraction of chromium extracted (α), the kinetics of reaction may be deduced. The isothermal kinetic data were fitted to equations of diffusion control, chemical control and the mixed control models.[10,11] The kinetic data showed best fit to the topochemical model involving surface reactions represented as,

$$1-(1-\alpha)^{1/3}= kt \qquad (3)$$

Where α is the fraction of reaction, k is the specific rate constant and t is the reaction time.

As shown in Figure 7, the straight line is obtained when $1-(1-\alpha)^{1/3}$ is plotted with t at different temperatures.
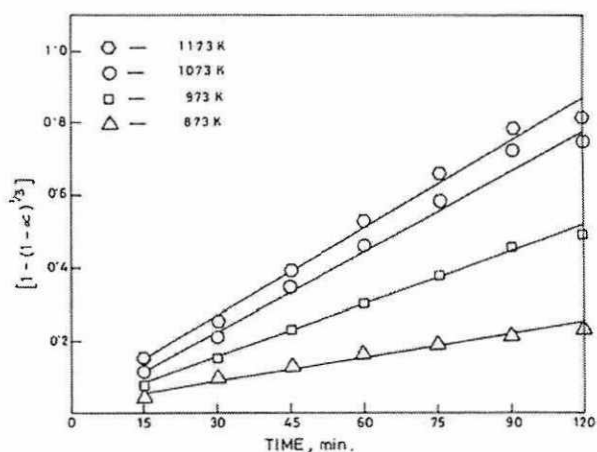
Fig.7. Kinetics plot for the extraction of chromium.

The derived values of slopes for each isotherm from the chemical control model were calculated and a plot of lnk vs 1/T was made as shown in Figure8.
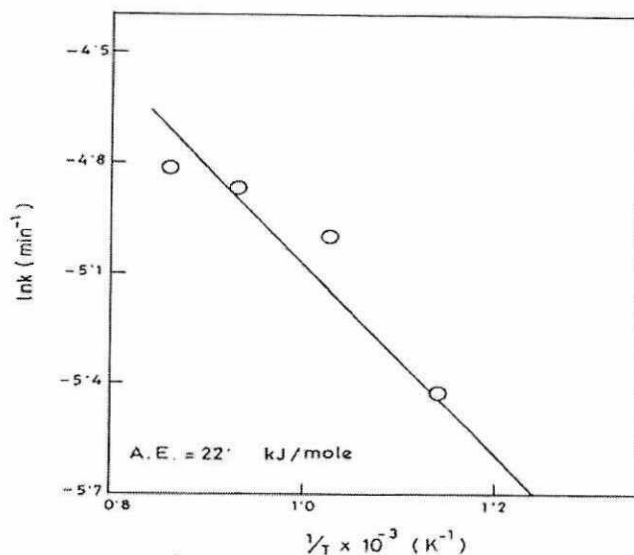

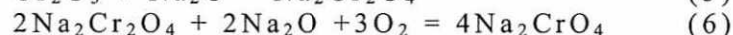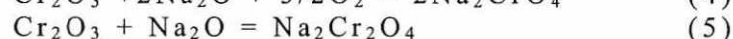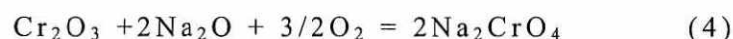Fig.8. Arrhenious plot for the extraction of chromium.

From the slope of the straight line, apparent activation energy value was derived from the Arrehenious relationship. The activation energy value calculated was 22 kJ mol^{-1}. The value of activation energy is well within the range of topochemical control model.

Purification of leach liquor

The presence of silica (1.36%) in the stainless steel dust was a major cause of leach liquor impurity. During soda ash roasting the silica converted to sodium silicate, which entered in to the solution after leaching of the roasted product. As such formation of sodium silicate in XRD analysis of the roasted product was not observed because of small quantity of silica present in the dust. But during filtration of leach liquor some amount of silica precipitation was noticed in the flask. Thus it was considered essential to remove the dissolved silica from the leach liquor. From the stock solution of leach liquor containing major amount of sodium chromate along with minor amount of sodium silicate, the silica was precipitated. The pH of the concentrated solution of sodium chromate (40 g/l) was found to be 8.2. When pH was lowered to 6, a white crystalline precipitate was obtained. After stirring at pH 6 and holding the leach liquor for 15-20 min total silica was precipitated. After filtration a clear solution of sodium chromate was obtained. By evaporation and crystallisation, a solid mass crystal of sodium chromate was obtained. The purity of the sodium chromate crystal was found 99.5%. The sodium chromate may be considered suitable for the use in various chemical industries.

Discussion

The results of XRD phase identification indicated that the stainless steel dust contained chromium as chromium oxide and iron as iron oxide. Based on XRD and SEM studies the main reactions involved during soda ash roasting are as follows[12]:

$$Cr_2O_3 + 2Na_2O + 3/2O_2 = 2Na_2CrO_4 \qquad (4)$$
$$Cr_2O_3 + Na_2O = Na_2Cr_2O_4 \qquad (5)$$
$$2Na_2Cr_2O_4 + 2Na_2O + 3O_2 = 4Na_2CrO_4 \qquad (6)$$

The XRD pattern of the dust roasted with sodium carbonate in air at 1073 K confirmed the presence of sodium chromate. The weight change along with endothermic peak in TG/DTA also indicated the formation of sodium chromate. This reaction might proceed with the formation of sodium chromite as an intermediate phase[13]. The result of roasting at different temperatures with time showed that the formation of sodium chromate was governed by topochemical reaction model. The activation energy value obtained (22 kJ mol^{-1}) was close to topochemical reactions. In the leaching of calcine the dissolution of silica was noticed. The leach liquor was therefore purified at pH 6 to remove silica which was followed by the formation of yellow crystalline sodium chromate by evaporation-crystallisation process.

Conclusion

Bench scale experiments conducted for the soda ash roasting of stainless steel dust and water leaching of the calcine yielded sodium chromate. Based on the foregoing discussion following conclusions may be drawn.

(i) maximum 95% sodium chromate formation is obtained by soda roasting at 1073 K in 90 min of reaction.

(ii) 2:1 molar ratio of sodium carbonate and chromium oxide of stainless steel dust is found optimum for high sodium chromate formation.

(iii) The kinetics of reaction indicates that it follows the topochmical kinetic model with surface reaction. An activation energy of 22 kJmol^{-1} is acquired in the soda roasting process.

(iv) The TG/DTA, XRD and SEM-EDX helped in understanding the progress of reaction during roasting process.

(v) The purified leach liquor produces sodium chromate of 99.5% purity by crystallisation.

Acknowledgements

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