

# THERMODYNAMIC EFFECTS OF TEMPERATURE DURING ROASTING OF CHROMITE FOR SODIUM CHROMATE SALTS FORMATION

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This paper aims to assess the potential effects of roasting temperature on the formation of sodium chromate ( $\text{Na}_2\text{CrO}_4$ ). To perform this task, chromite samples were complexed with NaCl at temperatures ranging from 900 °C to 1 200 °C in the presence of excess oxygen. These experimental conditions were set and assessed based on the predicted phase transformations using Facstage as a prediction tool. The scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) have revealed the roasting behaviour of chromite to be governed by a fully reacted outside layer and an unreacted core. As per the x-ray diffraction (XRD) results, at lower temperature settings, mineral phases such as hematite and chromium oxide reported as an indication of predicted oxidation of chromite. The key results indicate that the addition of NaCl reduces the equilibrium temperature, thereby fully decomposing the stable and refractory spinel structure of chromite at 1 200 °C.

*Keywords:* thermodynamics,  $\text{Na}_2\text{CrO}_4$ , roasting, equilibrium, x- ray research

## INTRODUCTION

The production of sodium chromate is because of soda ash roasting, wherein chromite is complexed with salts such as sodium carbonate in the presence of excess oxygen at temperatures ranging from 900 °C to 1 200 °C. The efficiency of this process is linked to the mineralogy of the chromite ore, subsequently to the silica content in the gangue. The aforementioned considerations have caused the subdivision of the soda ash roasting into lime-based and lime free oxidative roasting. The product from this reaction is a water-leachable compound that can further be dissolved in diluted sulfuric acid for the selective extraction of chromate salts.

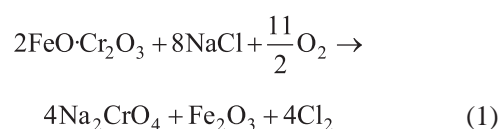
Although the oxidative alkali (lime-based) roasting of chromite has been proven fit for its purpose, since it successfully oxidizes the trivalent stable chromium ( $\text{Cr}^{3+}$ ) spinel into its hexavalent form ( $\text{Cr}^{6+}$ ), there are still environment related problems associated with this technique.

According to Parirenyatwa et al. [1], the traditional method of chromite processing results in the formation of chromite ore processing residues (COPR).

These processing residues contain a considerable amount of  $\text{Cr}^{6+}$ , which can further be considered toxic to both humans and the surrounding environment. As a result of the above, lime-free techniques have been con-

sidered suitable for chromite processing in both technical and environmental applications [1].

Considered as one of the most naturally occurring substances, sodium chloride (NaCl), has played indispensable roles to both human survival and industrial progress. NaCl has attracted a lot of interest in the modern world processing and manufacturing, owing it to its unique physicochemical and thermal properties, to which can be added to its readily availability, abundance, and purchasing cost [2]. As a result of the above, the application of this salt will be investigated on the roasting of chromite for the formation of chromate/dichromate salts, as per reaction 1 below.



The current paper focuses on assessing the thermodynamic effects of temperature on the roasting of chromite using NaCl for the formation of  $\text{Na}_2\text{CrO}_4^{2-}$  ions. This task will be achieved by comparison of the phase changes results obtained from Facstage and HSC against the observed experimental changes determined by characterization of the complex. Chemical composition changes, mineralogical and phase transformations will be assessed using x-ray fluorescence, XRD and SEM-EDS respectively before and after roasting.

## EXPERIMENTAL

The sample used in this study is a South African chromite concentrate of particle sizes below 106  $\mu\text{m}$

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and whose chemical bulk composition and mineralogical phases were identified and quantified using XRF, and XRD, respectively (Figure 1 and Table 1).

The micrographs depicting contrasting phases at different magnifications of the sample and their corresponding chemical compositions are depicted in Figure 2 below. These characterization results are explained in the results and discussion section. 50g of the chromite concentrate was stoichiometrically mixed with a known amount of NaCl and loaded in the laboratory furnace. The roasting process took place at temperatures ranges of 900 °C to 1 200 °C for 1 hour. After the thermal oxidation, the samples were allowed to cool at room temperature, thereafter, sent for analysis using the previously mentioned analytical techniques.

## RESULTS AND DISCUSSION

The feed prior the roasting process presents high content of sodium and chlorine, confirming the presence of the salt added. During roasting at elevated temperature, it was expected to see changes in chemical composition of the different components making up the feed, thereby substantiating phase changes. NaCl, usually expected to melt around 801 °C will further volatilise around 850 °C, which were predictions observed from Facstage (reaction module) and confirmed by the study of Wang et al. [3]. As observed in Table 1, the mass percentages of Na and Cl are drastically decreasing as a function of temperature increase.

As a result of the above, the roasted components with volatility lower than NaCl increase, suggesting solid-gas reactions at higher temperatures.

Table 1 XRF analysis of chromite feed and roasted complexes as a function of temperature increase.

Compound	/ Mass %				
	Feed	Temperature / °C			
		900	1000	1100	1200
Na <sub>2</sub> O	26,24	13,60	3,60	4,02	0,87
MgO	2,05	1,67	3,06	2,99	6,71
Al <sub>2</sub> O <sub>3</sub>	5,06	5,41	8,98	7,76	12,09
SiO <sub>2</sub>	0,76	1,18	1,55	1,46	1,77
Cl <sub>2</sub>	26,84	14,74	2,84	4,43	0,22
Cr <sub>2</sub> O <sub>3</sub>	23,80	30,90	42,65	41,76	43,76
Fe <sub>2</sub> O <sub>3</sub>	12,98	34,55	34,95	34,83	32,63

Chromite is considered a solid solution of 4 spinel structures, namely, FeAl<sub>2</sub>O<sub>4</sub>, MgAl<sub>2</sub>O<sub>4</sub>, FeCr<sub>2</sub>O<sub>4</sub>, MgCr<sub>2</sub>O<sub>4</sub>. It is therefore important to perform a study of the Gibbs energy, enabling predictions of the thermodynamical feasibility of the different reactions in the experimental temperature range. Figure 1 confirms the computed values using the equilibrium module of Facstage 8.2.

From the reactions described in Figure 1, it is noted that the thermal decomposition of chromite is thermodynamically not feasible, since its corresponding Gibbs energy is positive over the set range of temperatures. It

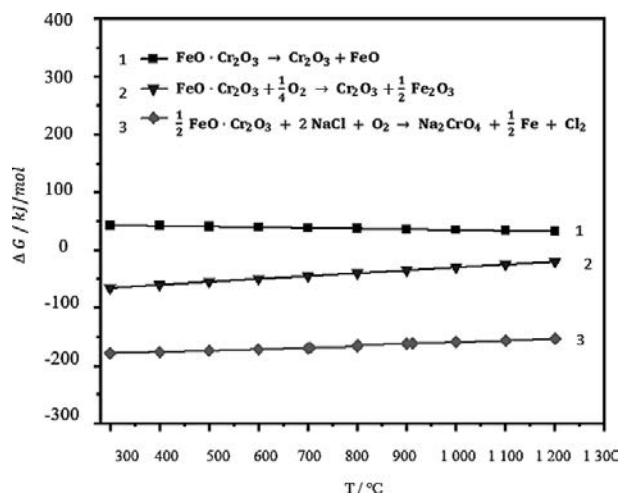


Figure 1 Gibbs energy vs temperature of the possible reactions during roasting.

is further noted that the addition of oxygen causes the decomposition of chromite (Gibbs is negative), thereby justifying the need of oxygen addition to the oxidative roasting environment.

Although the oxidation of chromite depicts thermodynamic favourability, the addition of the complexing agent (NaCl) shows relatively better thermodynamic feasibility over the studied range. This means that from the computed Gibbs values, the formation of the targeted sodium chromate salt will form favourably in comparison to the potential other reactions. The observed results are in accordance with Tian-gui et al. [4] despite the fact Na<sub>2</sub>CO<sub>3</sub> was used as the complexing agent.

The addition of NaCl, therefore pushes the equilibrium of reaction 1 towards the right, thereby favouring the formation of Na<sub>2</sub>CrO<sub>4</sub>.

Further mineralogical and phase analyses performed using XRD (Figure 2) display formation of new phases as the temperature increases between 900 and 1 200 °C.

The observed phase changes indicate the oxidation of Fe<sub>3</sub>O<sub>4</sub> for the formation of Fe<sub>2</sub>O<sub>3</sub> and formation of

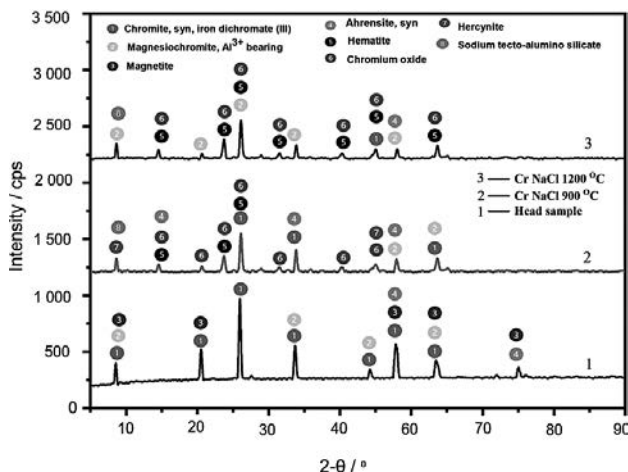
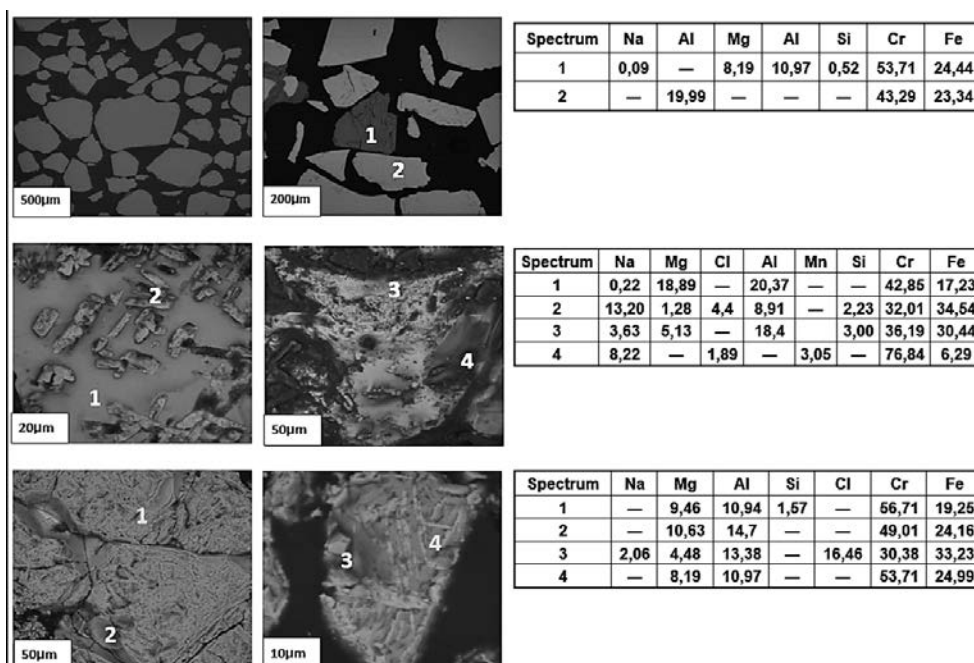


Figure 2 X-ray diffractograms of the raw (1) and roasted samples at temperatures of 900°C (2) and 1 200°C (3).

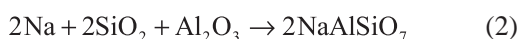


**Figure 3** SEM micrographs of the as received chromite sample (top), the roasted at 900 °C (middle) and 1 200 °C (bottom) and their corresponding EDS chemical composition.

$\text{Cr}_2\text{O}_3$ , which are considered main indications of the thermal decomposition of chromite.

Based on studies by [1, 4, 5], the formation of sodium chromate occurs in 2 steps, i.e., oxidation of  $\text{FeCr}_2\text{O}_3$ , thereafter the complexation of  $\text{Cr}_2\text{O}_3$  with the salt.

The XRD results corroborate with the suggested reaction pathway, where at 900 °C, the chromite oxide associated with hematite become the most dominant phase and the presence of sodium is observed in the form of sodium tecto-alumino silicate. This persistent presence of sodium can be attributed to the relatively high affinity of sodium towards aluminium and silica [3], as per reaction 2 below:



At higher temperature settings, the XRD results are characterised by the abundance of Al-bearing magnesi-chromite phases coupled with both hematite and chromium oxide, suggesting an even spreading on the roasted sample.

From the observed SEM results in Figure 3, at temperature 900 °C, a distinct crystal-like shape is observed, which can be attributed to the crystallinity of NaCl, as per the study by Sing et al. [6]. This is further confirmed by the EDS analysis, showing the highest concentrations of sodium chloride (13,20 % Na, and 4,4 % Cl) around spectrum 2 (red), revealing a probable excess of NaCl. Although the micrographs show abundance of sodium in a crystal form, the core of the particles appear unreacted in comparison to the outside layers.

The backscattered SEM results of the as received chromite shows a fairly even distribution of the minerals with less impurities such as Si, Mg, and Al, which are depicted by EDS spectra, corroborating to the XRF results.

According to Parirenyatwa et al. [1], during chromite roasting there is a formation of two distinct phases, an inner layer surrounding the of two distinguished phases with distinct chemical compositions. The EDS results may be used to confirm the above statement, looking at the proportion of chromite associated with the unreacted portion of the particle. This observation extends to the relatively lower concentrations of 18,4 %, and 5,13 % for Al and Mg, respectively on the outer layer, and relatively higher chromium concentrations (with no Al or Mg detection) in the inner core.

This brings about the need for understanding the kinetics of chromite roasting, which remain to date unclear to decipher.

Temperature effects are further noted when focusing on the bottom micrographs, depicting total thermal decomposition of the chromite's spinel structure which appear fully disintegrated, and even proportions of Cr are observed throughout. This decomposition is usually expected to take place at temperatures above 1 600 °C [7], thanks to its refractory behaviour. However, the addition of NaCl reduced the equilibrium temperature to 1 200 °C.

On the one hand, the corresponding EDS substantiate this even distribution, which is attributed to the full thermal decomposition of the chromite in oxidative conditions. On the other hand, spectrum 3 (blue) stands out, and depicts the presence of sodium (2,06 %) and chlorine (16,46 %). The high abundance of iron can be used as a further indication of a potential reaction with chlorine, therefore forming  $\text{FeCl}_2$ , which is considered water soluble.

The noticeable absence of sodium chloride at temperature 1 200 °C is attributed to its volatility at higher temperature, which hypothesises the solids-gas complexation reaction. These were confirmed by the predic-

tions made using Factstage, depicting a decrease in mole fraction of solid NaCl, thereby reporting to the gaseous phase.

The predictions and observed data corroborate to the extent of indication of the distinct phases available for reaction, and the roasting mechanisms associated with chromite roasting as a function of temperature increase.

Thus far, the formation of  $\text{NaCrO}_4^{2-}$  ions remain hypothetical, however performing the leaching experiments will decipher and deepen the understanding of chromite complexations in oxidative roasting conditions.

## CONCLUSIONS

The purpose of this paper was to study the thermodynamic effects of roasting temperature on chromite for the formation of  $\text{Na}_2\text{CrO}_4$ . Therefore, the following can be concluded:

- The addition of NaCl as a complexing agent makes the roasting reaction feasible.
- The roasting of chromite is governed by a fully reacted outside layer and an unreacted core.
- A temperature increase has caused phase transformation of chromite, thereby decomposing into  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .
- NaCl shifts the equilibrium temperature, thereby fully decomposing the spinel structure of the chromite.
- 1 200 °C is the temperature of full chromite decomposition, however predictions suggest unavailability of sodium chloride for the reaction since they report as gases.

## Acknowledgments

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**Note:** The responsible for English language is Meta Jonathan MVITA, Johannesburg.