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Escudero-Castejon, L, Sanchez Segado, S orcid.org/0000-0002-3511-0723, Parirenyatwa, S et al. (2 more authors) (2017) A Cr⁶⁺⁻ Free Extraction of Chromium Oxide from Chromite Ores Using Carbothermic Reduction in the Presence of Alkali. In: Applications of Process Engineering Principles in Materials Processing, Energy and Environmental Technologies, The Minerals, Metals & Materials Series. TMS 2017 146th Annual Meeting & Exhibition, 26 Feb - 02 Mar 2017, San Diego, CA, USA. Springer International , pp. 179-188. ISBN 978-3-319-51090-3

https://doi.org/10.1007/978-3-319-51091-0_16

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A Cr⁶⁺-FREE EXTRACTION OF CHROMIUM OXIDE FROM CHROMITE ORES USING CARBOTHERMIC REDUCTION IN THE PRESENCE OF ALKALI

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ABSTRACT

Oxidative alkali roasting of chromite is the state-of-the-art process for manufacturing chromium-containing chemicals, which involves dealing with serious environmental problems arising from handling Cr⁶⁺-containing wastes generated in this process. In this article a new method for the extraction of Cr₂O₃ from chromite ores is explained, based on the carbothermic reduction of concentrates in the presence of alkali investigated in the temperature range of 950-1050°C. Under these conditions, the iron oxides present in the ore body are reduced to metallic iron and the resulting separation of chromium complex occurs by forming sodium chromite (NaCrO₂). The reduced samples are magnetically separated for the recovery of an iron-rich fraction, and a non-magnetic fraction containing NaCrO₂, MgO and other impurities. The further treatment of the non-magnetic fraction by leaching yields a Cr₂O₃-rich product of approximately 85% purity, with remaining alumina, alkali and magnesia. The main advantage of the process is that, under reducing and subsequent leaching conditions, the oxidation of Cr³⁺ to Cr⁶⁺ is completely avoided; thereby decreasing the risk of land, air and water pollution.

KEYWORDS

Chromite ore, carbothermic reduction, alkali, chromium(VI), chromium extraction, chromium oxide.

INTRODUCTION

The future manufacturing of nonferrous metals is dependent on significant improvement of the traditional beneficiation processes by minimizing the generation of hazardous wastes and the energy consumption. Although the chromium chemicals industry has been reducing the environmental impact by designing safer disposal procedures for process waste and handling, the landfill sites require ongoing maintenance [1]. Only a fraction of chromium containing wastes are recycled in the industry, which implies that there is no long-term solution for the management of hexavalent chromium.

Reactive metal oxides, namely Cr_2O_3 , because of their multiple valences determined by the 3d-electronic structure, form a range of complex oxides in nature; which in case of chromium occurs as chromite spinel $(\text{Fe},\text{Mg})(\text{Cr},\text{Al},\text{Fe})_2\text{O}_4$ [2]. Six different spinels (FeCr_2O_4 , MgCr_2O_4 , FeAl_2O_4 , MgAl_2O_4 , MgFe_2O_4 and Fe_3O_4) coexist in the complex chromite spinel forming a solid solution.

Worldwide manufacturing of sodium chromate, sodium dichromate, chromic acid and many other chromium chemicals relies on the alkali roasting of chromite in oxidising conditions, which yields water soluble sodium chromate (Na_2CrO_4). Silica is often present in chromite and it can vary between 2 wt.% in S. African ores and more than 8 wt.% in lower grades of chromites, used for chemicals manufacturing. Although the S. African ores are most widely used, there is a general tendency in the sector to use indigenous resources for chromium chemicals, which has then implications on using more energy for handling and managing chromium (6+) wastes. As a result of increasing silica, which forms a viscous silicate liquid, the oxygen transport during oxidation is reduced and there is higher consumption of alkali as it is required to neutralize silica [3, 4]. Hence, the extraction efficiency of chromium decreases with increasing silica content [5], and consequently, the generation of hazardous chromite ore processing residue (COPR) containing toxic Cr^{6+} have not been eliminated and it stands for the main limitation of the alkali roasting process.

Besides the use of chromite ores for chromium chemicals, the most important application of chromite is in the production of high-grade ferro-chromium, which is used in the metallurgical industry for manufacturing of stainless steels and chromium-containing metal alloys [6]. Ferro-chromium is produced by smelting of chromite ore in reducing atmosphere in an arc submerged furnace with coke at high temperatures (above 1600°C), with partial solid state pre-reduction of chromite. The reduction of chromium oxide takes place as shown in reaction (1):



where $[\text{C}]_{\text{Fe}}$ and $[\text{Cr}]_{\text{Fe}}$ represent the carbon and chromium in the alloy. The equilibrium constant for reaction (1) may be expressed as:

$$k = \frac{(P_{\text{CO}})^3 \cdot (a_{[\text{Cr}]_{\text{Fe}}])^2}{(a_{[\text{C}]_{\text{Fe}}})^3 \cdot a_{\text{Cr}_2\text{O}_3}} ; \quad (2)$$

where a_i is the activity of species i ; and P_{CO} is the equilibrium partial pressure of CO gas. As it is evident from equation (2), the activity of carbon must be kept high so that higher Cr can be retained in the alloy phase because $P_{CO} \propto a_{[C]_{Fe}}$ and $a_{[Cr]_{Fe}} \propto (a_{[C]_{Fe}})^{\frac{3}{2}}$ if $a_{Cr_2O_3}$ and P_{CO} are considered fixed at a given temperature. However, the presence of high amounts of carbon may lead to the formation of chromium carbides which are undesirable for the formability of stainless steel products. The production of Fe-Cr needs expensive metallurgical coke, cannot use chromite fines and requires a great supply of electrical energy for operating the electric arc furnace [7].

In this study, the production of chromium(III) oxide based on the reduction of chromite ores in the presence of alkali with carbon at moderate temperatures (950-1050°C) was investigated. The reaction of chromium oxide with Na_2CO_3 to form sodium chromite ($NaCrO_2$) occurs in reducing conditions with simultaneous reduction of iron oxides to metallic iron, following reaction (3).



The reduction of chromite under these conditions does not suffer from the complex balance between high carbon activity and partial pressure of CO gas, since the chromium oxide activity is lowered by forming the alkali chromite. Furthermore, the generation of Cr^{6+} -species is eliminated in this process due to the presence of a reducing atmosphere throughout the alkali complexation process at elevated temperature. The purpose of this investigation is therefore to demonstrate a new process methodology that does not yield Cr^{6+} containing waste in solid, liquid or gaseous forms, and therefore excludes the dependency on waste handling. The chromium(III) oxide derived from this process may then be used as raw material for the manufacturing of chromium chemicals, stainless steels, chrome metal or other chromium-containing alloys. The proposed flowsheet and the fundamentals of the different stages of the process are discussed in this manuscript.

EXPERIMENTAL

The ore used in this study was S. African chromite ore of the following composition 48.8% Cr_2O_3 , 31.3% Fe_2O_3 , 7.03% MgO , 7.15% Al_2O_3 , 3.45% SiO_2 and 0.54% CaO . Sodium carbonate (Na_2CO_3) and activated charcoal of analytical grade were also employed in alkali reduction experiments. For the reduction experiments, the as-received mineral was mixed with alkali (Na_2CO_3) and carbon (activated charcoal) using a certain mineral:alkali:carbon weight ratio. Mixtures were heated in a tube furnace under isothermal reducing conditions for 2.5 hours, in argon atmosphere and at temperatures ranging between 900°C and 1050°C.

Reduced samples were ground and magnetically separated. During magnetic separation the sample was sprayed with water to wash-off the non-magnetic fraction and dissolve the water-soluble components. The non-magnetic fraction, rich in $NaCrO_2$, was leached first in water and subsequently in acid media. Either oxalic acid or H_2SO_4 solutions were used as acids

in leaching experiments. Both water and acid leaching were carried out in a leaching vessel with continuous stirring, at 50°C and controlling pH.

RESULTS AND DISCUSSION

Carbothermic Reduction of Chromite Ore in the Presence of Alkali

During reduction in the presence of alkali, the iron present in the spinel is reduced to metallic form (Fe), and chromium oxide present in chromite solid solution reacts with the Na₂O produced from the decomposition of sodium carbonate and forms sodium chromite (NaCrO₂), as previously shown in equation (3). The carbon dioxide, which is a waste otherwise, combines with excess carbon and yields CO gas.

The equilibrium reduction condition of chromite in the presence of alkali may be explained on the basis of the Na-Fe-Cr-O-C predominance area diagram shown in Figure 1. From this figure, it is apparent that metallic Fe co-exists with NaCrO₂ (area 4) at 1050°C (1323 K) for a range of partial pressures of CO and CO₂. Reduction of iron oxide takes place by shifting the equilibrium condition corresponding to area 1 to area 4, resulting in the decreasing value of P(CO)₂. NaCrO₂ is stable at these temperatures and reductive pressure conditions; thereby ensuring that the Cr⁶⁺ state remains unstable.

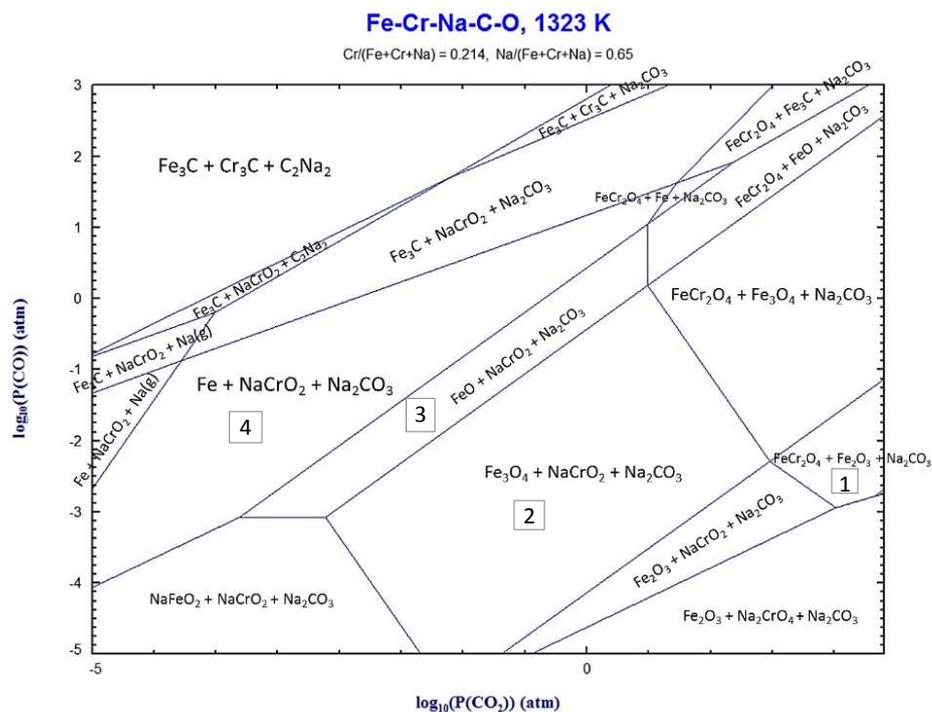


Figure 1- Predominance diagram of the Na-Fe-Cr-O-C system at 1323K (1050°C) computed by Fact-Sage 6.4 software [8]

The aim of the alkali reduction stage is to form a magnetic metallic iron-rich fraction and a non-magnetic fraction containing sodium chromite, which can be magnetically separated. Images from scanning electron microscopic (SEM) analysis and the energy dispersive X-ray elemental mapping of reduced chromite samples are shown in Figure 2. The elemental mapping illustrates that the brighter phase corresponds to metallic Fe formed during reduction, while the darker grey phase is rich in NaCrO₂. Sodium aluminate is also present in the reduced product as a result of the chemical reaction of aluminium oxide with excess Na₂CO₃, following reaction (4).



NaAlO₂ is water soluble and it can be separated readily from the reaction product. A part of sodium carbonate may react with MgO and silica to form complex sodium magnesium silicates. Magnesium oxide (MgO) and calcium carbonate (CaCO₃) are also present as products of reaction.

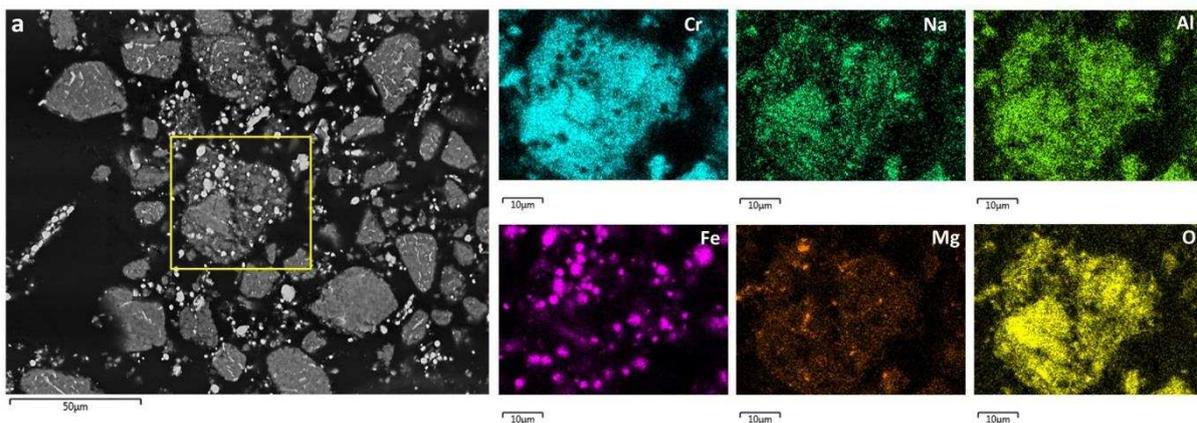


Figure 2- Scanning electron microscopy image (a) of a chromite reduced sample with Na₂CO₃ and activated charcoal in argon atmosphere at 1050°C for 2.5 hours; and energy dispersive X-ray elemental maps of Cr, Na, Al, Fe, Mg and O of the selected area

Wet Magnetic Separation

The X-ray powder diffraction patterns of a reduced sample, magnetic fraction and non-magnetic fraction are compared in Figure 3 in which NaCrO₂, Fe, NaAlO₂, MgO and CaCO₃ were the main phases identified in the reduced sample pattern (a). This is good agreement with the elemental mapping results shown in Figure 2.

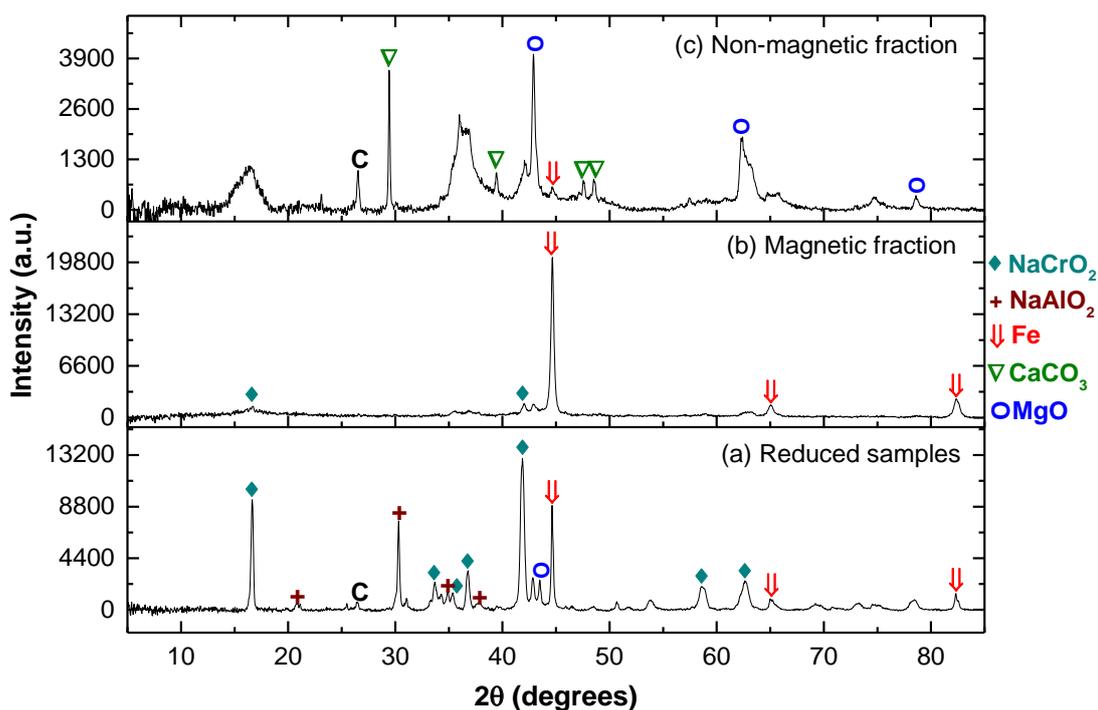


Figure 3- X-ray powder diffraction (XRPD) patterns of reduced sample (a), magnetic fraction (b) and non-magnetic fraction (c) obtained from the reduction of chromite ore with sodium carbonate and activated charcoal (1050°C, 2.5 hours), followed by wet magnetic separation

For an efficient magnetic separation, it is necessary to optimize the formation of metallic Fe by adjusting the operation parameters of the reduction process. In Figure 3, it can be seen that the magnetic fractions still contain residual sodium chromite after the separation, as low-intensity peaks for NaCrO_2 were identified in pattern (b). This is also confirmed by the comparative analysis of the microstructures of the magnetic fraction (left) and the non-magnetic fraction (right) shown in Figure 4, in which extensive entrapment of metallic iron within NaCrO_2 particles and sintering between both phases are evident. The compositions of the magnetic and non-magnetic samples analysed by XRF are shown in Table 1, and these data are compared with the chemical composition of the initial chromite ore. The magnetic fraction contains 21.1% Cr_2O_3 , being most of it in the form of trapped NaCrO_2 with a minor quantity of chromium in the metallic iron matrix.

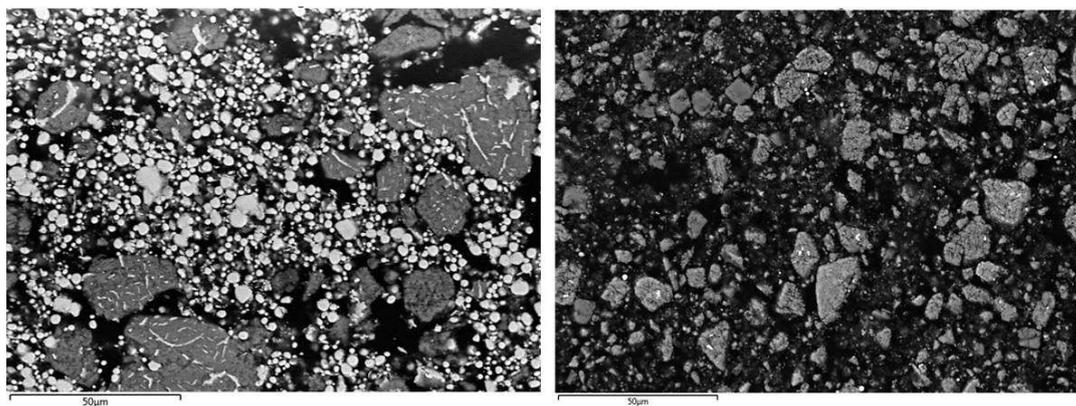


Figure 4- Scanning electron microscopy images of magnetic fraction (left) and non-magnetic fraction (right) samples obtained after two steps magnetic separation of chromite samples reduced with Na_2CO_3 and activated charcoal at 1050°C for 2.5 hours

Table 1- XRF analysis of as-received chromite ore, magnetic and non-magnetic fractions after reduction of chromite ore with Na_2CO_3 and charcoal at 1050°C for 2.5 hours followed by magnetic separation

wt. %	Cr_2O_3	Fe_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	CaO
Chromite	48.80	31.30	---	7.03	7.15	3.45	0.54
Magnetic fraction	21.10	71.20	1.60	1.99	1.85	0.45	0.59
Non-magnetic fraction	50.20	6.16	7.42	13.30	7.01	4.34	6.63

This tendency of entrapment and sintering apparently impedes complete recovery of NaCrO_2 into the non-magnetic fraction. The efficiency of the magnetic separation improves with increasing particle size of metallic iron, and thus the particle size dependence of Cr-entrapment as sodium chromite in the iron matrix is a key aspect for achieving high chromium recovery.

In Figure 3, it could be seen that the XRPD pattern (c) of the non-magnetic fraction is not completely crystalline. Diffraction peaks of sodium chromite, which is the main product expected in this fraction, could not be identified possibly because of the non-crystallinity of NaCrO_2 . However, evidence of the presence of NaCrO_2 in the non-magnetic fraction is given in the SEM image and elemental mapping of a non-magnetic fraction sample presented in Figure 5. X-ray fluorescence results in Table 1 showed that the non-magnetic fraction contains 50.2% Cr_2O_3 ; and the remaining impurities are, from higher to lower wt.%, MgO , Na_2O , Al_2O_3 , CaO , Fe_2O_3 (which may be in form of metallic iron) and SiO_2 .

Since magnetic separation is carried out with water, part of the unreacted Na_2CO_3 and the water soluble compounds formed during reduction, namely NaAlO_2 and water soluble silicates, will solubilise at this stage yielding an alkaline solution. The treatment of this solution in order to recover the alkali will be explained below in this text.

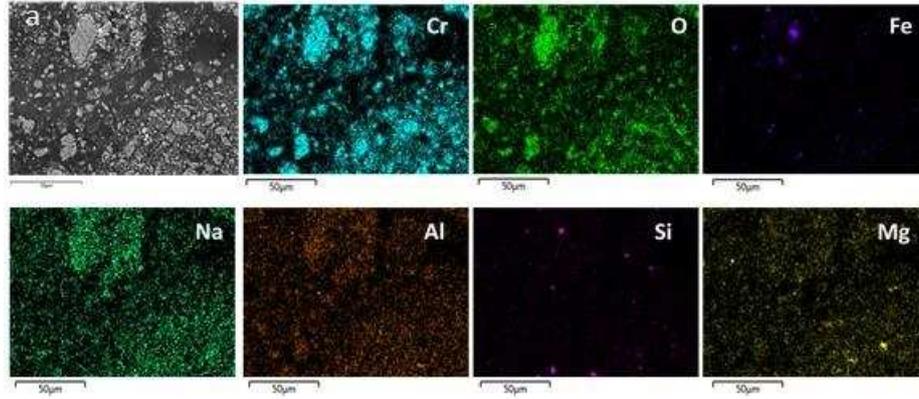


Figure 5- Scanning electron microscopy image (a) and energy dispersive X-ray elemental maps of Cr, O, Fe, Na, Al, Si and Mg, of a non-magnetic fraction sample obtained after chromite reduction with Na_2CO_3 and activated charcoal at 1050°C for 2.5 hours followed by magnetic separation

Treatment of the Non-magnetic Fraction

A Cr_2O_3 -rich product can be extracted from the non-magnetic fraction by different leaching steps. The first leaching step was performed with water by removing as much sodium-bearing compounds as possible from the non-magnetic fraction. This is essential for the process since, if most of the sodium is extracted at this point, the alkali can be recovered and recycled back into the process, which will then help decreasing the consumption of acid during acid leaching.

The residue after water leaching is subsequently leached with acid with the aim of removing the remaining sodium ions from the partially leached sodium chromite ($\text{Na}_{1-x}\text{CrO}_2$). The remaining iron and any water insoluble silicates present in the non-magnetic fraction may be removed at this stage for obtaining an enriched Cr_2O_3 residue. Sulfuric acid and oxalic acid were tested for acid leaching, achieving 83-85% and 80-82% Cr_2O_3 -rich products, respectively. In Table the chemical compositions of the non-magnetic fraction and the water and acid leached residues obtained are compared, showing a significant enrichment of the residue after the leaching stages. The main impurities remaining on the enriched products after leaching with H_2SO_4 are Al_2O_3 and Fe_2O_3 , whereas when leaching with oxalic acid the content of CaO is also significantly high.

Table 2- Chemical compositions of the non-magnetic fraction, water leached and acid leached Cr_2O_3 residues using either sulfuric or oxalic acid. Samples were analysed by XRF

wt. %	Cr_2O_3	Fe_2O_3	Na_2O	MgO	Al_2O_3	SiO_2	CaO
Non-mag fraction	50.20	6.16	7.42	13.30	7.01	4.34	6.63
Water leached residue	68.30	5.30	1.83	9.68	6.04	3.64	3.08

Sulfuric leached residue	83.60	2.66	1.65	1.49	4.79	0.53	2.25
Oxalic leached residue	81.50	2.17	1.41	1.82	6.07	0.27	4.77

Proposed Process Flowsheet

Based on the experimental results presented in this text, a novel process for extraction of chromium oxide from chromite ores is proposed, and its flowsheet is presented in Figure 6

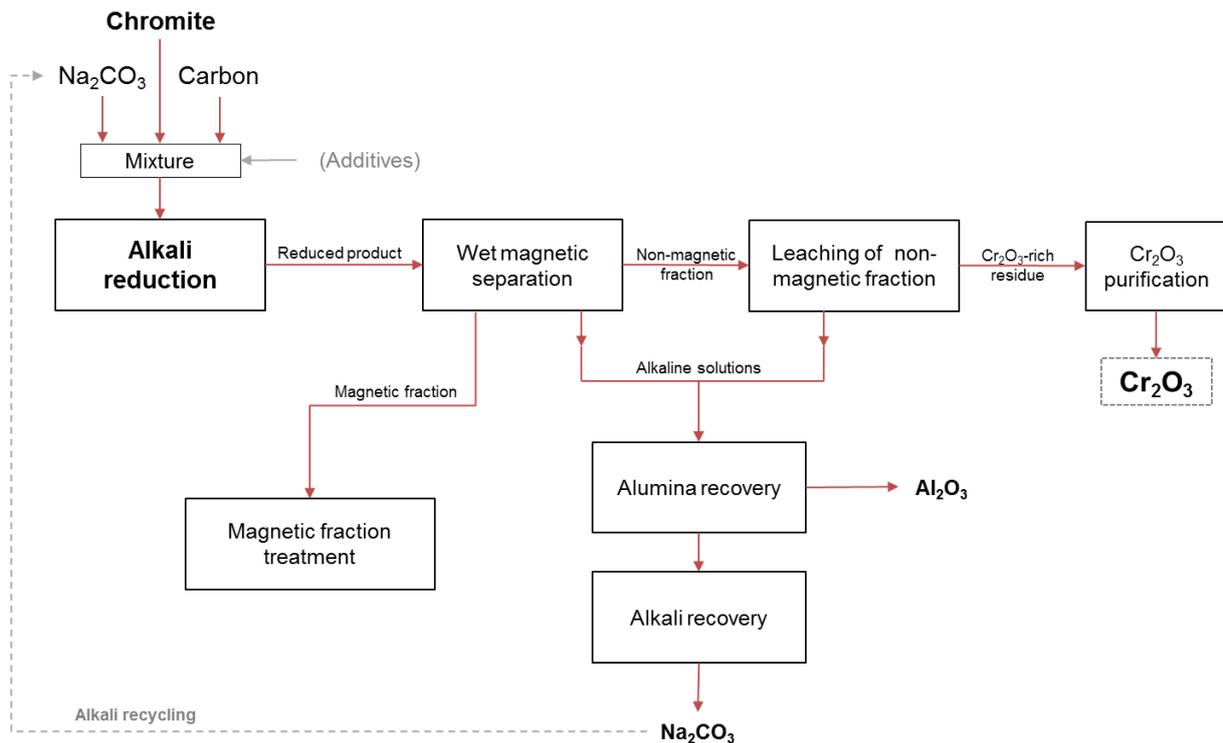


Figure 6- Process flowsheet including the main stages of the alkali reduction process

The first step of the new process design consists on the reduction of chromite in the presence of Na_2CO_3 and activated charcoal ($T = 950^\circ\text{C} - 1050^\circ\text{C}$), as explained before in this text. Reduced samples were cooled down to room temperature and ground using a mortar and pestle to liberate Fe particles. On the next step, reduced samples are magnetically separated using water which yields a Fe-rich magnetic fraction, a NaCrO_2 -rich non-magnetic fraction and an alkaline solution.

It was shown in Table 1 that the magnetic fraction contains $\approx 20\%$ Cr_2O_3 , and therefore, it is worthwhile considering the recovery of chromium oxide from this fraction, which needs to be further investigated. An option would be to treat this magnetic fraction at high temperature in order to separate the remaining NaCrO_2 (into slag) from the metallic Fe. The NaCrO_2 slag could be recycled back into the process for extraction of chromium, or fed into a ferrochromium alloy making plant.

The non-magnetic fraction is subjected to water leaching, generating a solid precipitate rich in Cr_2O_3 and a solution which is highly alkaline. The leachate solution obtained is rich in alumina, alkali and contains some silica, and may be combined and treated with the highly alkaline solution obtained from the wet magnetic separation stage for potential recovery of alkali. Alumina is precipitated from the solutions by CO_2 bubbling. Sodium species as NaHCO_3 , which can be then recycled back into the reduction stage, are recovered from the remaining solution by evaporation. Maximization of the alkali recovery is a key aspect of the process from an economical point of view.

Water leaching is followed by leaching in acid media, giving as a result a Cr_2O_3 -rich product of up to 85% purity. Further purification is required in order to achieve high purity chromium oxide.

CONCLUSIONS

A novel process for extraction of chrome oxides from chromite ores has been investigated. The process is based on the carbothermic reduction of chromite ore with solid carbon (activated charcoal) in the presence of an alkali in the temperature range of 950°C to 1050°C . The magnetic separation of reduced samples with water leaching yields a non-magnetic fraction residue which is the main source of Cr_2O_3 . The leaching of the Cr_2O_3 residue with oxalic and sulphuric acid in one step produces better than 80% pure Cr_2O_3 . So far it is evident from the analysis that there was no evidence for the presence of Cr^{6+} in the process from the leaching or reduction stage.

Optimization of the different steps of the process is now required, with special emphasis on the separation of iron from NaCrO_2 during magnetic separation and further purification of the Cr_2O_3 -rich product.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from a consortium of UK industry and the EPSRC standard grants (GR/T19889/01 and GR/L95977/01) and PhD studentships for research which were initiated in 1997 at the University of Leeds. AJ also acknowledges the support from the European Union's Marie Curie Fellowship grant number 331385 for Dr Sanchez-Segado.

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