



Utilisation of pre-oxidised ore in the pelletised chromite pre-reduction process



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ABSTRACT

Ferrochromium is a vital alloy mostly used for the production of stainless steel. It is produced from chromite ore, the only economically exploitable natural chromium resource, through carbothermic smelting in submerged arc or direct current furnaces. The pelletised chromite pre-reduction process is currently the industrially applied ferrochromium production process with the lowest specific electricity consumption. Results obtained from this study proved that the pre-oxidation of chromite ore prior to milling, agglomeration and pre-reduction significantly enhances the level of chromite pre-reduction achieved in the pelletised chromite pre-reduction process. The optimum pre-oxidation temperature was established as the temperature where a balance was achieved between maximising iron (Fe) migration to the surface of ore particles that were pre-oxidised, while avoiding the formation of free eskolaite (Cr_2O_3). For the case study metallurgical grade chromite ore considered, the optimum pre-oxidation temperature was found to be 1000 °C. Utilising such pre-oxidised ore could theoretically lead to an improvement of approximately 8.5% in the specific electricity consumption and a 14% decrease in the lumpy carbonaceous material required during submerged arc furnace smelting of pelletised chromite pre-reduced feed.

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1. Introduction

Ferrochromium (FeCr) is mostly used for the production of stainless steel, which is vital in various applications (Cramer et al., 2004; Gasik, 2013). Ferrochromium is produced from chromite ore, which is the only economically exploitable natural chromium (Cr) resource (Misra, 2000). At present, global Cr resources are estimated to be between 9 and 12 billion tonnes. South Africa (RSA) holds the vast majority of estimated chromite resources, i.e. ~6.9 billion tonnes (OCC, 2014). In 2012, RSA produced ~10 million tonnes of chromite ore, representing ~41% of the world production. Of the ~10 million tonnes of ore produced, ~55% were exported, which implies that ~28% of ore consumed in the rest of the world in 2012 originated from RSA. RSA is also one of the major producers of FeCr, with production in 2012 accounting for 32% of the total global estimate (ICDA, 2013).

Chromite ore is mainly converted to FeCr through carbothermic smelting in submerged arc furnaces (SAFs) or direct current furnaces (DCFs) (Beukes et al., 2010). The majority of RSA chromite ore is relatively friable (Beukes et al., 2010; Glastonbury et al.,

2010). Generally, the use of fine chromite (<6 mm) in SAF smelting is restricted, since fine materials raise the risk of the furnace bed to sinter. Consequently, evolving process gases are trapped, leading to bed turnovers or furnace eruptions that can have devastating consequences (Beukes et al., 2010; Riekkola-Vanhanen, 1999). Therefore, fine ore is agglomerated (e.g. pelletised) before being charged into an SAF.

Ferrochromium production using SAF smelting is a fossil fuel (carbon reductant) and electric energy intensive process. Therefore, production cost depends heavily on energy and raw material prices. International trends to increase energy security in conjunction with increasing energy costs have placed an emphasis on conducting research related to process optimisation, process efficiency and efficient energy utilisation. Holappa (2010) reported the specific electricity consumption (SEC) and carbonaceous reductant consumption of conventional open SAF smelting of lumpy and fine ore (without agglomeration and pre-heating) to be 3.8–4.5 MW h/t FeCr and 0.5–0.7 t reductant/t FeCr, respectively.

A number of processes have been developed to reduce SEC, with the pelletised chromite pre-reduction process considered to be the industrially applied option with the lowest SEC (McCullough et al., 2010; Naiker, 2007; Naiker and Riley, 2006). In the pelletised chromite pre-reduction process, metallurgical grade chromite ore (<1 mm), a clay binder and a carbon reductant are dry milled to

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particle size of 90% < 75 μm , followed by disc pelletisation and pre-heating, before being fed into a rotary kiln where the chromite is pre-reduced (also referred to as solid state reduction). The partially reduced pellets are then fed hot, immediately after exiting the kiln, into closed SAFs (Beukes et al., 2010; Naiker, 2007). Apart from lower SEC, the pelletised chromite pre-reduction process option also holds other significant advantages, which include lower SAF lumpy reductant consumption, exploitation of lower cost fine reductants and energy sources such as anthracite (instead of coke) and oxygen (O_2), 100% agglomerate feed, Cr recoveries in the order of 90% and the ability to produce a low silicon (Si)- and sulphur (S)-containing FeCr product (McCullough et al., 2010; Naiker, 2007; Takano et al., 2007).

Pre-oxidation as a treatment prior to smelting in the SAF is a commercially applied process. In the oxidative sintering process (Outotec, 2015), which has been the most commonly applied process over the last decade in the South African FeCr industry, milled chromite ore is sintered in pelletised form. This sintering process is essentially an oxidative process, during which the small amount of carbon present in the uncured pellets is oxidised to sinter the pellets (Beukes et al., 2010; Niemelä et al., 2004). SEC for SAF FeCr production with oxidative sintered pellets is ≥ 3.1 MW h/t FeCr, which is an improvement from the conventional SAF smelting of ores.

Zhao and Hayes (2010) investigated the effects of additional oxidation on the microstructure and reduction (as occurring in the furnace smelting process) of oxidative sintered chromite pellets. They found that pre-heating the pelletised ore at temperatures between 1000 and 1200 $^{\circ}\text{C}$ in air increased the reducibility of the chromite in the smelting furnace. They attributed this increased reducibility to the increase in the effective surface area created due to the shear mechanism generating smaller particles, i.e. the transformation of magnetite (Fe_3O_4) to hematite (Fe_2O_3). The rapid transformation to the Fe_2O_3 phase occurs through a solid state shear mechanism that results in the preferential growth on the planes in the crystals. The strain induced at the $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ phase boundary and the preferential reduction of Fe_2O_3 can result in the mechanical break-up of the crystal grains, thereby increasing the effective surface area for reduction (Zhao and Hayes, 2010).

From the abovementioned, it is evident that the oxidation/sintering of chromite prior to smelting in an SAF can potentially have significant SEC advantages. However, pre-oxidation of chromite ore, prior to being used in the pelletised pre-reduction process, has not been investigated before. In this paper, results are presented that demonstrate how pre-oxidation can improve the extent of pre-reduction, which will further improve the SEC of the pelletised chromite pre-reduction FeCr production process. The objectives were to (i) present the new suggested process, i.e. pre-oxidation of chromite ore prior to pelletised pre-reduction, (ii) assess how to optimise pre-oxidation conditions to maximise the benefit of using pre-oxidised chromite ore, and (3) indicate the possible practical advantages and disadvantages of this process option by considering factors such as SEC, carbonaceous reductant consumption, breaking- and abrasion strengths, as well as the formation of hexavalent chromium, Cr(VI), which is considered a human carcinogen (Beaver et al., 2009; Thomas et al., 2002).

2. Materials and methods

2.1. Materials

The raw materials utilised in the industrially employed pelletised chromite pre-reduction process consist of upgraded fine chromite ore (typically metallurgical grade chromite ore or upgraded UG2 process residue from the Platinum Group Metals industry), a clay binder and a fine carbonaceous reductant. Raw

materials used in this study were obtained from a large South African FeCr producer, applying the pelletised chromite pre-reduction process. Metallurgical grade chromite ore (<1 mm), anthracite breeze (reductant) and attapulgitic clay (binder) utilised by this FeCr producer were acquired. The same raw material samples were used by Kleynhans et al. (2012), who presented a comprehensive chemical and surface analysis of all these materials, as well as X-ray diffraction (XRD) and ash fusion temperature analyses of the clay binder. Therefore, the material characterisations and methods applied are not repeated here, but only a synopsis of the chemical composition of the three raw materials and the proximate analyses of the anthracite breeze are presented in Table 1.

Ultra-pure water from a Milli-Q water purification system (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used to pre-wet materials prior to pelletisation. Instrument grade nitrogen (N_2) gas (Afrox) was utilised in all pre-reduction experiments.

Several Cr(VI) analyses were conducted. Calibration of the analytical instrument was performed using a reference standard (Spectroscan) with a certified concentration of $1009 \pm 5 \mu\text{g/mL}$ chromate (CrO_4^{2-}). Ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) (Merck) and a 25% ammonia (NH_3) solution (Ace) were used to prepare the eluent. The post-column reagent was prepared using 1,5-diphenylcarbazide (Fluka Analytical), 98% sulphuric acid (H_2SO_4) (Rochelle Chemicals) and HPLC grade methanol (Ace). Sodium hydroxide (NaOH) (Promark chemicals) and sodium carbonate (Na_2CO_3) (Minema) were used to prepare a Na_2CO_3 -NaOH buffer to extract Cr(VI) from the solid samples.

2.2. Methods

2.2.1. Pre-oxidation of chromite ore

Pre-oxidation of the chromite ore was carried out in an Elite BR15/5 chamber furnace fitted with a programmable temperature controller. 100 g of metallurgical grade chromite ore (<1 mm) was placed in a ceramic (99.8% Al_2O_3) boat, positioned centrally inside the furnace chamber and heated in a normal gaseous atmosphere (air) during each pre-oxidation test. For each temperature profile, the furnace controller was set to ramp up at its maximum heating rate from room temperature to a desired maximum temperature (i.e. 800–1500 $^{\circ}\text{C}$) and then to remain constant at the maximum temperature for a further 10 min, after which the furnace was switched off. The furnace door was then opened to aid in rapid cooling to room temperature. These pre-oxidation temperature profiles are graphically presented in Fig. 1.

2.2.2. Material preparation and pelletisation

The preparation of raw materials for pre-reduction was conducted similar to the procedures previously described by

Table 1

Chemical analyses (wt.%) of chromite ore, anthracite breeze (reductant) and attapulgitic clay (binder), as well as the proximate analysis of the anthracite breeze (air dry basis) used in this study (from Kleynhans et al., 2012).

	Chromite ore	Anthracite breeze	Attapulgitic clay
Cr_2O_3	45.4	–	–
FeO	25.4	1.6	6.0
Al_2O_3	15.2	3.1	14.7
MgO	9.8	0.4	5.3
SiO_2	1.7	10.0	46.9
CaO	0.2	0.8	5.6
P	<0.01	0.01	<0.01
S	<0.01	0.6	<0.01
Fixed carbon	–	75.1	–
Inherent moisture	–	0.3	–
Ash	–	17.8	–
Volatiles	–	6.9	–

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