

THE INFLUENCE OF CaCO_3 ADDITION AND CLAY BINDER SELECTION ON ELECTRICITY EFFICIENCY AND OTHER OPERATIONAL ASPECTS DURING PRE-REDUCTION OF PELLETISED CHROMITE

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ABSTRACT

Production of ferrochrome is an energy intensive process. Pelletised chromite pre-reduction is most likely the ferrochrome production process with the lowest specific electricity consumption, i.e. MWh/t ferrochrome produced. Higher chromite pre-reduction levels correspond to lower specific electricity consumptions. In this paper the effect of CaCO_3 addition and clay binder selection on pelletised chromite pre-reduction is presented. Results indicated that CaCO_3 addition significantly enhances the level of chromite pre-reduction achieved within a given time and temperature horizon. However, CaCO_3 addition caused severe decreases in both compressive and abrasion strengths of pre-reduced pellets, which is unlikely to be negated by mitigation measures. The addition of CaCO_3 in the pelletised chromite pre-reduction process will therefore most probably result in the formation of excessively fine feed materials. In practise, this reduces the usefulness of this technique for submerged arc furnace ferrochrome production significantly, since excessive fines in the feed material are likely to result in increased operational instabilities, equipment damage and safety risks. TGA and thermochemical calculations also indicated that CO_2 released from the CaCO_3 will result in additional carbon consumption, which is an additional negative associated with its use as an additive during pre-reduction of composite chromite pellets. Although the research work covered in this paper was not specifically aimed at obtaining mechanistic information, thermo-mechanical analysis indicated that especially iron pre-reduction rates were enhanced by CaCO_3 addition. It was also proved that clay binder selection not only influence the physical strength of the pre-reduced pellets, but also the level of achievable pre-reduction. Additionally, increased addition of clay binder to the composite pellet was found to result in progressive decline in the degree of chromite pre-reduction achieved within a specified time-temperature reference frame.

KEYWORDS: Chromite pre-reduction, CaCO_3 , clay binder, electricity consumption.

1. INTRODUCTION

Reducing specific electricity consumption (SEC), i.e. electrical energy consumed per ton of FeCr produced, has long been a driving factor within the ferrochromium (FeCr) industry. Recently it was demonstrated how the steep rise in electricity cost in South Africa have impacted negatively on the South African FeCr industry [1]. This has resulted in a near stagnation, or even contraction in the South African FeCr output, with significant increase in Chinese alloy production. The pelletised chromite pre-reduction process is considered to be the FeCr production process option with the lowest SEC [1, 2]. Utilising typical South African chromite ore the SEC of the pelletised chromite pre-reduction process is approximately 2.4 MW h/t FeCr. When comparing this to the SEC for DC furnace operations of > 4.5 MW h/t FeCr [3], the oxidative sintered process of

>3.1 MW h/t FeCr [4] and conventional SAF production of 3.9-4.2 MW h/t FeCr [2], it becomes clear that the pelletised chromite pre-reduction process option holds significant SEC advantages. In this paper the effect of CaCO_3 addition and clay binder selection on the pelletised chromite pre-reduction process is presented. CaCO_3 is used as a flux in FeCr smelting operating with a basic slag, while clay is used as a binder in the pelletising process. These materials therefore do not constitute the addition of foreign materials. However, their appropriate and optimised addition can probably significantly assist overall process efficiency.

2. EXPERIMENTAL

The case study materials and experimental techniques used were similar to that presented in two recent publications [1, 5].

2.1. Materials

Samples of metallurgical grade chromite (<1 mm), anthracite breeze and two clays, i.e. attapulgite and bentonite, were obtained from a large South African FeCr producer, applying the pelletised chromite pre-reduction process. The characteristics, e.g. chemical, surface chemical, proximate, ultimate, mineralogical phase compositions, ash fusion temperatures, water loss and loss of ignition (LOI) of these raw materials have been published [1]. Industrial Analytical (Pty) Ltd supplied SARM 8 and SARM 18 that were used as reference materials in the analysis of carbonaceous reductants and chromite containing materials, respectively. Analytical grade CaCO_3 (Merck) was used as an additive during some pre-reduction experiments. Ultra-pure water (resistivity $18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used for all procedures requiring water. Instrument grade synthetic air and nitrogen (N_2) gas were supplied by Afrox.

2.2. Pelletising

Different mixing ratios of the three components present in the pre-reduced pellets (chromite ore, anthracite and clay) were made up, according to the objectives of specific experiments. 3-4 wt% clay addition is used in the industrial process [1]. It was therefore decided to conduct experiments in the 2.5-5 wt% clay addition range. A 10 wt% clay addition was also included to help identify trends that might be difficult to recognise within a more limited range. The anthracite was kept constant at 20 wt% (~15 wt% fixed carbon) in all experiments. The rest of the mixtures were made up with the chromite ore. In experiments where CaCO_3 was added as an additive, a pre-determined wt.% CaCO_3 was added according to the requirement of the particular experiment.

All raw material mixtures were dry milled to the particle size specifications applied for industrial pre-reduction feed material, i.e. 90% smaller than $75 \mu\text{m}$ [1]. A Siebtechnik laboratory disc mill with a tungsten carbide grinding chamber was used for this purpose. A Malvern Mastersizer 2000 was used to verify the particle size distribution of the pulverised material.

The milled material was pressed into cylindrical pellets with an LRX Plus strength testing machine (Ametek Lloyd Instruments) equipped with a 5 kN load cell and a Specac PT No. 3000 13 mm die set [1, 5]. For each batch of pellets prepared 50 g of dry mixed raw material was pre-wetted with 5 mL of water and mixed thoroughly. 3.2 g of pre-wetted material was then placed in the die set and compressed at a rate of 10 mm/min until a load of 1500 N was reached. Although this process was time consuming (each pellet made individually), this technique was preferred over conventional disc pelletisation, since it ensured consistent density, form and size, which allowed the monovariance investigation of other process parameters.

2.3. Pre-reduction setup

During each pre-reduction experiment 10 uncured pellets were placed on a coorstek AD-998 (99.8% AlO_2) plate, which were subsequently placed inside a tube furnace (Lenton Elite, UK model TSH15/75/610) fitted with a Shunk recrystallised alumina tube.

Ceramic heat shields were inserted at both ends of the furnace tube to improve the effective length of the tube with a stable temperature and to protect the stainless steel caps that were fitted onto both sides of the ceramic tube to seal the ends. The stainless steel caps had a gas inlet on the one side and an outlet on the other side. Each batch was then treated according to a pre-programmed high temperature profile.

The gaseous atmosphere inside the furnace tube was controlled by applying a steady N_2 flow-rate of 1 NL/min.

An inert gaseous atmosphere (N_2) was preferred during the pre-reduction experiments, since pre-reduction as a result of chromite interaction with the carbonaceous reductant present in the material mixture was of interest and not pre-reduction due to the presence of an external reducing gaseous atmosphere. Before each pre-reduction experiment commenced the tube furnace, already loaded with pellets, was flushed with N_2 to displace air inside the tube.

The temperature profile utilised was compiled to simulate the temperature profile applied during the industrial pelletised pre-reduction process [1, 5]. The profile consisted of three segments, i.e. i) heating the pellets from room temperature to 900°C over a period of 30 minutes, ii) heating from 900 to 1300°C over a period of 50 min, iii) and finally cooling the pellets inside the tube furnace in the inert atmosphere. The base case chromite pre-reduction level achieved (i.e. 0 wt.% CaCO_3 and 3.5 wt.% attapulgite clay as binder) with this high temperature profile was 46.5%, which correlated well with the average level of pre-reduction achieved at one of the large South African FeCr smelters applying the pelletised chromite pre-reduction process.

2.4. Analysis of pre-reduction

The extent of chromite pre-reduction was determined chemically according to the method described by Kleynhans et al. [1].

2.5. Other techniques applied

The compressive strengths of the pre-reduced sintered pellets were tested with an Ametek Lloyd Instruments LRXplus strength tester [1, 5]. The abrasion resistance test apparatus utilised was based on a downscaled version of the European standard EN 15051 rotating drum [6].

The drum was rotated at 40 rpm. A batch (10 pellets) of the pre-reduced pellets was abraded for 1, 2, 4, 8, 16 and 32 min. After each time interval, the material was screened using 9.5, 6.7 and 1.18 mm screens. The over- and under-sized materials were then weighed and all the material returned to the drum for further abrasion, until the final abrasion time was reached.

The dimensional changes of the pellets being pre-reduced *in situ* was recorded with a Seiko Instruments Inc. TMA/SS 6100 thermo-mechanical analyser (TMA), interfaced with SII EXSTAR 6000 [1, 5]. All TMA experiments were conducted under inert atmospheric conditions (N_2), similar to the conditions applied during pre-reduction experiments conducted in the tube furnace.

HSC Chemistry 7.0 [7] was used to conduct thermochemical calculations used to interpret and explain certain results.

3. RESULTS AND DISCUSSIONS

3.1. Effect on pre-reduction and SEC

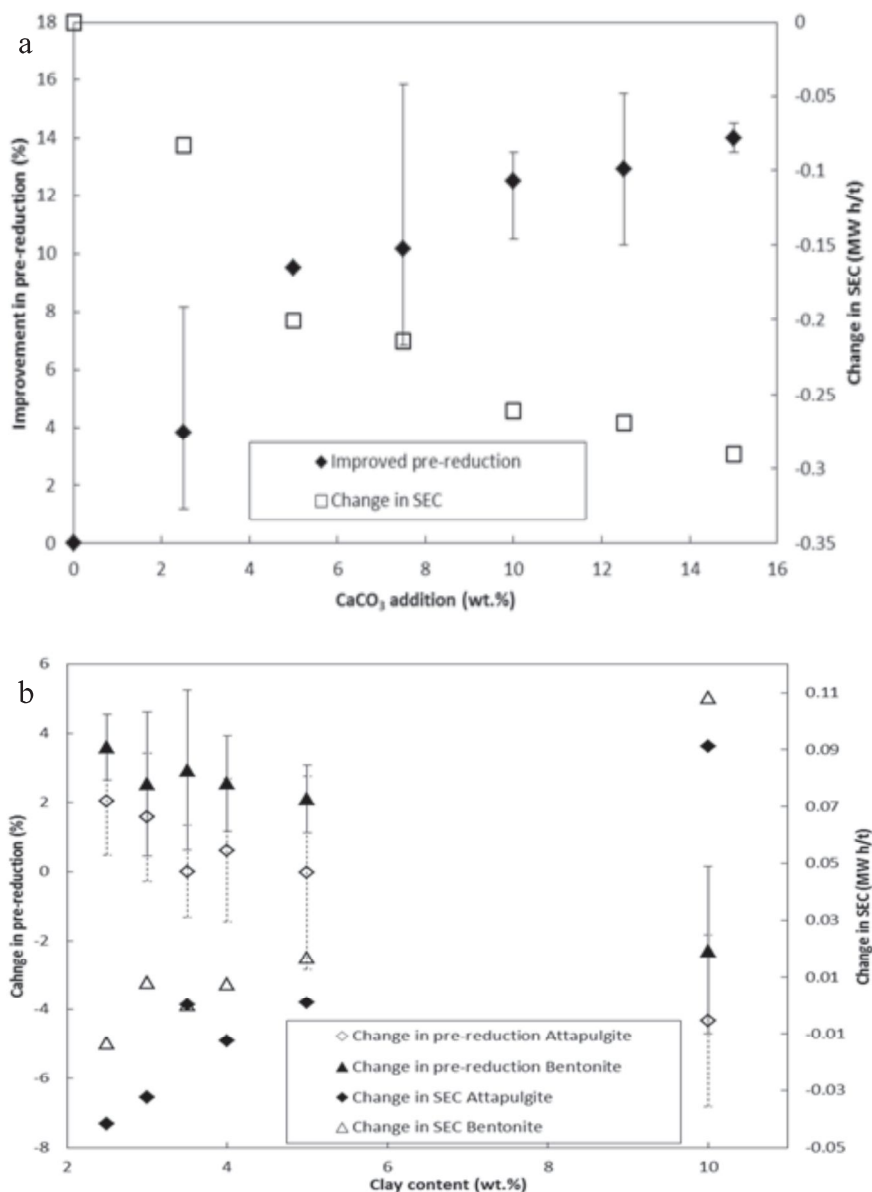
The effect of CaCO_3 addition on the level of achievable chromite pre-reduction, with the specific experimental temperature profile employed is illustrated in figure 1a. It is evident that CaCO_3 addition had a positive effect on the extent of chromite pre-reduction. The intent of this paper was not specifically aimed at deriving mechanistic information on the effect of CaCO_3 during pre-reduction. Such investigations have previously been conducted where CaO was added [8-10]. It is, however, useful to compare the improvement in pre-reduction levels observed experimentally, with that published previously. For this purpose data from studies in which the conditions, i.e. additive addition and maximum temperature, that correlated best with the experimental conditions were cited. Sundar Murti et al. [8] observed approximately 2.5% absolute improvement in pre-reduction with 8 wt.% CaO addition after 35 min exposure at 1275°C , while Van Deventer [10] reported approximately 18.6% absolute improvement in pre-reduction with 10 wt.% CaO addition after 100 min exposure at 1400°C . Since Ding and Warner [9] did not investigate a base case, i.e. 0 wt.% CaO addition, no improved pre-reduction value could be cited from their work. Experimentally 12.5% improvement was observed with 10 wt.% CaCO_3 addition. The experimental data therefore seems to correlate quite well with that reported by Van Deventer [10], but seems to exceed that reported by Sundar Murti et al. [8]. It should however be noted that in both the afore-mentioned cited studies the levels of chromite pre-reduction were derived from gas evolution and/or gravimetric methods, while the levels of pre-reduction presented in this paper were quantitatively determined.

Thermochemical calculation of the delta Gibbs free energies (ΔG) [7] for the reactions relevant to chromite pre-reduction calculated for 1300°C (maximum temperature during pre-reduction experiments), confirmed that CaCO_3 addition lowered ΔG for both the formation of the metal and metal carbide phases from the various oxides and the chromite spinel [5].

Reconstruction of the data published previously [11] and empirical fitting of this reconstructed data, allowed the estimation of improvement in SEC if CaCO_3 would be used as an additive on an industrial scale to improve chromite pre-reduction (figure 1a). From this data it is evident that the addition of CaCO_3 as an additive to the pelletised chromite pre-reduction process could lead to significant SEC improvements in FeCr production. The improvement/decrease in the levels of pre-reduction achieved for the two different clay binders and clay contents from 2.5 to 10 wt%, are shown in figure 1b. From the data it is evident that higher clay contents resulted in lower pre-reduction levels for both clays, with correlating higher SEC. This is significant within the industrial process, since higher clay contents are on occasion utilised to achieve improved green strength of the uncured pellets.

Another significant observation from the data in figure 1b is that there seems to be a difference between the performances of the two clays used in this case study with regard to pre-reduction levels achieved. Although some overlaps are observed between error bars, it is clear that the average pre-reduction of the bentonite containing pellets was consistently higher than that of the attapulgite containing pellets. It was calculated that the bentonite containing pellets had an average of 1.7% higher chromite pre-reduction [1]. This is significant, since this specific attapulgite clay was at the time of the inception of this study the preferred option at the South African FeCr smelters applying the pre-reduction process. The reason for the better performance of the bentonite containing pellets could be attributed to two possible reasons, i.e. i) the bentonite had a lower melting point than the attapulgite, which may imply that the bentonite had already melted during the pre-reduction process, hence serving as a flux that promotes metal reduction, or ii) the minerals present in the two clays can possibly contain materials that could either catalyse or inhibit the pre-

reduction of chromite [1]. Several studies have been published indicating that various substances could have catalytic or inhibiting effects on chromite pre-reduction.



- a - Improvement in pre-reduction compared to the base case scenario of 46.5% prereduction (primary y-axis). The corresponding calculated change in SEC (secondary y-axis), is also shown
- b - Change in pre-reduction due to clay selection and content (primary y-axis). The corresponding calculated change in SEC (secondary y-axis), is also shown

Figure 1

3.2. Effect on pellet strength

From an operational and safety perspective it is important to minimise the fraction of fine materials being fed into a SAF. Pelletised feed material ensures a permeable furnace bed, without gas eruptions and bed turnovers, as well as associated improved efficiencies. It was therefore

important to determine the effect of CaCO_3 addition on the compressive and abrasion strengths of pelletised pre-reduced chromite pellets. The effect of CaCO_3 addition on compressive and abrasion strengths of the cured pre-reduced pellets are illustrated in figure 2a and 2b, respectively.

From the data presented in figure 2a and 2b it is evident that the addition of CaCO_3 has a detrimental effect on both the compressive and abrasion strengths of pre-reduced chromite pellets. However, there does not seem to be a definite trend with regard to higher CaCO_3 addition leading to decreased pre-reduced pellet strength. 7.5 wt.% CaCO_3 addition had the least effect on both compressive and abrasion resistance strength. Yet, even at this best case scenario the pre-reduced pellets only had a third of the compressive strength and abraded approximately 2.4 times faster than pre-reduced pellets not containing CaCO_3 . The pre-reduced pellet strength could be improved by two mitigating measures, i.e. increased strength from a thin outer oxidative layer that characterise industrially produced pre-reduced pellets and the selection of an optimum clay binder [1]. However, it is unlikely that the significant reduction in strength observed due to the addition of CaCO_3 , can be totally mitigated.

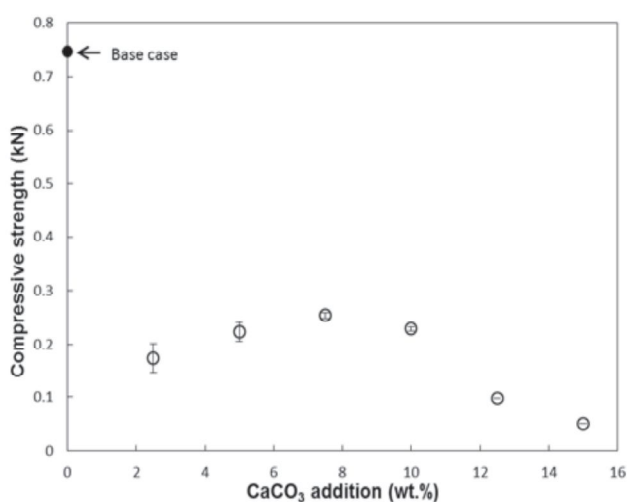


Figure 2a: The effect CaCO_3 addition has on compressive strength [5]

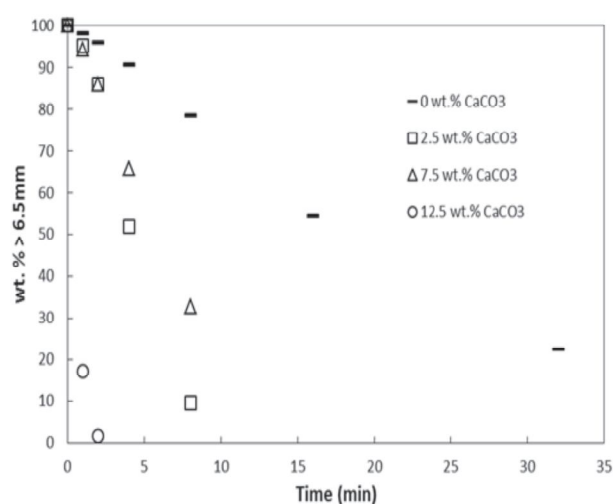


Figure 2b: The effect CaCO_3 addition has on the abrasion strength [5]

The effect of clay binder selection on cured compressive and abrasion strengths are illustrated in figure 3a and 3b, respectively. By comparison of the compressive strengths of the two case study clays, it is clear that the bentonite clay was superior. The compressive strength of the bentonite containing pre-reduced pellets generally improved with increased clay content. Increased attapulgite content, however, did not result in any significant increase in compressive strength of the pre-reduced pellets. Increasing the attapulgite clay content of the industrial pre-reduced pellets may therefore not result in a stronger pellet, although it might aid the green strength, which was not considered in this study. Similar to the compressive strength results, the abrasion resistance strength of the bentonite containing pellets outperformed the attapulgite containing pellets.

3.4. Thermo-mechanical analysis (TMA)

In figure 4a and 4b the dimensional changes (averages of three separate experimental runs for each condition) of chromite pellets being pre-reduced *in situ* in the TMA instrument, containing different weight percentages of CaCO_3 and clay binders are presented. Figure 4a clearly indicates that all pellets, irrespective of CaCO_3 content, responded very similar up to approximately 600°C,

i.e. small shrinkage up to approximately 120°C that could possibly be ascribed to moisture loss, followed by thermal expansion up to approximately 600°C. From the onset of iron pre-reduction at approximately 710°C [12] up to approximately 1200°C significant shrinkage of the pellets occurs. It was also evident that the rate of shrinkage of CaCO₃ containing pellets was higher than pellets without CaCO₃ as an additive. CaCO₃ containing pellets also exhibited an additional expansion above 1200 °C, which was not observed for non-CaCO₃ containing pellets. From the TMA data two important deductions can be made. Firstly, the increased rate of shrinkage of CaCO₃ containing pellets in the iron pre-reduction temperature range (indicated by steeper slopes), indicates that CaCO₃ addition specifically enhances iron pre-reduction.

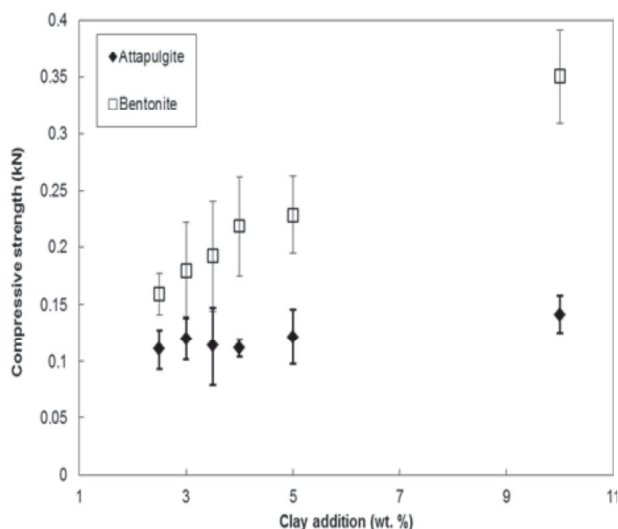


Figure 3a: The effect of clay selection and wt.% addition on compressive strength [1]

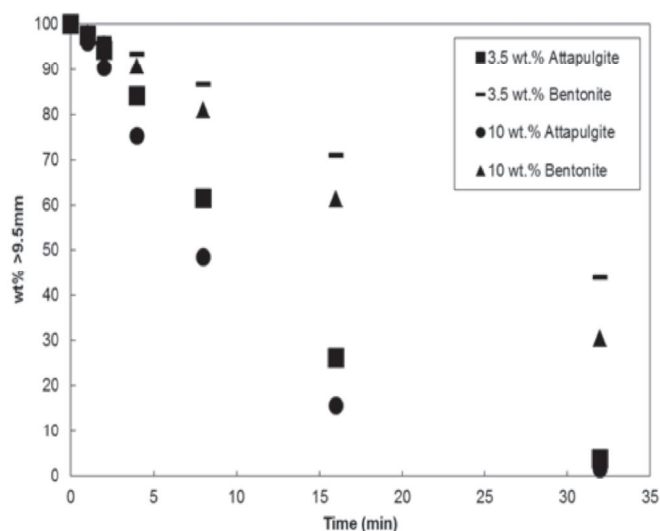


Figure 3b: The effect of clay selection and wt.% addition on the abrasion strength [1]

This confirmed earlier postulations that CaO specifically enhances chromite pre-reduction via the enhanced oxidation of divalent iron to trivalent iron and/or CaO entering the spinel lattice and releasing divalent iron [9]. Apart from this mechanistic relevant information, it can also be stated from the TMA analysis that the additional expansion observed for CaCO₃ containing pellets above 1200°C will have a negative effect on the physical strengths of pre-reduced pellets. Consecutive expansions and contractions weaken pre-reduced pellets. This at least partially explains why CaCO₃ addition resulted in reduced compressive and abrasion strengths (figure 2a and 2b). Although it cannot be deduced from the TMA results, it is also likely that the additional gas released from CaCO₃ could weaken the pre-reduced pellets. CaO addition as previously investigated [8, 9, 10] could therefore be a better option as an additive. However, none of these previous studies made reference to the effect of CaO addition on agglomerate strength. It is also unlikely that CaO, instead of CaCO₃, addition would be economically a more feasible option. CaO is a more expensive raw material than CaCO₃ and usage of CaO would also require additional undercover storage (e.g. physical infrastructure expansions), since contact with moisture results in the exothermic formation of Ca(OH)₂.

The TMA results (figure 4b) of all the pellets pre-reduced *in situ* containing either bentonite or attapulgit with the different clay wt% indicated the same initial trends – small shrinkage up to about 120°C that could probably be ascribed to moisture loss, followed by thermal expansion up to approximately 600°C. After 700°C, more significant shrinkage occurred for the attapulgit containing pellets. In the range 900-1200°C, the attapulgit containing pellets had shrunk

significantly more than the bentonite containing pellets. This additional shrinkage of the attapulgite can be related to the LOI of the attapulgite (13.04%) measured at 1000°C, which was significantly higher than the LOI of bentonite (7.69%). Although the TMA results cannot be directly related to hot pellet strength, larger variation in thermal dimensional behaviour could lead to weaker hot pellet strength. Therefore, although not quantitatively investigated, there is some indication that the hot strength of the attapulgite pellets could be weaker than the bentonite containing pellets.

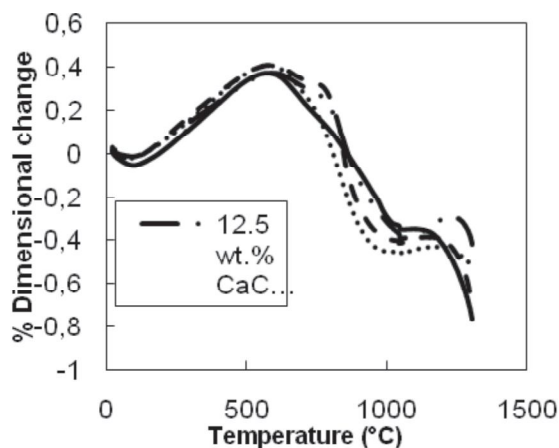


Figure 4a: Effect of wt.% CaCO_3 addition on the percentage dimensional change of pellets being pre-reduced *in situ* [5]

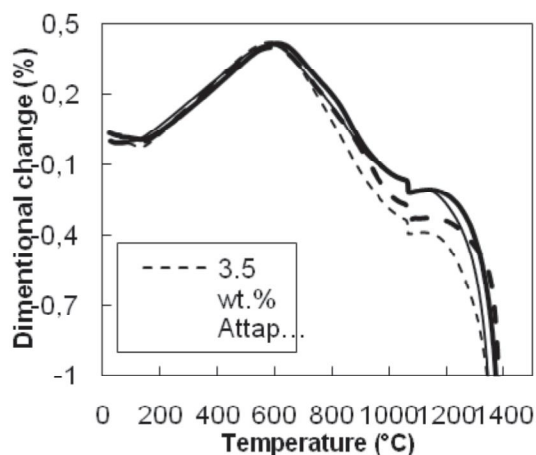


Figure 4b: Effect of wt.% clay addition on the percentage dimensional change of pellets being pre-reduced *in situ* [1]

3.5. Additional considerations

According to TGA results obtained, only approximately 2% of the initial weight of the CaCO_3 utilised as an additive in this study was lost at 700°C, while all the CO_2 had been released at 807 to 837°C (depending on the gaseous atmosphere). According to ΔG calculations of the Boudouard reaction, the endothermic formation of CO from CO_2 and C is the dominant reaction above 700°C. The use of CaCO_3 as an additive in composite pellets containing carbon will therefore result in the consumption of additional carbon during pre-reduction.

In order to explain the better performance of the bentonite compared to the attapulgite in compressive strength and abrasive resistance strength tests, scanning electron microscopy (SEM), electron dispersion X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD) and ash fusion analyses were performed. Visual inspection with SEM (e.g. observing bridge formations, pore sizes, densities, etc) and chemical surface analysis with SEM-EDS did not provide any conclusive results. As expected, XRD analysis indicated that the smectite clay group minerals were the largest component in both clays. However, the attapulgite clay had considerably higher smectite group content than the bentonite. Considering only these results, the attapulgite clay may be mistakenly regarded as the better binder. Limitations of the Rietveld method prevented further breakdown of the smectite group, therefore qualitative XRD analyses were also conducted. Qualitative results indicated that the attapulgite contained palygroskite, which confirms its status as an attapulgite clay. In contrast the bentonite contained montmorillonite, but not palygroskite. The afore-mentioned quantitative smectite mineral contents of the two clays can therefore be ascribed to mainly palygroskite in the attapulgite and montmorillonite in the bentonite. However, explaining why the bentonite seems to be a better binder in the pellets, based only the above-mentioned mineralogical information would be presumptuous. Therefore, ash fusion tests were also conducted to derive parameters that could maybe clarify the previous observations. The ash fusion temperatures

indicated that the bentonite had lower deformation, softening, hemispherical and fluid temperatures. This can possibly give some practical explanation as to why the bentonite performed better in the compressive and abrasion resistance strength tests. A lower melting point (construed as incorporating all four measured ash fusion temperatures) implies that bentonite could possibly start forming bridges between the particles at lower temperatures than attapulgite. It is also notable that the fluid temperatures of the attapulgite were above 1300°C, implying that the possibility exists that it was not completely liquefied under the experimental conditions.

4. CONCLUSIONS

It was proven that CaCO_3 addition could enhance the level of chromite pre-reduction achieved in the pelletised chromite pre-reduction process. This could have a corresponding positive effect on the SEC. However, CaCO_3 addition resulted in severe decreases in the compressive and abrasion strengths of pre-reduced pellets. Mitigation measures are unlikely to prevent excessive fine material formation of CaCO_3 containing pre-reduced pelletised feed material. This renders this technique much less useful for SAF FeCr production. TGA and thermochemical calculations indicated that CO_2 released from the CaCO_3 will result in additional carbon consumption within the composite pellets. The reducing agent incorporated into the composite pellets is usually a cheaper source of carbon, than lumpy reducing agents used during the subsequent smelting process. TMA analysis indicated that especially iron pre-reduction rates were enhanced by CaCO_3 addition. Also, TMA analysis indicated that pre-reduced pellets containing CaCO_3 undergo an additional expansion during pre-reduction, which is likely to contribute to the reduced physical strength of pellets.

The results presented also proved that the case study attapulgite clay was inferior to the bentonite clay in all the properties measured. It was also shown that higher clay content, e.g. to increase pellet green strength, will result in lower chromite pre-reduction. The results clearly indicated that it is unlikely that the performance of a specific clay binder in this relatively complex process can be predicted based on the chemical, surface chemical and mineralogical characterisation of the clay. Experimental monovariance evaluation of clay performance needs to be evaluated in order to distinguish which clay will be best suited.

5. ACKNOWLEDGEMENTS

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