

The use of hydrogen as a reductant in the smelting industry

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Dissertation accepted in partial fulfilment of the requirements for the degree *Master of Science in Chemistry* at the North-West University

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Graduation December 2022

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SOLEMN DECLARATION

I, **Jamey Davies**, declare herewith that the dissertation entitled: **The use of hydrogen as a reductant in the smelting industry**, which I herewith submit to the North-West University (NWU) as completion of the requirement set for the degree **Master of Science in Chemistry**, is my own work, unless specifically indicated otherwise, has been text edited as required, and has not been submitted to any other tertiary institution other than the NWU.



Signature of student

12 August 2022

Date

Signed in **Potchefstroom** at the **North-West University** on **12 August 2022.**

ACKNOWLEDGMENTS

Colossians 3:17 - *“And whatsoever ye may be doing, in word, or in work, all things, [do] in the name of the Master Yahshua, giving thanks unto the Divine Father through Him.”*

I want to thank Yahweh the almighty God, for every challenge, failure, and victory I faced as this all helped me to understand a bit more about the true definition of humbleness, perseverance, and faith. **All the glory to God!**

I would like to thank my Supervisor, Dr. Stephanus Petrus du Preez, for the opportunity, and willingness to always help and advise me when needed.

I want to thank my parents, Franshwa and Su-maré for all their unconditional love and support which contributed to the person I am today. To my sister and best friend, Sue-nique for all the motivation and encouragement.

A Special thanks to Ralph Glastonbury, for always making time to help, guide, and encourage me.

I also want to thank Trygve Schanche and Merete Tangstad for sharing their knowledge and expertise as well as guiding me with absolute humbleness and patients.

Lastly, I would like to thank the Research Council of Norway (RCN) and HySA Infrastructure Centre of Competence, South Africa for financial support throughout the duration of the MSc study.

PREFACE

This dissertation was submitted in article format, as stipulated by the North-West University (NWU) under the General Academic Rules (A-rules, approved on 21/09/2017) designated for post-graduate curricula. The A-rules prescribed that “... *where a candidate is permitted to submit a dissertation in the form of a published research article or articles or as an unpublished manuscript or manuscripts in article format and if more than one such article or manuscript is used, the dissertation must still be presented as a unit, supplemented with an inclusive problem statement, a focused literature analysis, and integration and with a synoptic conclusion ...*”. Therefore, the articles incorporated in this dissertation were ready for submission and/or submitted and/or accepted and/or published in a specific journal. The conventional experimental, results, and discussion sections are excluded from the dissertation since the relevant information is presented in each specific article (Chapters 3, 4, and 5). Aside from the articles, separate background, motivation, and objectives (Chapter 1), a literature survey (Chapter 2), and project evaluation and prospects (Chapter 6) were added to the dissertation. Some of the information in Chapters 1, 2, and 6 were also presented in the article chapters (Chapters 3, 4, and 5). Hence, similar text and ideas in the chapters and articles do occur. By the time the dissertation was submitted, Chapters 3 and 4 has been published as an original full-length article to *Minerals*, and Chapter 5 was prepared to be submitted as an original full-length article to *Materials and Metallurgical Transactions B*. Numbering in this dissertation has been adopted for subsections, figures, tables, and equations, to ensure uniformity. The references for all the Chapters follow the guidelines set out by the North-West University. All co-authors have granted their permission for the articles to be used in this MSc dissertation and the author consent forms are attached in the next section.

Peer-reviewed articles and the manuscript submitted for publication are listed below:

- J. Davies, D. Paktunc, J.J. Ramos-Hernandez, M. Tangstad, E. Ringdalen, J.P. Beukes, D.G. Bessarabov, S.P. du Preez. The use of hydrogen as a potential reductant in the chromite smelting industry, *Minerals* 2022, 12, 534, doi:<https://doi.org/10.3390/min12050534>
- J. Davies, M. Tangstad, E. Ringdalen, J.P. Beukes, D.G. Bessarabov, S.P. du Preez. The effect of pre-oxidation on the reducibility of chromite using hydrogen: A preliminary study. *Minerals* 2022, 12, 911, doi:<https://doi.org/10.3390/min12070911>.
- J. Davies, M. Tangstad, T. L. Schanche, S.P. du Preez. Pre-reduction of United Manganese of Kalahari ore in CO/CO₂, H₂, and H₂/H₂O gas atmospheres, submitted to *Metallurgical and Materials Transactions B* 2022

Conference presentations related to this MSc dissertation are listed below:

- J. Davies, S.P. du Preez. The use of hydrogen as a chromite reductant. E-Book of abstracts: HYPOTHESIS XVI, November 8–10, 2021, Online. p. 50–51. Available at: <https://www.hypothesis.ws/index.php/my-menu/download/summary/33-hypothesis-xvi/878-book-of-abstracts> (accessed on 25/05/2022)
- J. Davies. Pre-reduction of United Manganese of Kalahari ore in CO/CO₂, H₂, and H₂/H₂O gas atmospheres. NTNU/SINTEF webinar series in Metal production, April 22, 2022.
- J. Davies. Pre-reduction of United Manganese of Kalahari ore in CO/CO₂, H₂, and H₂/H₂O gas atmospheres. SFI Metal Production Spring meeting at NTNU. April 26, 2022.

STATEMENT BY CO-AUTHORS

This section summarises the statements of consent from the co-authors of the below-mentioned journal articles (published or as to be published), that Jamey Davies may submit these articles as chapters in her dissertation, towards the fulfilment of the requirements for the degree *Master of Science in Chemistry*.

- J. Davies, D. Paktunc, J.J. Ramos-Hernandez, M. Tangstad, E. Ringdalen, J.P. Beukes, D.G. Bessarabov, S.P. du Preez. The use of hydrogen as a potential reductant in the chromite smelting industry, *Minerals* 2022, 12, 534, doi:<https://doi.org/10.3390/min12050534>
- J. Davies, M. Tangstad, E. Ringdalen, J.P. Beukes, D.G. Bessarabov, S.P. du Preez. The effect of pre-oxidation on the reducibility of chromite using hydrogen: A preliminary study. *Minerals* 2022, 12, 911, doi:<https://doi.org/10.3390/min12070911>.
- J. Davies, M. Tangstad, T. L. Schanche, S.P. du Preez. Pre-reduction of United Manganese of Kalahari ore in CO/CO₂, H₂, and H₂/H₂O gas atmospheres, submitted to *Metallurgical and Materials Transactions B* 2022

I, Prof. Merete Tangstad, hereby grant Jamey Davies permission to submit the above-mentioned journal articles, of which I was a co-author, as chapters towards her Master's dissertation.

Prof. Merete Tangstad



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ABSTRACT

Both the smelting of chromite and manganese (Mn) ores consume a significant amount of carbon (C) and electrical energy. The smelting processes contribute to the elevation of carbon dioxide (CO₂) emissions in the atmosphere as stable metal oxides are reduced to their metallic states via the removal of oxide atoms via a carbothermic reaction. The incorporation of hydrogen as a reductant during the smelting process will not only reduce the C footprint but may also contribute to lowering material and energy consumption during smelting procedures. This dissertation presents the use of hydrogen as a reductant during the reduction of chromite and Mn-ore.

The effect of hydrogen as a reductant on the reducibility of chromite was investigated in Chapter 3. Also, thermodynamic modelling, the influence of time, and particle size on the reduction of chromite by hydrogen were studied. The chromite was reduced with pure hydrogen at 750 mL/min flowrate at 1100 °C for 30 min. It was determined that at the experimental conditions the iron (Fe)-oxide constituency in chromite could be metalized and removed with hot-acid leaching, while the chrome (Cr)-oxide constituency did not undergo metallization. However, the removal of Fe leads to the formation of eskolaite-type phase ((Cr_{1.4}Al_{10.6})O₃) which may be unfavorable for the reducibility of chromite. As the reduction time increased the %Fe metallization increased near-linearly. Also, the particle size had a noticeable effect on the %Fe and Cr metallization.

Chapter 3 showed that the Fe-oxide constituency of chromite could be metalized by hydrogen with relative ease. In Chapter 4, several techniques were employed to optimize the %Fe metallization during chromite reduction with hydrogen at 1100 °C. The effect of hydrogen availability was explored. The results revealed that an increase in hydrogen flowrate significantly improved the %Fe metallization, while Cr metallization remained relatively unchanged (and close to 0%). Furthermore, chromite was pre-oxidized, which altered the

structure of the chromite spinel, before reduction using hydrogen. This alteration improved the reactivity of chromite with hydrogen. Also, the effects of pre-oxidation and reduction time, and chromite particle size were investigated. By pre-oxidizing the chromite before being subjected to hydrogen, the reduction time could be reduced from 180 to 60 min, while maintaining similar levels of Fe-metallization. For instance, unoxidized ore reduced for 180 min achieved a Fe metallization of 92.1%, whereas chromite pre-oxidized for 60 min and reduced for 60 min reached 77.5% Fe metallization. An increase in pre-oxidation time from 60 to 240 min had no significant impact on the reducibility of chromite using hydrogen. However, an increase in Fe metallization was observed with a decrease in particle size. A similar observation was made for Cr metallization; however, Cr metallization did not exceed 2.0 % (which was significantly lower than Fe metallization).

The influence of hydrogen on the degree and rate of pre-reduction in Mn-ore was investigated in Chapter 5. The Mn-ore was treated using three atmospheres, i.e., 100% H₂, 70% H₂ 30% H₂O, and 70% CO 30% CO₂ at 4 L/min during the isothermal pre-reduction process performed at 700, 800, and 900 °C. A thermogravimetric (TG) furnace (furnace coupled with a TG analyzer) was employed for the pre-reduction of the ore. The weight loss and off-gas composition were measured and quantified. The results revealed that the utilization of hydrogen significantly increased the degree and rate of pre-reduction and carbonate decomposition. Furthermore, the utilization of 100% H₂ allowed the Fe-oxides to completely reduce to metallic Fe. The metallization of the Fe-oxide was shown to be thermodynamically and kinetically possible. The study also showed that the utilization of hydrogen as a reductant did not affect the decrepitation and porosity of United Manganese of Kalahari (UMK) ore after the pre-reduction process.

Key words: Chromite, manganese ore, hydrogen, pre-reduction, ferrochrome, UMK ore, metallization, carbonates, decomposition, water vapor, carbon dioxide, carbon monoxide.

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CHAPTER 1: BACKGROUND, MOTIVATION, AND OBJECTIVES

1.1. Project background and motivation

Both chromium (Cr) and Mn are essential constituents of modern-day steels, making the production thereof equally important. For instance, the stainless steel industry consumes the majority of produced Cr (which improves its corrosion resistance),^[1-4] whereas approximately 90% of globally produced Mn is consumed by the steel industry to produce mechanically strong steels.^[5-7]

Cr is a multipurpose element that is used in several modern industries, e.g., metallurgical, chemical, and refractory.^[2] In modern-day society, Cr is a crucial component in many alloys, mainly stainless steel. The inclusion of Cr in steel alloys increases the corrosion resistance of the alloy, with surface chemistry often pacified by a Cr-rich oxide layer. The extent of corrosion resistance may be adjusted by controlling the chemical composition of the bulk material, the thickness of the passivation layer, and/or by modifying the morphology of the layer either electrochemically, through thermal treatment, or by passivation using nitric acid (HNO₃).^[8,9]

Mn is included in the steel industry as a steel constituent mainly as a ferroalloy, while approximately 3% of all Mn is used in aluminium alloys.^[7,10] On average 7.5 kg Mn/ton of steel is required.^[7] Therefore, Mn production has to match the ever-increasing steel requirements. Mn is responsible for lowering the brittleness while enhancing the strength, corrosion, hardness, and abrasion resistance of steel.^[5,7,10] Mn also contributes to the efficiency of the smelting process, while stabilizing the chemical conditions in the melt.^[10] Furthermore, stainless steel accounts for approximately 2% of the globally produced steel, mainly utilizing Cr and nickel as alloying elements. The addition of 4 – 16% of Mn can partially or entirely replace the Ni content of stainless steel.^[7]

During both Cr and Mn production processes, the only new source of Cr and Mn units are chromite and a relatively wide variety of Mn-ores, respectively. For Mn-ores, the composition of the ores may differ, specifically the oxidation state of Mn and the percentage of carbonates it contains.^[7] However, their subsequent smelting procedures remain similar. Approximately 1.6 MWh of energy is required to produce 1 ton of liquid Mn-alloy (76% Mn, 17.5% Fe, 6.5% C) at 1400 °C from MnO, FeO and C.^[11] In both cases, the ores have to be smelted via energy-intensive carbothermic processes. Both ores are mainly smelted in electrical submerged arc furnaces (SAFs). A significant amount of C is consumed to reduce the stable metal oxides to their metallic states and by doing so, large quantities of C are released to the atmosphere in the form of carbon dioxide (CO₂).^[2,7,12]

Considering this, there is a need to investigate alternative processes that either (but ideally) consume less energy or have a smaller C footprint.^[13] For this reason, this dissertation investigated the incorporation of hydrogen as a chromite and Mn-ore reductant to reduce energy and C consumption during smelting procedures. It was considered that a pre-smelting step would be the most feasible approach, considering the high temperatures associated with chromite and Mn-ore smelting. More so, preliminary thermodynamic calculations showed that Cr³⁺, in its oxide form, is not readily reduced by hydrogen, while it promotes the Fe reduction inside the chromite (Section 3.4.1). Furthermore, according to thermodynamics the higher Fe- and Mn-oxides will reduce to their lower oxides in a hydrogen atmosphere.

1.2. Problem statement

Limited to no peer-reviewed literature is available on the use of hydrogen as a reductant during chromite and Mn-ore smelting. As far as the authors could assess, the majority of work is done on C-based reduction (both solid and gaseous C sources), and in cases where hydrogen forms part of an investigation, it is typically included to evaluate the effects thereof on non-smelting properties (pre-treatment process) and as a co-reductant (in addition to a C-based

reductant). For instance, Qayyum and Reeve (1976) investigated the pre-reduction of chromite in methane (CH_4)-hydrogen gas mixtures.^[14] A CH_4 -hydrogen gas mixture was also used to explore the behavior of the pre-reduction of Cr-oxide (Cr_2O_3).^[15] Jozwiak et al. (2007) investigated the reduction of Fe-oxides in hydrogen and CO atmospheres.^[16] But none of these studies considered the pre-reduction of chromite in a pure hydrogen atmosphere.

Some studies incorporated hydrogen into the gas mixture for the pre-reduction of Mn-ore but none of these studies used 100% hydrogen as a reductant. More so, no studies (as far as the candidate could assess) have been performed on using UMK (South Africa) ore as the case study ore; though, other Mn-ores such as Comilog (Gabon), Nchwaning (also known as Assmang, South Africa), and Mamatwan (South Africa) ore have been evaluated. For instance, Bhalla and Eric (2015) used CH_4 as the reducing gas during the pre-reduction of Mamatwan ore.^[17] Ngoy et al. (2020)^[18] and Schanche and Tangstad (2021)^[19] incorporated different amounts of hydrogen in a CO/CO_2 gas mixture for the pre-reduction of Mn-ores (Comilog and Nchwaning), and Larssen and Tangstad (2022) introduced hydrogen and water vapor to the CO/CO_2 gas mixture to investigate the potential effect of moisture on the pre-reduction kinetics of Comilog and Nchwaning ore.^[20] Therefore, it was decided to pre-reduce chromite and UMK ore with 70% and/or 100% hydrogen to evaluate the influence of hydrogen on the pre-reduction of chromite and UMK ore without the influence of other reductants such as C and CO. A 70% H_2 30% H_2O atmosphere was considered as this atmosphere had a comparable partial O_2 ($p\text{O}_2$) pressure to the reference 70% CO 30% CO_2 atmosphere.

1.3. Project objectives

The main objective of this study is to investigate the potential of hydrogen as a reductant during the solid-state reduction of chromite and Mn-ore. The following detailed objectives are listed as follows, and are presented as chromite- and Mn-related objectives:

Chromite-ore-related objectives:

- 1) Perform fundamental thermodynamic calculations to better understand the aspects that govern the behavior of the chemical species partaking in the reaction,
- 2) Determine the effect of reduction parameters on the extent of Fe and Cr metallization in chromite,
- 3) Evaluate the effect of pre-oxidation of chromite on its reducibility by hydrogen.

Mn-ore-related objectives:

- 4) Investigate the effect of temperature and hydrogen as a reductant on the degree and rate of pre-reduction in UMK ore,
- 5) Evaluate the total CO₂ formation from carbonate decomposition when 100% H₂ and 70% H₂ 30% H₂O gas atmospheres are used as reductants during the pre-reduction of UMK ore,
- 6) Evaluate the decrepitation and porosity of UMK ore after pre-reduction at different temperatures in three different gas atmospheres.

1.4. Dissertation outline

This dissertation comprises of six chapters. An overview of each chapter is given below.

Chapter 1 gives an overview of the chromite and Mn-ore smelting industry, and subsequently gives a detailed explanation of the motivation behind the utilization of hydrogen as a reductant during the pre-reduction of chromite and UMK ore. The project background and motivation for the study are given in Section 1.1, and the problem statement is presented in

Section 1.2. The project objectives are addressed in Section 1.3. The chapter concludes with a dissertation outline in Section 1.4.

Chapter 2 provides a review of the literature applicable to the topic of the dissertation. It consists of the following sections: General information on Cr (Section 2.1), South Africa's FeCr industry (Section 2.2), previous studies on the pre-reduction of chromite ore (Section 2.3), main processes and techniques (Section 2.4), foundational aspects of chromite reduction using carbon (Section 2.5), parameters affecting chromite's pre-reduction (Section 2.6), effect of oxidation on the reducibility of chromite ore (Section 2.7), Mn-ore (Section 2.8), previous studies on Mn-ores (Section 2.9).

Chapter 3 presents an experimental chapter, published as a full-length scientific article. The chapter shows how hydrogen is used as a chromite reductant. It explains thermodynamically and kinetically how hydrogen facilitates the reduction of the Fe-oxide constituent of chromite, while the Cr-oxide constituent remains relatively unaffected. Some of the Fe-oxides were reduced to metallic Fe and subsequently removed by hot-acid leaching. Subsequently, the Fe contents were determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). The chapter also shows what influence time and particle size have on the reducibility of chromite. Scanning electron microscopy (SEM) and energy dispersive x-ray spectrometer (EDX) were used to gain insight into the mobility of the various chromite constituents, mainly Fe. X-ray powder diffraction (XRD) analysis was used to determine the mineralogical changes occurring within the chromite spinel during reduction, and quantitative Rietveld refined XRD analysis was performed on as-received, treated, and leached chromite particles.

Chapter 4 presents an experimental chapter, prepared as a full-length scientific article. This chapter was mainly dedicated to exploring the effect of pre-oxidation on the reducibility of chromite by hydrogen. Chromite was pre-oxidized at 1100 °C for 60 min and subsequently

reduced in hydrogen at 1100 °C for 60 min. It was determined in Chapter 3 that hydrogen facilitates the metallization of the Fe-oxide constituency of chromite. However, pre-oxidation was incorporated to determine if the Fe-constituency could be metalized under milder conditions when compared to unoxidized ore, as well as to determine if Cr-oxide was affected (i.e., if any Cr-oxide metallization occurred). The formed metallic Fe was removed through hot acid leaching and the Fe contents were determined using ICP-OES. Also, the effect of hydrogen flow rate on the reducibility of chromite was investigated by reducing samples at a hydrogen flow rate of 150 and 750 ml/min. SEM equipped with EDX was used to determine the surface and subsurface characterization of unreduced, reduced, and pre-oxidized/reduced chromite particles in backscattered and secondary electron mode. The crystalline phase analysis of bulk samples was determined by XRD analysis. In addition, the effect of reduction time, pre-oxidation time, and temperature were investigated.

Chapter 5 presents an experimental chapter, prepared as a full-length scientific article. This chapter describes the pre-reduction of UMK ore in CO/CO₂, H₂, and H₂/H₂O gas atmospheres. A TG furnace was used to investigate the solid-gas pre-reduction reactions of UMK ore (9.5 – 16 mm) in three different gas atmospheres, i.e., 70% CO 30% CO₂, 70% H₂O 30% H₂, and 100% H₂ at three target temperatures, i.e., 700, 800, and 900 °C. Factsage and HSC chemistry 10 thermodynamic programs were used for the calculation of stability diagrams (Fe-O and Mn-O) and pO₂ pressure (for each gas atmosphere), respectively. HSC Chemistry 10 was also used to calculate the stability diagram of selected carbonates. Chemical analysis was performed on raw and pre-reduced ores by X-ray fluorescence (Bruker AXS S4 Pioneer X-Ray fluorescence spectrometer) using the fused bead technique. The excess oxygen was measured with permanganometric titration, and the C concentration was analyzed with a LECO (Combustion-IR) instrument. The loss on ignition (LOI) was thermogravimetrically measured to a stable weight at 950 °C in air. XRD analysis was

performed to determine which elements were still present inside the pre-reduced ore. Electron probe microanalysis (EPMA), SEM, and EDS were used to determine any difference in microstructure between the samples reduced in different gas atmospheres. Porosity measurements were also performed on raw ore and pre-reduced samples by the ratio between the absolute and apparent density. In addition, the decrepitation of the reduced samples was measured after the experiments by sieving the charge through a sieving stack consisting of 9.5, 6.7, 4.75, 3.15, 1.6, and <0.5 mm sieves.

Chapter 6 presents the conclusions of this study, based on the results described in Chapters 3 – 5, and concerning the study objectives presented in Section 1.3. The dissertation concludes with mention of some implications for practical applications and then recommendations for possible future research.

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CHAPTER 2: LITERATURE SURVEY

The literature study presented in this dissertation focused on the two ore-types, i.e., chromite and Mn-ore. Though these ores differ significantly from each other, the smelting procedure used to produce FeCr and ferromanganese (FeMn) is relatively similar. Nevertheless, the ores were presented and discussed separately. Considering that Chapters 3 and 4 presented experimental chapters on chromite, and only Chapter 5 on Mn-ores, a larger part of Chapter 2 was dedicated to chromite when compared to Mn-related literature. More so, chromite involves various pre-smelting procedures that are not used by the FeMn industry, which was included in this dissertation. In addition to this, the use of hydrogen as a reductant was discussed where relevant for each of the ore types.

2.1. General information on Cr

In 1766 Johann Gotlob Lehmann described and analyzed a new mineral, crocoite from the Beresof mine in Siberia, for the first time.^[1,2] This bright red-orange mineral, crocoite (natural lead chromate, PbCrO_4), was found to be the first Cr-containing compound.^[1] The French chemist, Louis Vauquelin and L.C.H. Macquart concluded that crocoite contained lead oxide, aluminum, and about 38% of oxygen.^[1] In 1797 Vauquelin isolated the Cr metal, by reacting crocoite with hydrochloric acid and letting the lead chromate precipitate.^[1,3] Subsequently, charcoal was used to reduce the green solid and upon cooling some metallic needles together with half of the original mass were noted.^[3] This led to Vauquelin discovering that crocoite was combined with an oxide of an unknown metal, now known as Cr.^[3] In the following year (1798), Martin Heinrich Klaproth together with Tobias Lowitz was able to isolate Cr metal from chromite ore as well as Cr-Fe ore deposits.^[1] Thenceforth, chromite was used as the only commercial source of Cr.^[1]

Further investigation was done by the French scientist Henri Moissan who discovered an alloy, which he called ferrochrome (FeCr).^[4] He produced the FeCr via heating Cr-containing ore and Fe in a furnace using C as a reductant.^[4] From here on Cr could be used in steel, however, the large-scale use of Cr was limited until the development of the aluminothermic method in the early 1900s and the utilization of the electric arc furnace that can smelt chromite ore into FeCr.^[1,3] The development of stainless steel created the true significance of Cr.^[3] Harry Brearley accidentally discovered the first stainless steel in 1913.^[3,5]

Cr has several different oxidation states, ranging from -2 to +6, of which the most stable oxidation state is +3 (Cr^{3+}).^[3,5] Out of the twenty-six known isotopes of Cr, there exist four natural isotopes: ^{50}Cr (4.3%), ^{52}Cr (83.8%), ^{53}Cr (9.6%), and ^{54}Cr (2.4%).^[3,5] Of these natural isotopes ^{50}Cr is radioactive and has a long half-life of 1.8×10^{17} years.^[5] Chromite is the primary economically exploitable source of new Cr units,^[6-8] which formed through solidification of lava or magma (relatively high in Fe-rich pyroxene and olivine minerals) involving volcanic or plutonic processes, meaning it is of igneous origin.^[1,3] Chromite primarily occurs in mafic and ultramafic rocks as crystal amasses through magmatic crystallization.^[3] A relatively significant fraction of viable global chromite ore reserves, estimated at approximately 70%, is located in South Africa's Bushveld Igneous Complex (BIC).^[9]

Pure chromite has a composition of AOB_2O_3 , where A is the divalent cation that can be Fe^{2+} or Mg^{2+} and B is the trivalent cation that can be Fe^{3+} , Cr^{3+} , or Al^{3+} , but is typically given as FeCr_2O_4 (considering that non-Fe and -Cr elements are viewed as unwanted elements). Chromite belongs to the spinel group and its space group is $\text{Fd}3\text{m}$.^[10] Naturally occurring chromite is characterized by the interchange between Fe^{2+} and Mg^{2+} , as well as between Cr^{3+} , Al^{3+} , and Fe^{3+} , with the following universal formula: $(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al}, \text{Fe}^{3+})_2\text{O}_4$.^[11-13] The spinel chromite structure belongs to the cubic system and is shown in Figure 2-1, where there

are 32 oxygen atoms assembled in the central plane of the cubic structure, leading to the formation of 64 tetrahedral gaps and 32 octahedral gaps. In the classic chromite spinel, among these cavities, eight of the tetrahedral sites are occupied by Fe^{2+} and sixteen of the octahedral sites are occupied by Cr^{3+} .^[14]

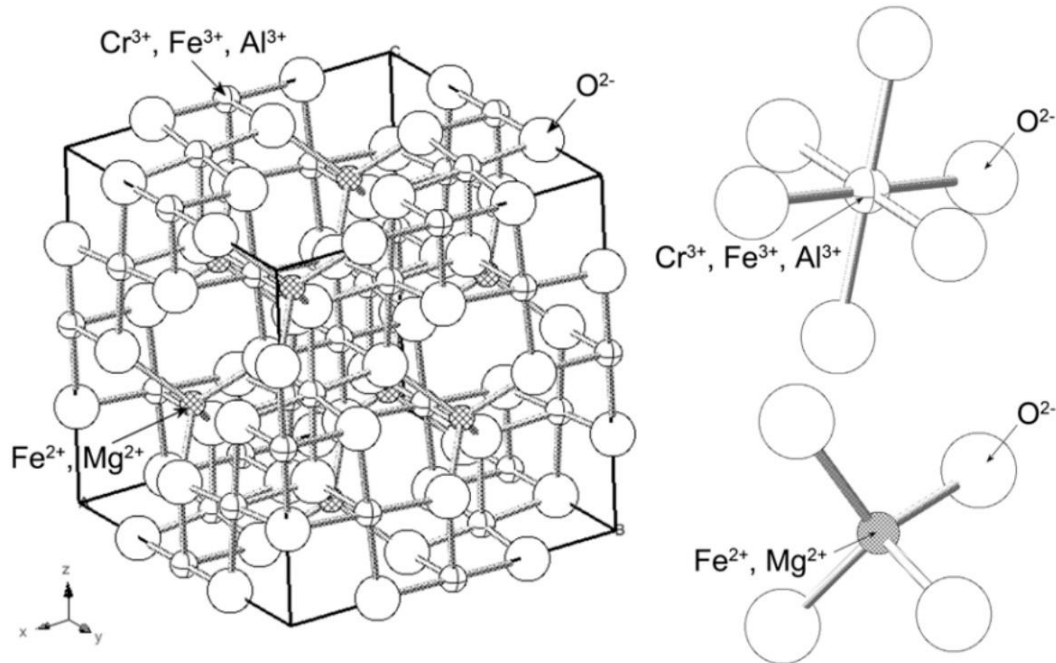


Figure 2-1 A graphic representation of the compact spinel lattice structure of chromite.^[14]

The dissimilarities in the chemical composition of chromite, e.g., amounts of tetrahedral occupying Mg^{2+} and octahedral occupying Al^{3+} , Cr/Fe ratio, influence the relative ease of metallization/reduction of chromite.^[15] For instance, the reducibility of the spinel will increase when Al^{3+} is substituted by Fe^{3+} in the octahedral sites, and when Mg^{2+} is substituted by Fe^{2+} in the tetrahedral sites.^[15] The presence of Mg^{2+} and Al^{3+} adversely affects the reducibility; Canaguier (2018) found that an Mg-containing chromite spinel, i.e., $(\text{Fe}^{2+}, \text{Mg}^{2+})\text{Cr}_2\text{O}_4$, had greater resistance to reduction when compared to an Al-containing spinel, i.e., $\text{Fe}(\text{Cr}^{3+}, \text{Al}^{3+})_2\text{O}_4$.^[16] Chromite's relative resistance towards reduction can be determined by its refractory index expressed in Equation 2-1:^[15]

$$\text{Refractory index} = \frac{\text{wt.\% Cr}_2\text{O}_3 + \text{MgO} + \text{Al}_2\text{O}_3}{(\text{Fe}_{\text{total as FeO}}) + \text{SiO}_2} \quad (\text{Equation 2-1})$$

The three main geological settings where chromite deposits are found: (i) stratiform-type deposits account for more than 90% of the recognized Cr ore resources found in the BIC in South Africa, the Great Dyke in Zimbabwe, and the Kemi intrusion of Finland, (ii) podiform-type or alpine-type deposits are responsible for about 10% of the world's Cr ore resources found in the island arcs and the major tectonic belts (Appalachian Mountain, Tethyan mountain chains, and the Ural Mountains), and (iii) lateritic (placer) deposits formed through the weathering of Cr-bearing peridotites. However, the utilization of this deposit is not known to be profitable.^[1,17]

2.2. South Africa's FeCr industry

2.2.1. Production history of FeCr

Before 1973 the U.S.A., Western Europe, and Japan imported the required quantities of chromite ores from developing countries (i.e., Zimbabwe, South Africa, and Brazil). The imported chromite ore was smelted and FeCr alloys were generated for the various metallurgical industries.^[18] In Scandinavian countries and Canada, hydroelectric energy was relatively readily accessible for smelting chromite ores.^[18]

After 1973 the situation in which the developed countries produced FeCr changed. The price of oil escalated, the promulgation of stringent regulations about atmospheric pollution control increased in developed countries, and the search for laborers that are willing to work in a dirty and hazardous industry was difficult.^[18] As a result, developing countries initiated the export of FeCr alloys to the developed countries, where previously only chromite ores were exported.^[18] The reason is that regulations governing atmospheric pollution were usually not so strict in developing countries as they were in developed countries, and the local labor in developing countries is more accessible than in developed countries.^[18]

Of the globally mined chromite, approximately 90% to 95% is utilized for the production of several grades of FeCr.^[8,19,20] The four grades of FeCr are low C (0.015 – 1% C, 56 – 70% Cr), intermediate C (1 – 4% C, 56 – 70% Cr), high C (4 – 6% C, >60% Cr) and charge (6 – 8% C, 50 – 60% Cr) FeCr.^[21] FeCr is a crude alloy produced through the energy-intensive carbothermic smelting of chromite.^[19,20] FeCr mainly consists of Fe and Cr (50 – 70%) with smaller amounts of C (0.02 – 9%) and silicon (0.6 – 6%).^[19,22] The amount of C and silicon present in the FeCr is dependent on the grade or type of alloy and impurities such as sulfur, phosphorous, and titanium.^[22]

About 80% to 90% of FeCr (consisting of approximately 45 – 80% Cr)^[19] is mainly used as the Cr-source during the production of stainless steel, with a Cr content ranging between 12 – 30%.^[19] The notable growth in stainless steel demand, which was estimated at 10.6% (56.3 million tons) in 2021^[23], is due to its wide range of applications which in turn expedites the importance of its precursor, i.e., FeCr.^[7,24] FeCr is primarily produced in several different types of furnaces such as semi-closed SAFs, closed SAFs, and closed direct current (DC) arc furnaces.^[12,19]

The smelting of chromite is a highly endothermic reaction and requires a constant temperature of >1440 °C. The smelting of chromite is however determined by the furnace type used, the smelting regime of the specific furnace, and the furnace charge.^[22] In addition, elevated temperatures are required to separate the metallic and slag phases in their liqueous states.^[25,26] The chromite smelting process has two distinctive disadvantages. It requires high energy consumption (up to approximately 4.6 MWh/ton of FeCr produced, depending on furnace type and smelting regime employed), and causation of greenhouse gas emissions (1 ton of CO₂ per ton of FeCr produced).^[27,28]

The low historical cost of electricity together with the large amounts of chromite ore available in South Africa contributed to the country's leading role in FeCr production,

accounting for 33% of the 4.8 million tonnes of FeCr produced globally in 2012.^[29] However, the electricity shortages, poor transportation infrastructure, and higher production costs caused South Africa to lose its leading position to China in 2013.^[29,30] Figure 2-2 shows how FeCr production increased in China from 2010 to 2012 while it decreased in South Africa. Nevertheless, South Africa will remain a significant producer of FeCr as these two countries account for more than two-thirds of the total FeCr production globally. In 2017 the global production of FeCr was estimated to be 11.7 million tonnes^[31,32] and that it would increase by approximately 3.6% every year due to the growing necessity of FeCr.^[31,32]

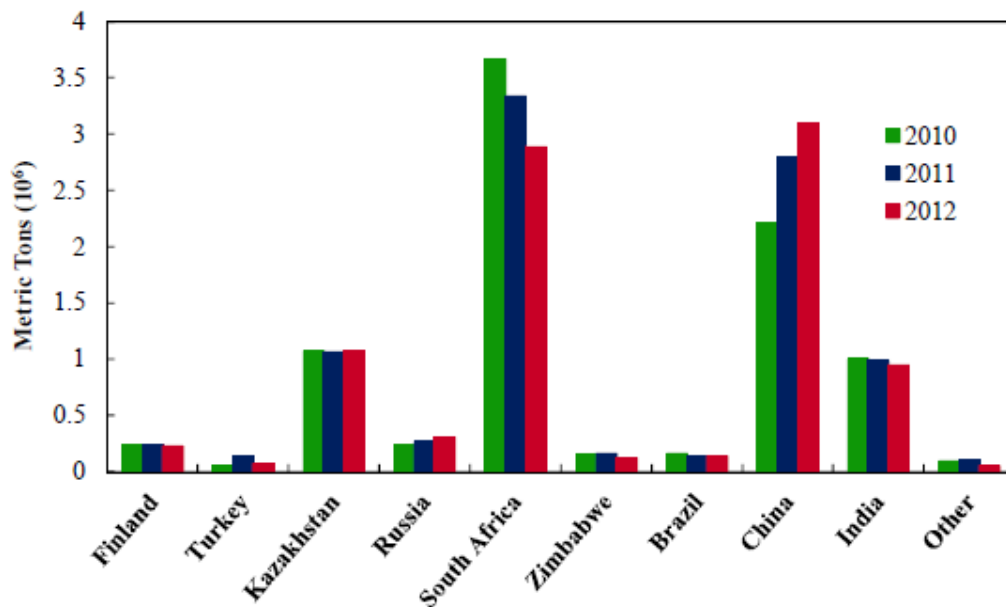


Figure 2-2 The global high C charge grade FeCr production for 2010 to 2012.^[33,34] The image was reused, without alterations, from <http://hdl.handle.net/10394/12084> (date of access: 07/07/2022).

2.2.2. Economic and market considerations

Although most of this study is technically orientated, a section on the economic and market considerations of the South African FeCr industry is discussed. South Africa contains the world's largest chromite reserves. The majority of South Africa's chromite reserves occur

in the northern part of South Africa, in the BIC.^[9,18] Figure 2-3 graphically presents the expansion of the BIC as well as the locations of FeCr smelters.

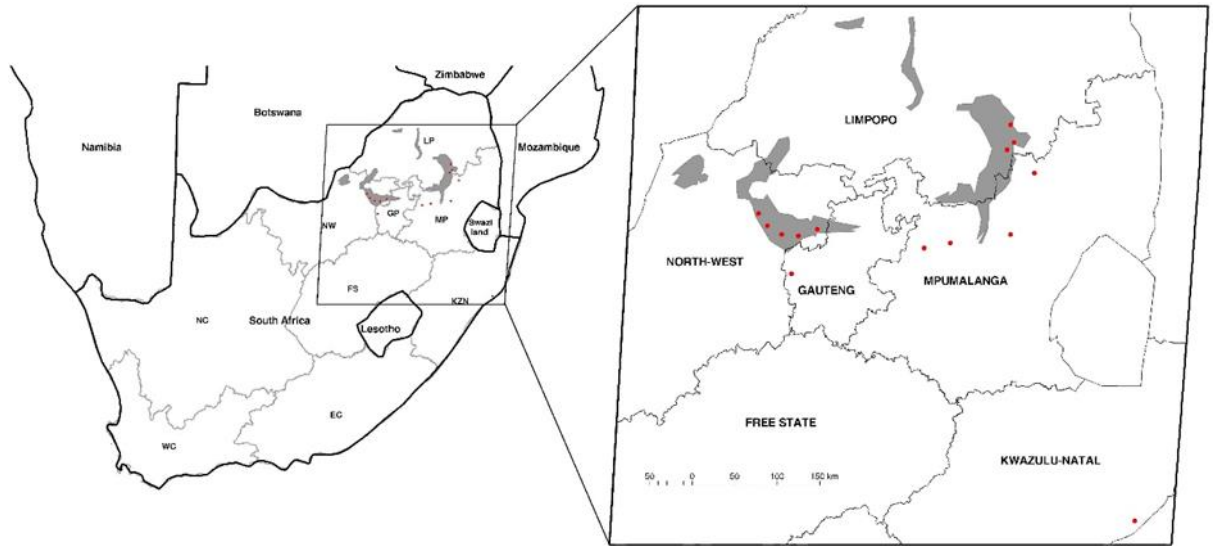


Figure 2-3 A graphical illustration of the extent of the BIC (grey areas) and the positioning of FeCr smelters in South Africa (red dots). Google Earth was used to determine the location of the various FeCr smelters, and the map was compiled with Matlab.^[35]

The BIC is a saucer-like, layered igneous mass and stretches for about 400 km from the east to the west as well as from north to south of South Africa.^[18] The BIC is the largest example of a stratiform type chromite deposit.^[36] The BIC accommodates several seams that are of economic interest, such as the Lower Group 6 (LG6), the Middle Group 1 and 2 (MG1 and 2), and the Upper Group 2 (UG2) seams.^[36] LG and MG seams are usually mined for their Cr content, while the UG2 seam is primarily exploited as a source of platinum group metals (PGM's) containing minerals.^[36] To remove PGMs from the UG2 ore generally involves the liberation of the PGM-based sulfide through milling, followed by the recovery of the PGM concentrate via flotation.^[36] The PGM concentrate contains undesirable chromite, for this reason, the PGM recovery circuits are specifically designed to ensure that the chromite gets rejected to the tailings stream.^[36] The chromite in the PGM tailings can be utilized as feedstock for FeCr manufacturing, after beneficiation to increase the Cr content.^[36] Each seam has its

own Cr/Fe ratio: The LG6 seam has a Cr/Fe ratio of 1.5 to 2.0, MG1 and MG2 seams have ratios of 1.5 to 1.8, and the UG2 seam has a ratio of 1.3 to 1.4.^[37]

The total chromite ore imports from South Africa to the Chinese market have risen from 36% to 70% in the years 2010 to 2016, respectively. South Africa was the primary producer of FeCr in the world, while after 2012, China was known as the leading FeCr and stainless steel producing country in the world.^[38,39]

Currently, the FeCr producers in South Africa are facing several challenges such as increasing electricity costs, lower selling prices due to the high import rates of chromite by China, a decline in beneficiation of FeCr in South Africa, and elevated labor costs.^[39] These challenges show that the current FeCr smelting technologies used in South Africa will likely not be able to sustain the local FeCr industry for the coming thirty years.

The most popular processing technologies currently used by South African FeCr producers include the Outotec process, the Premus process (used by Glencore Alloys), conventional furnaces (semi-closed SAFs, used by Glencore and Samancor), and DC arc furnace (used by Samancor and Mogale Alloys). These processes are discussed in detail in Section 2.4.2. All these production technologies require different energy supplies and reductant consumption. The DC arc and Premus furnaces utilize fewer reductants when compared to the other smelting regimes, while also operating more efficiently. Higher capital input is however required in both cases.^[40,41]

The market share of FeCr production in China increased from 5% in 2001 to 25% in 2010 while South Africa decreased from 50% to 42% in the same period. The market share of South African FeCr further decreased to 36% in 2011, while China increased by 5% to achieve a market share of 30%.^[40] Ferrochrome smelters created more job opportunities per ton exported than chromite mines. Furthermore, it is expected that if the beneficiation of FeCr stopped, South Africa's gross domestic product (GDP) may be negatively impacted.^[40]

2.3. Foundational aspects of chromite reduction using carbon.

Considering the idea of using hydrogen as a reductant (and very likely the use thereof during pre-reduction procedures), one has to understand what is meant by the term pre-reduction (also referred to as the solid-state reduction of chromite) in terms of FeCr production. Two terms are generally used to express the extent of Fe and Cr reduction – either in terms of lowering the oxidation state (e.g. Fe_2O_3 (Fe^{3+}) reduced to FeO (Fe^{2+})) or metallization (e.g. Cr_2O_3 reduced to Cr^0).^[42] Barnes et al. (1983) defined “degree of reduction” and “metallization” as the following:^[42]

Reduction (R) can be associated with the removal of oxygen and is defined in terms of the oxygen mass loss expressed in Equation 2-2:^[42]

$$\%R = \frac{\text{Mass of oxygen removed}}{\text{Original removable oxygen}} \times 100 \quad (\text{Equation 2-2})$$

In this case, where solid C is used as a reductant, CO will form as a product and for this reason, the reduction can also be described as:

$$\%R = \frac{\text{Mass of CO evolved}}{28/16 \times \text{original removable oxygen}} \times 100 \quad (\text{Equation 2-3})$$

The extent of metallization (M), is defined by Barnes et al. (1983) as:^[42]

$$\%M = \frac{\text{Cr}^0 \text{ and Fe}^0}{\text{Cr}_{\text{tot}} + \text{Fe}_{\text{tot}}} \times 100 \quad (\text{Equation 2-4})$$

Where Cr^0 and Fe^0 are the total amounts of metalized Cr and Fe, and Cr_{tot} and Fe_{tot} are the total Cr and Fe contents of the respective chromite. Furthermore, Barnes et al. (1983) proposed that there is no linear relationship between reduction and metallization due to the reduction of Fe_2O_3 to FeO , metallization of FeO to Fe , and Cr_2O_3 to Cr which happens simultaneously.^[42] However, there is a close similarity between the complete removal of oxygen and complete metallization, as 100% reduction corresponds to 100% metallization.^[42]

Algie and Finn (1984) explained the three stages of chromite reduction as follows: at first, the Fe^{3+} is reduced to Fe^{2+} , followed by the reduction of Fe^{2+} to metallic Fe. After

approximately 50% of the Fe was metalized, Cr^{3+} was metalized to Cr^0 . After the Fe reduction was complete, 60% Cr reduction was achieved.^[43,44]

Soykan et al. (1991) also proposed a reduction mechanism of chromite as well as the subsequent formation of Cr- and Fe-carbides during carbothermic smelting. The reduction mechanism proceeds as follows:^[37] at the surface of the chromite particle the Fe^{2+} is metalized to Fe, the Cr^{2+} ions migrate from the outer phase to the transition phase (between the inner and outer phase) via solid-state diffusion, at the transition phase the Fe^{3+} ions reduce to Fe^{2+} ions according to the following reaction:^[37]



The round and square brackets refer to the tetrahedral and octahedral sites of the spinel lattice, respectively. Furthermore, the generated Fe^{2+} ions migrate from the transition phase to the surface of the particle. After the Fe is completely reduced, the remaining Cr^{2+} and Cr^{3+} ions are reduced to metallic Cr, creating a Fe-and Cr depleted spinel of MgAl_2O_4 .^[37]

The use of C as a reductant during chromite smelting is well understood, hence more detailed expressions have been developed. However, in the current study the %Fe and Cr metallization was of significance and expressed individually according to Equation 2-5:

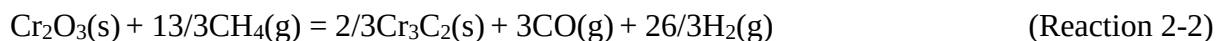
$$\% \text{Fe and Cr metalization} = \frac{\text{Solubilized Fe and Cr}}{\text{Total Fe and Cr content}} \times 100\% \quad (\text{Equation 2-5})$$

where the metalized Fe and Cr fractions of the reduced chromite (defined as the fractions of leached Cr and Fe, as determined by ICP–OES analysis) are represented by the solubilized Fe or Cr value, which is divided by the total amount of Fe or Cr present in the untreated chromite ore.

2.4. Previous studies on the pre-reduction of chromite ore

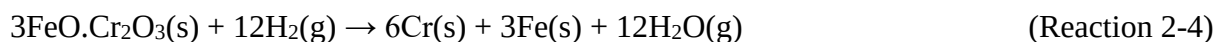
Historically, several different reductants (of which only a few are mentioned in the dissertation) were investigated for the pre-reduction of chromite:

In the utilization of CH₄-hydrogen gas as a reductant, the Fe- and Cr-oxides were converted to carbides.^[45,46] It was found by Read et al. (1974) that CH₄ gas was the source of C that diffused into the oxide. The overall reduction reaction of Cr-oxide by using CH₄ gas as a reducing agent is given below:^[45,46]

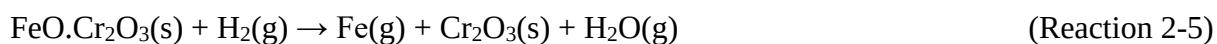


Read et al. established that the reaction rate was independent of the CH₄ partial pressure (range of 0.02 – 0.25 atm) and that the pre-reduction reaction in the presence of CH₄ gas was comparable to the non-isothermal reduction of Cr-oxide by solid C and hydrogen gas in the atmosphere.^[45,46]

Qayyum and Reave (1976) investigated a modified reduction mechanism where the experimental conditions involved high temperatures and CH₄/H₂ ratios, where CH₄ was unstable.^[45,47] The following two reactions were proposed:^[47]



To alleviate some of the C dependence of chromite smelting, the use of hydrogen gas to reduce the Fe-fraction of chromite was suggested. The reduction of pure chromite by hydrogen is expressed by Reaction 2-4 which shows the stoichiometric reaction. In practicality Reaction 2-4 is limited to the reduction of only the Fe fraction as proposed by Boericke and Banger (1945) through Reaction 2-5:^[48]



Reaction 2-5 shows the selective reduction of Fe in pure chromite by hydrogen.^[48] From here Chu and Rahmel (1979) reported that Cr₂O₃ could be reduced by hydrogen above 1027 °C.^[49]

Hydrogen and carbon monoxide (CO) was used as reductants, however, it was found that only Fe-oxides were reduced with this combination.^[45,47] Anacleto and Ostrovski (2004)

state that the temperatures had to be above 1113 °C for the reduction of Cr₂O₃ with hydrogen and CO.^[45]

A recent patent suggested that SiC Composite should be incorporated into the formation of sintered and/or pre-reduced chromite agglomerates (typically briquettes or pellets) as the reductant in the FeCr production process. Pfeiffer and Cookson (2015) showed that incorporating the proposed SiC composite during the pellet curing process initiated the pre-reduction process. The partial pre-reduction during pellet curing can reduce the material and energy dependence during smelting.^[50]

At present, the most common, commercially employed reductant for the pre-reduction of chromite is either in the form of coke or anthracite.^[42] These carbonaceous reductants can reduce the Cr- and Fe-oxide constituency of chromite to their metallic states (Cr and Fe) or their carbide states (Fe₃C and Cr₃C₂).^[51] The following reactions show how the reduction process proceeds when only C is used as the reducing agent:^[42]



According to Reactions 2-5 to 2-7, CO is formed and will be present in significant quantities in the off-gas. Due to the highly toxic nature of CO, the off-gas needs to be oxidized before being released into the atmosphere that further leads to environmental complications.^[19]

2.5. Main processes and techniques

2.5.1. Chromite ore mining and beneficiation

Chromite ore is mainly recovered using underground and open-cast mining, depending on the resources and materials available in that location.^[52] Large amounts of chromite ores are mined and beneficiated via several Cr beneficiation plants worldwide to feed the customized needs of different FeCr smelters.^[17] These mining and refining operations of chromite form

significant amounts of fines, subsequently leading to difficulties regarding handling, storage, and environmental aspects.^[17] It is found that the tailings, generated during chromite ore beneficiation, contain more than 25% of the mineral value (mainly Cr and Fe).^[17] The high demand for FeCr production was the drive behind the recovery of chromite values from the rejected tailings, which in turn forced beneficiation plants to operate optimally.^[7,17,24]

The purpose of the beneficiation operations is to separate and concentrate valuable minerals from waste materials and prepare ore for subsequent refinements.^[17,53] Beneficiation activities (preparation for FeCr smelting), change the mineral values by decreasing (crushing and grinding) the particle size of chromite and/or agglomerating these particles (pelletizing and briquetting). These activities will facilitate upcoming processes or increase the Cr₂O₃ content of specific chromite streams.^[53]

Chromite beneficiation is important for upcoming smelting processes and various beneficiation methods are used, based on the ores' origin and the end-use requirement (pre-reduction or oxidative sintering).^[53] Coarse ore is manually sorted, while fine ore is gravity separated (separation of particles by weight and density). Heavy-media separation (also called sink-and-float separation, based on the density of the particle) is used to separate the lumpy ore that is mixed with the host rock.^[53] Furthermore, chromite minerals are liberated from host rocks through crushing and gravity separation.^[53] A common chromite beneficiation flow chart is represented in Figure 2-4.

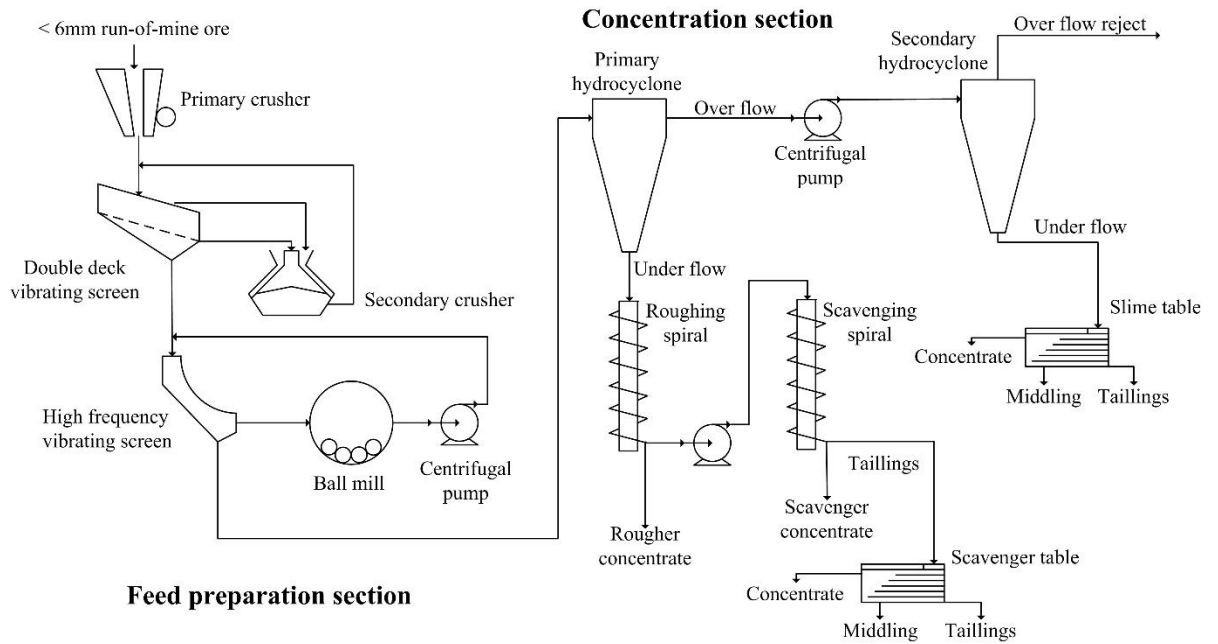


Figure 2-4 General process flow chart for chromite beneficiation process to produce typical metallurgical grade chromite concentrate.^[17]

Figure 2-4 indicates that the beneficiation process is divided into two sections: (i) At the feed preparation section (comminution), the material is prepped for the operations to follow. In this section, the run-of-mine (ROM) chromite ore (defined as ore as-recovered during mining and before further processing) is screened from 75 – 220 mm followed by the crushing process via the primary and secondary crusher and the screening to generate the <3 mm size fraction.^[17] Thereafter the <3 mm, size fraction particles are ground to <1 mm and then beneficiated through the concentration section.^[17] The <1 mm size, upgraded chromite ore is also classified as metallurgical-grade ore and usually contains approximately $\geq 45\%$ of Cr_2O_3 , however, in some cases, lower-grade ore may be produced.^[54] (ii) In the concentration section the <1 mm size fraction is upgraded through conventional gravity techniques, such as the spiral concentrator and shaking table.^[17] Gravity techniques are well established and broadly accepted for the concentration of chromite ore but it becomes inefficient and complex when <75 μm size particles are treated.^[17]

Gravity concentrations is a group of methods that uses density differences between mineral particles to separate and recover desirable mineral particles. Particles with different densities will act uniquely against the forces of gravity depending on the viscosity of the environment, resistance to the motion in a viscous environment, density, weight, particle size, and shape or a pertinent combination of them.^[55] The gravity concentration method operates on 6 – 150 mm size particles, which are considered coarse particles. On the other hand, spirals, jigs, and shaking tables are utilized in the case of finer particles. However, it is difficult to recover finely disseminated ores due to their intrinsic complications.^[17] Therefore, every individual gravity separation technique only performs to its utmost efficiency under specific operating conditions and particle size fractions.^[17]

2.5.2. FeCr production processes

As mentioned earlier, open/semi-closed and closed SAFs and DC arc furnaces are smelting methods employed for the production of FeCr in South Africa.^[56] Figure 2-5 presents the differences between the semi-closed SAF and closed furnaces (such as closed SAFs and DC furnaces).

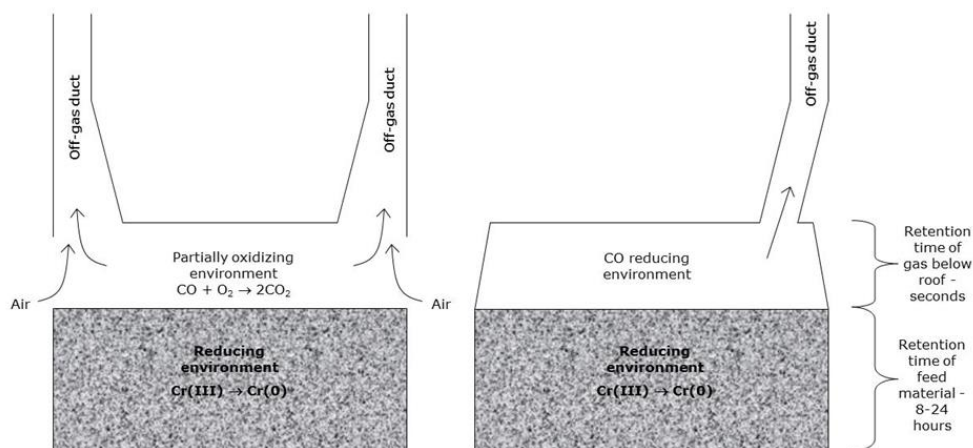


Figure 2-5 Simplified illustration of a semi-closed SAF (left) and a closed SAF (right).^[56]

The terms open/semi-closed and closed indicate how the ambient air enters (or is prevented from entering) the furnaces.^[56] In open/semi-closed furnaces, CO-rich off-gas is

combusted above the furnace bed before being extracted, in comparison to closed furnaces where the CO-rich off-gas is extracted without being combusted.^[56] The significant quantity of highly toxic CO gas present in the off-gas requires oxidation before being released into the atmosphere and is typically flared. Though, in some cases, the CO gas is utilized as a fuel source. A large amount of CO₂ generation poses an environmental concern which is the motivation behind finding a non-carbonaceous reductant to curve C release. Figure 2-6 presents a diagram of the process steps typically used by the South African FeCr industry.^[6]

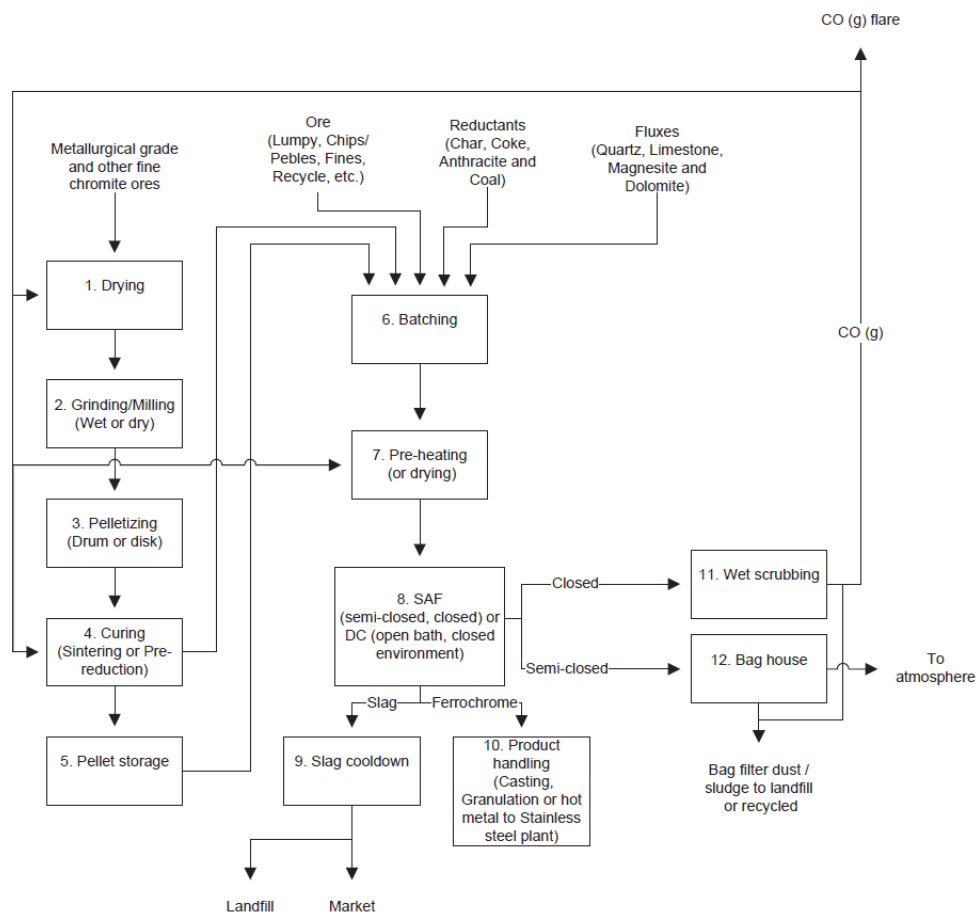


Figure 2-6 A flow diagram adapted by Beukes et al. (2017)^[56] from Riekkola-Vanhanen (1999)^[19] and Beukes et al. (2010)^[6], indicating the most common Process Steps utilized by the South African FeCr industry.

Generally, four relatively well-defined process combinations are utilized by the South African FeCr producers:^[6]

(i) The traditional open/semi-closed SAF operation coupled with bag filter off-gas treatment is the earliest technology used in South Africa for the production of FeCr.^[6,56,57] In this type of operation it is preferred to use coarse chromite ($6 \text{ mm} \leq \text{size} \leq 150 \text{ mm}$), coarse reductants, and fluxes as the coarse nature of the feed material allow generated off-gas (from the smelting process) to freely move through the furnace bed.^[19,56] Sintering of the furnace bed is therefore prevented, eliminating blowouts and bed turnovers.^[19,56] However, it is not impossible to include a small fraction of fines (typically $\leq 6 \text{ mm}$) in open/semi-closed SAFs, it does however increase the risk of bed sintering.^[56] The Process Steps used are 6, 8 – 10, and 12 (Figure 2-6).^[56] In some cases, open/semi-closed SAFs are fed with pelletized chromite (pre-reduced or oxidatively sintered pellets). Hence, Process Steps 1 – 5 may also be included.^[56] The chromite is milled before the pelletization process, increasing the surface area of the chromite particles where the reduction process proceeds during smelting. Furthermore, pelletization is implemented due to the friability of South African chromite ore. Also, the agglomeration in the form of pelletization will enable the formation of a permeable bed that will allow gasses to pass through the chromite particles during smelting.^[56] Open/semi-closed SAFs typically operated on an acid slag with a basicity factor (BF) < 1. Equation 2-6 defines the BF:^[6,56]

$$\text{BF} = \frac{\% \text{CaO} + \% \text{MgO}}{\% \text{SiO}_2} \quad (\text{Equation 2-6})$$

The open/semi-closed SAFs will only temporarily operate with a BF > 1 due to two reasons: (i) to compensate for refractory linings that are in a sub-standard condition, because the liquidus temperature of basic slag is higher than that of acidic slag, or (ii) when the build-up of sulfur in the slag needs to be removed.^[6,56]

(ii) Closed SAFs consuming oxidatively sintered pelletized feed, coarse reductants, and fluxes (known as the Outotec process, applied at Tornio).^[6,56] This SAF is explained by Process Steps 2 – 6, and 8 – 11, with or without 7 in Figure 2-6.^[56] However, this operation technology

is also employed by green and brownfield expansions in South Africa.^[6,56] Usually in green field FeCr operations the pelletizing and sintering sections (Process Steps 3 and 4) are amalgamated with closed SAFs, and wet venturi scrubbing is responsible for off-gas cleaning.^[6,56] When SAFs are fed with oxidatively sintered pellets it normally functions on an acid slag, where the BF is <1 .^[6,56]

(iii) Closed SAF operations that consume pre-reduced pelletized feed, coarse reductants, and fluxes are commercially referred to as the Premus Process (Process Steps 1 – 4, 6, and 8 – 11, with or without 5 in Figure 2-6). The Premus Process is applied at Glencore Alloys (historically known as Xstrata Alloys) in South Africa.^[56,57] During the Premus Process, the pre-reduced pelletized feed is usually fed hot and directly after pre-reduction to the relevant furnace.^[6,56] The furnace operates on a basic slag ($\text{BF} > 1$), and wet venturi scrubbing is responsible for off-gas cleaning.^[6,56] A basic slag is utilized due to its high conductivity, this is necessary since fewer carbonaceous reductants are added during the smelting process due to the pre-reduction of chromite.^[56,58] Due to prior pre-reduction this process option has the lowest specific electricity consumption (SEC) (approximately 2.4 MWh/t FeCr)^[59] and the highest capital requirement.^[56]

(iv) DC arc furnace operation is the operation type that can solely be supplied with fine material (including chromite, carbonaceous reductants, and fluxes).^[6,56] Process Steps include 6, 8 – 11, with or without Step 7.^[56] DC arc furnaces are utilized in various smelters in Kazakhstan and South Africa.^[56] These types of furnaces utilize a basic slag regime with a $\text{BF} > 1$ and wet venturi scrubbing is used for off-gas cleaning.^[6,56] It is found that DC arc furnace operations have the highest SEC, hence, pre-reduction of the chromite ore is implemented before smelting to reduce the SEC.^[56,60] However this has only been investigated on an academic level and not commercially.^[56,60]

2.6. Parameters affecting chromite's pre-reduction

2.6.1. Effect of the chemical composition of chromite

The reduction rate of Fe and Cr within chromite is dependent on the solid-state diffusion of Fe^{2+} and Cr^{3+} respectively through the faulty spinel lattice of the chromite ore. The diffusion of Fe^{2+} through the chromite particle towards the surface is relatively fast but still slower than the metallization of Fe at the rim of the particle. The absence of the Fe^{2+} ions creates a faulty spinel lattice through which Cr^{3+} can migrate, however, the migration of Cr^{3+} is much slower than that of Fe^{2+} . The migration of Cr^{3+} leads to a kinetically inert spinel structure, with Mg^{2+} in tetrahedral sites and Al^{3+} and Cr^{3+} in octahedral sites. According to Dawson and Edwardst (1987) the diffusion of Cr^{3+} halts when the ratio of M^{2+} and M^{3+} ions in the structure returns to the normal spinel. Therefore, it is found that the reduction of chromite rich in Mg- and Cr-oxides is more complicated than the reduction of chromite rich in Fe and Al.^[61]

It is worth noting that the octahedral sites in South African chromite ore contain a relatively low Cr content (between 0.59 – 0.62 mol Cr) when compared to the chromite ore from Brazil, Turkey, and Kazakhstan which contains 0.70 – 0.77 mol Cr. The remainder of the octahedral sites in South African ore is occupied by Al^{3+} and low amounts of Fe^{3+} (around 0.06 mol).^[62] The presence of Al^{3+} adversely affects the reducibility of chromite. Similar to Al^{3+} , the presence of Mg^{2+} present in the tetrahedral sites will stabilize the spinel against reduction.^[63]

2.6.2. Effect of time, temperature, and particle size

Currently, chromite can be pre-reduced to levels of approximately 60%, which corresponds to a near 100% Fe metallization, and approximately 30% Cr metallization. The pre-reduction of chromite does however proceed at a relatively slow rate due to the presence of Cr-oxide. The pre-reduction kinetics cannot be accelerated as pre-reduction procedures are typically limited to real-world operational temperatures of approximately 1350 °C.^[61] This

temperature is selected to prevent partial melting of the pellets (i.e., pellet softening) and dam-ring formation within the pre-reduction kilns. The formation of excessive dam-rings necessitates its removal, which halts pre-reduced pellet production. This in turn forces SAFs operating on these pellets to consume lumpy chromite, which reduces the specific SAF's metallurgical efficiency to decrease.^[61]

Nevertheless, Hazar (2007) found that by elevating the reduction temperature, the reduction of Fe^{3+} to Fe^{2+} and the migration of Cr^{3+} and O^{2-} through the chromite particle accelerates. Hence, the reduction rate increased with an increase in temperature.^[44] Furthermore, the study showed that the size of the chromite particle influenced the rate of reduction. It was found that the reduction rate increased as the particle size decreased. Smaller particles provide more chromite/reductant contact points which supply more surface area for the reaction to proceed on. Also, smaller particles allow shorter diffusion paths for Cr^{3+} , Fe^{2+} , and O^{2-} ions to migrate through the chromite particle.^[44]

2.6.3. Effects of additives on pre-reduction

Neizel et. al. (2013) investigated the incorporation of calcium carbonate (CaCO_3) in pelletized chromite pre-reduction. Usually, CaCO_3 is used as a flux during the reduction process but in this case study, it was employed as a pellet constituent. It was found that the level of chromite pre-reduction intensified (from approximately 47% to 60%) with the addition of CaCO_3 which could lead to lower energy demands during the smelting process of chromite. However, the inclusion of CaCO_3 in the pelletized chromite pre-reduction process can likely lead to the formation of large amounts of fine feed materials which can lead to increased operational instabilities. Furthermore, the addition of CaCO_3 would cause a decrease in compressive and abrasion strength of chromite, which could lead to the reformation of chromite fines. The pre-reduced pellets containing CaCO_3 only had a third of the compressive strength of the pre-reduced pellets without CaCO_3 .^[64]

Sodium-based additives such as sodium borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), sodium sulfate (Na_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and sodium nitrate (NaNO_3) were added to C-containing chromite ore pellets. The addition of all the sodium-based additives enhanced the reducibility of chromite ore, with sodium borate delivering the best performance out of all the additives.^[65] The sodium-based additives react with the octahedrally coordinated ions (i.e., Al^{3+} and Cr^{3+}) in chromite, hence the tetrahedrally coordinated cations (i.e., Mg^{2+} and Fe^{2+}) are left behind as monoxide phases. This change in the chromite crystal structure improves the reduction mechanism.^[27]

A study conducted by Van Deventer (1988) revealed that some additives can decrease the reducibility of chromite. In this study, chromite was mixed with graphite (reductant) and various additives, such as SiO_2 , Al_2O_3 , K_2CO_3 , Na_2O_2 , CaO , MgO , Fe , and Cr , subsequently, the mixture was reacted isothermally under argon. It was found that all the additives had a positive influence on the Boudouard reaction, however, only MgO and Al_2O_3 had an inhibiting effect on the carbothermic reduction reaction of chromite. The inhibiting effect could have been due to the additives reacting to form olivine ($\text{MgO} \cdot \text{Al}_2\text{O}_3$), Fe , Fe_3C , and $(\text{Cr}, \text{Fe})_7\text{C}_3$. There was also evidence of MgO inhibiting the decomposition of the chromite spinel which will cause a delay in the reduction reaction of chromite.^[66]

The addition of fluoride fluxes (e.g., NaF - CaF_2 and CaF_2) was investigated by Dawson et al. (1987). The authors found that the flux responded as a solvent for the spinel constituents of chromite, causing the Fe^{2+} and Cr^{3+} and O^{2-} ions to dissolve in the melt and diffuse to the place where reduction proceeded (the location where the melt and a particle of the reductant are in direct contact). However, the non-reducible cations e.g., Mg^{2+} and Al^{3+} also dissolved in the melt due to their solubility, which precipitated as spinel at energetically favorable sites. The model discovered by the authors makes it possible to find the correct composition of flux addition that could increase the reduction rate of chromite effectively.

Dawson et al. (1987) proposed the flux composition should be as follow: i) its liquids temperature should be lower than the operating temperature, ii) It should be able to dissolve in a substantial amount of Al and Mg oxides while not elevating the solidus temperature and, iii) the melt should have a viscosity low enough to facilitate the rapid diffusion of the ions. Three distinguishable processes are involved with the addition of flux: firstly, the spinal constituents are dissolved, followed by the migration of the ions through the liquid phase, and lastly, the reduction reaction occurs at the surface of the chromite particle.^[61]

2.7. Effect of oxidation on the reducibility of chromite ore

A separate section is dedicated to the discussion on the effects of chromite's oxidation before reduction, as oxidized chromite is less resistive to reduction when compared to unoxidized chromite. Pre-oxidation has shown its success by being a commercially applied process during oxidative sintering where pellets are sintered to improve their mechanical strength. Oxidative sintering is one of the most popular employed processes in South Africa's FeCr industry. During this process, chromite is milled, pelletized, and then sintered.^[36,67,68]

An in-depth adventitious process of oxidation on the reducibility of chromite (Sukinda, India) is explained by Kapure et al. (2010). The oxidizing atmosphere created in the oxidation process provides an intrinsic driving force that promotes the $\text{FeO} \rightarrow \text{Fe}_2\text{O}_3$ phase (an exsolution sesquioxide phase) change. Furthermore, the chemical potential of the applied oxygen encourages the migration of Fe^{2+} ions from the center of the chromite particle to the surface where the solid-gas interface is located. The migration and oxidation of Fe during the oxidation process proceed as follow:



Where O_o^{2-} represents oxygen anions on the cubic closed-packed lattice, $\text{V}_{\text{cat}}^{\text{n}}$ is cation vacancy, h^* is referred to as a hole, and e^- is an electron. The study concluded that together with

the conversion of Fe^{2+} to Fe^{3+} , cation vacancies formed which eased the migration of Fe in the chromite particle and subsequently improved the reactivity of chromite.^[69]

Borra et al. (2010) studied the impact of pre-oxidation on phase composition and morphology of chromite from Sukinda, India. The authors found that a Fe_2O_3 -rich sesquioxide phase was visible in the Widmanstätten structure presented by the bright lines on chromite particles as can be seen by the SEM image (Figure 2-7a) and EDS analysis (Figure 2-7b) presented in Figure 2-7.

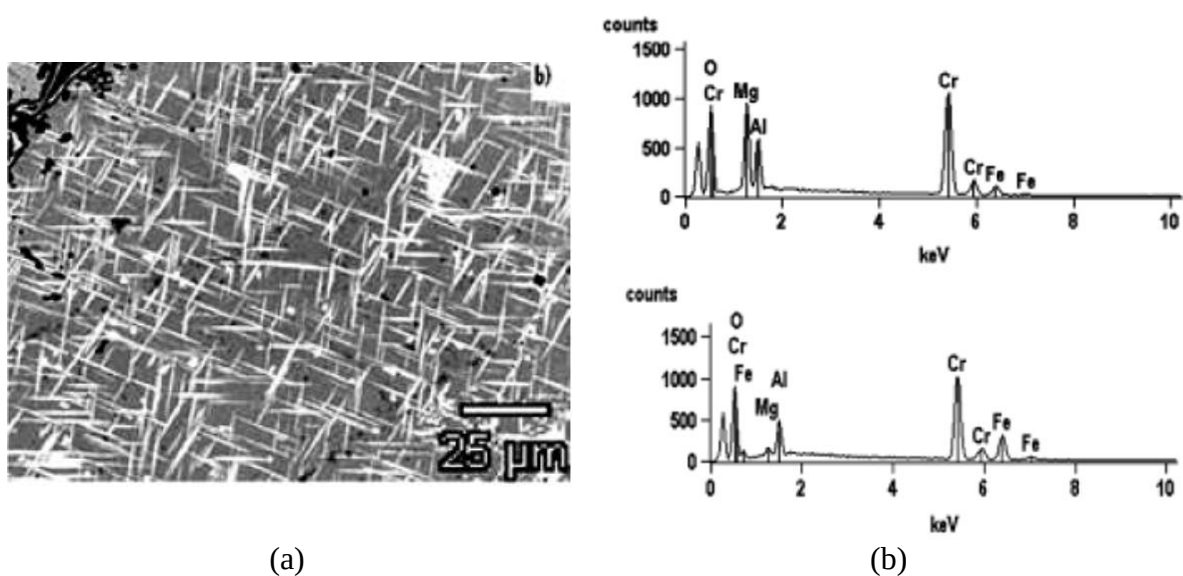


Figure 2-7 SEM image (a) of the Widmanstätten structure on oxidized chromite particles and the EDS analysis (b) of the dark matrix (top spectrum) and bright phase lines (bottom spectrum) shown in (a).^[70]

Borra et al. (2010) concluded from Figure 2-7 that the Fe-rich Widmanstätten structure precipitates out of the Mg-rich matrix onto the [111] crystallographic planes of the spinel. There was a correlation between the [111] planes of the spinel and the [0001] planes of sesquioxide regarding the close packing positioning of oxygen ions, which was responsible for the common orientation of sesquioxide lamellae along the [111] plane of the spinel matrix. At the crossing of two or more lamellae, tapered terminals were formed, which indicated a

diffusion-controlled process.^[11,70] A similar Widmanstätten structure was observed in several other studies.^[71-73]

Zhao and Hayes (2010) conducted a study where pre-oxidized chromite pellets were reduced using CO gas. During the pre-oxidation process, Fe_3O_4 was converted to Fe_2O_3 through a solid state shear mechanism forming a separate phase on the closely packed planes in the crystals. The Fe_2O_3 phase increased with an increase in temperature. The oxidation of Fe^{2+} to Fe^{3+} enhanced the degree of subsequent Fe metallization.^[72]

An investigation by Kleynhans et al. (2016) focused on the pre-oxidation of chromite before milling, agglomeration, and pre-reduction procedures. The study showed that pre-oxidation had an adventitious effect on the reducibility and metallization of chromite. However, it was discovered that the oxidation temperature had a significant effect on how much the reducibility of chromite was influenced. The chromite was pre-oxidized at several temperatures (800 – 1500 °C), from where it was determined that the optimum temperature for pre-oxidation was 1000 °C. Eskolaite formation was initiated at temperatures >1000 °C causing a decrease in the chromite's reducibility, due to having a higher reduction temperature than chromite. For this reason, Kleynhans et al. (2016) defined the optimum pre-oxidation temperature (1000 °C) as the temperature where maximum Fe migration to the surface of the chromite particle is achieved, while free eskolaite formation is avoided.^[58]

Biswas et al. (2018) investigated pre-oxidized Indian chromite ore and found that the phase transformation of chromite spinel to sesquioxide phase is controlled by the oxidation of Fe^{2+} to Fe^{3+} ions. It was concluded that the phase transformation of chromite spinel expedites as the oxidation time and temperature increased up to 120 min and 1000 °C, respectively.^[73]

Du Preez et al. (2019) focused on the oxidative sintered pellet production process and found that after pre-oxidation Fe_2O_3 -rich sesquioxide phases were present in the chromite ore. It is known that such phases have a lower smelting temperature than chromite which could

elevate the metallurgical efficiency and subsequently lower the energy consumption of the respective smelter operating on the ore.^[12]

2.8. Manganese ore

This and the proceeding sections are dedicated to Mn-ore, the second ore considered in this dissertation. As stated earlier, Mn-ore differs substantially from chromite; however, its smelting procedure is comparable to that of chromite. The importance of Mn-ore in steelmaking is of global relevance.

2.8.1. Natural occurrence and properties of manganese

Pure Mn metal is greyish white and known to be harder and more brittle than Fe. Mn is the 12th most abundant element, making up approximately 0.1% of the earth's crust. Metallic Mn has a specific gravity in the range of 7.21 – 7.44 kg/dm³ depending on its allotropic form. The element has a melting and boiling point of 1244 and 2060 °C, respectively.^[74]

The Hotazel Formation of the Proterozoic Transvaal Sequence (Voëlwater Subgroup) consists of mixed volcanogenic-chemical sediments. The world's largest Mn-ore repositories are held in these sediments. The Mn-containing rocks from the Proterozoic Transvaal Sequence can be found in three distinctive structural basins, known as the Kalahari, Avontuur, and the Leinster basins. However, the Kalahari basin is the only basin utilized for mining Mn-ore, being the source of 77% of the world's Mn-ore.^[75,76] Two-thirds of the Kalahari basin consists of carbonate (CaCO₃, MgCO₃)-rich ore, known as the Mamatwan-type environment. The remaining third of the basin, the Wessels-type environment, holds Mn- and Fe-rich ore.^[75]

Mn-ore can be classified into different types based on the oxidation state of the Mn, i.e., oxidized ores (MnO₂), semi-oxidized ores (Mn₂O₃), semi-oxidized sinter ores (Mn₃O₄), and carbonate ores (MnCO₃).^[77] In this dissertation, the UMK ore is considered the vase study ore and is known to be a semi-oxidized ore, with a high carbonate content, from the Mamatwan-

type environment of the Kalahari Basin in South Africa. The UMK ore is mined at the Hotazel mine located in the Mamatwan-type environment.^[75]

2.8.2. Ferromanganese process

Furnaces employed for the smelting of Mn-ores can be divided into four zones. Of these four zones, pre-reduction occurs in the first three of them. In each of the zones, a specific reaction occurs, which is based on the relevant temperatures in that zone, and the reactants present therein. The “drying, calcination and heating zone” (Zone 1) involves low temperature (25 – 192 °C) reduction of MnO_2 to Mn_2O_3 . Zone 2 is known as the “gas reduction zone” where Mn_2O_3 and Fe_2O_3 are reduced, and dolomite is decomposed. In the “direct reduction zone” (Zone 3) the reduction of Mn_2O_3 and Fe_2O_3 occur at the same time as the Boudouard reaction.^[74] Zone 4 is referred to as the “coke bed” or “smelting reduction zone” where the Mn-metal is produced.^[74] Figure 2-8 is a schematic illustration of a typical SAF used for FeMn production that includes the four furnace zones and the respective temperature range.

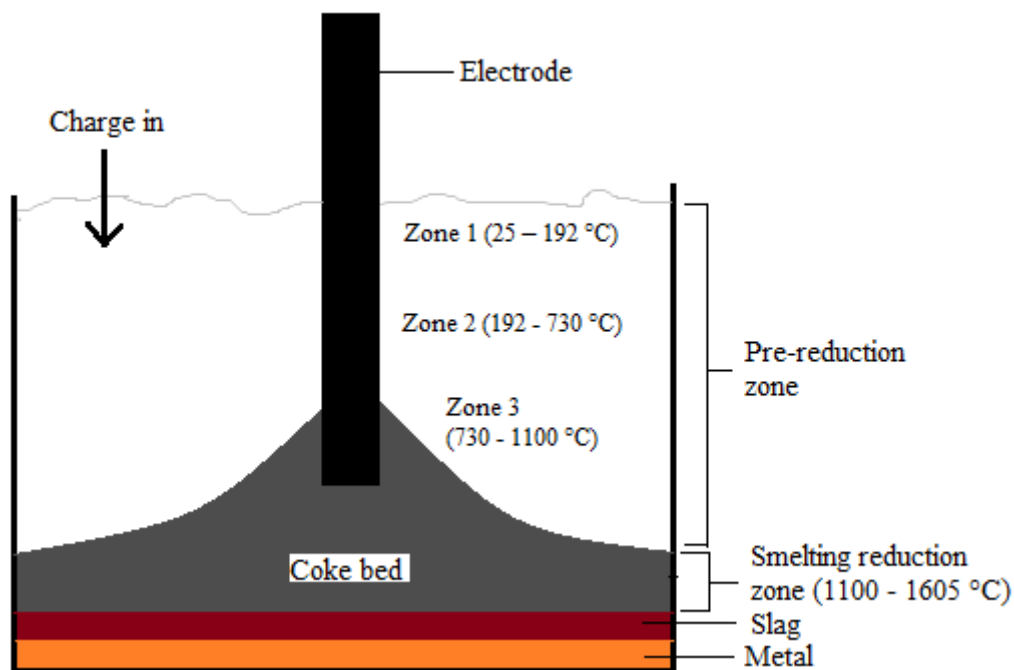
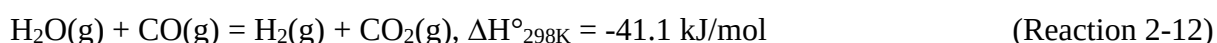


Figure 2-8 Schematic illustration of the various zones present in a SAF during FeMn production. The schematic is based on the information given in ^[74].

Water evaporation (Reaction 2-11) is the first reaction to occur after the furnace charge is heated to approximately 200 – 400 °C.^[74] Moisture originates from two sources in this case; i) moisture on the charge material surfaces as a result of wetting (e.g., terrestrial rain), and ii) crystalline moisture. Surface moisture evaporates at approximately 100 °C, whereas crystalline moisture will only evaporate in the temperature range of 200 – 400 °C.^[74] Reaction 2-11 is endothermic, hence a lower water content is desired as this will result in lower power consumption.^[74]

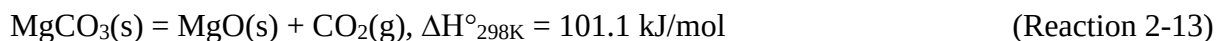


At temperatures below 700 °C, some of the evaporated water will react with CO to form hydrogen and CO₂ (Reaction 2-12). This reaction is known as the water-gas shift reaction (WGSR). It is likely that the water vapor source, as discussed above, allows Reaction 2-12 to proceed. It is however noted that the relatively small amount of hydrogen measured in the off-gas during Mn-ore smelting may originate from the decomposition of volatile organic compounds present in the carbonaceous reductants used during smelting and from the electrode paste. The WGSR is given as follows:^[74]

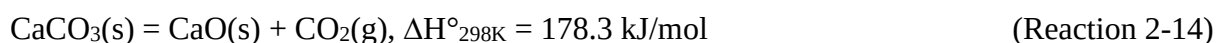


The decomposition of all the carbonates is endothermic, resulting in higher energy consumption of the furnace. Magnesium carbonate (MgCO₃) will decompose following Reaction 2-13. The amount of Mg present in the charge is determined by the type of ore, as well as the basicity demands of the slag.^[74] Slag basicity can be defined as the mass ratio between the basic and acid oxides such as (Calcium oxide (CaO) + Magnesium oxide (MgO)/Silicon dioxide (SiO₂)).^[78] The composition of the slag plays a vital role in the extent of Mn recovery, metallic yield, and feasibility of high C FeMn smelting. Mn recovery is promoted by an increase in the activity of Mn-oxide in the slag melt which is determined by the slag composition. The presence of basic oxides, i.e., CaO and MgO, improves the activity

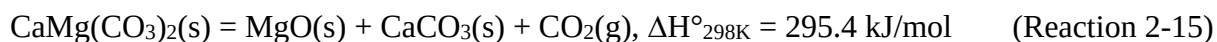
of MnO. However, a high CaO and MgO content will also increase the viscosity of the slag which will reduce the reduction of Mn.^[78] Hence, it is important to determine the optimum slag basicity for maximum Mn recovery and metallic yield. The decomposition of MgCO₃ initiates in the temperature range of 150 – 400 °C.^[74]



The decomposition of calcium carbonate (CaCO₃) is shown in Reaction 2-14. The composition of the charge determines the amount of CaCO₃ present in the charge. The CaCO₃ will decompose at approximately 900 °C.^[74]



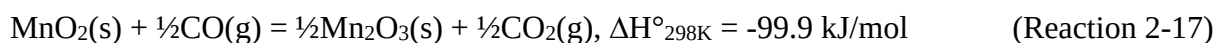
Dolomite (CaMg(CO₃)₂) is a mineral comprised of calcium magnesium carbonate and starts to decompose at a temperature of approximately 500 °C (Reaction 2-15). The resulting decomposition of dolomite yields MgO and CaCO₃.^[74] The CaCO₃ decomposes as indicated by Reaction 2-14.

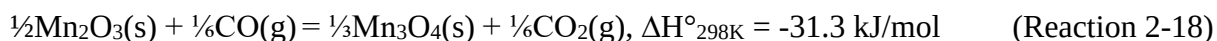


Soot may precipitate on the surface of the particles in the temperature range of 500 to 600 °C following Reaction 2-16. The soot-containing particles are carried to the bottom of the furnace where the temperature is higher. In the presence of oxides, the soot is gasified to CO₂.^[74] This reaction will not have a significant effect on the overall stoichiometry or coke consumption of the process. The process will only transfer heat from the lower part to the upper part of the furnace.^[74]

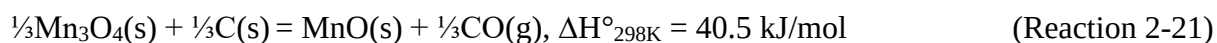


The Mn-ore mainly consists of higher Mn-oxides (MnO₂, Mn₂O₃, and Mn₃O₄) which can relatively easily be reduced in solid-state when exposed to CO. These reduction reactions (Reactions 2-17 to 2-19) are all exothermic and supplies heat to the charge.^[74]





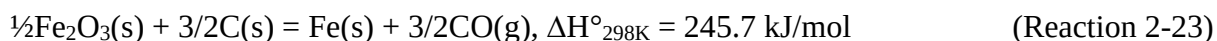
At temperatures above 800 °C, the reduction of Mn_3O_4 (Reaction 2-19) and the Boudouard reaction (Reaction 2-20) proceed simultaneously at the surface of the coke bed.^[74] Hence, some of the CO_2 that forms from Reaction 2-19 reacts with C to form CO (Boudouard reaction). This is known as direct reduction where Mn_3O_4 is directly reduced to MnO in the presence of C following Reaction 2-21.^[74] The direct reduction reaction is endothermic due to the Boudouard reaction being highly endothermic. In addition, C is also consumed during the direct reduction reaction, thereby increasing the overall energy and C consumption.^[74]



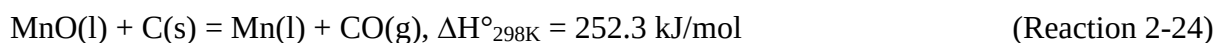
Fe-oxide (specifically in the Fe^{3+} state) is also present in Mn-ore and the reduction of Fe and Mn occurs simultaneously. Solid-state reduction of the Fe-oxide proceeds according to Reaction 2-22. The complete reduction of Fe-oxide is also exothermic.^[74]



The reduction of Fe-oxide by solid C is also possible when a similar scheme is followed as previously shown for Mn (Reaction 2-21). Hence the reaction is strongly endothermic.^[74]



Fe-oxides can be fully reduced to Fe through gas reduction; however, this is not possible for Mn-oxides due to MnO being much more stable than FeO. The final reduction of MnO to metallic Mn will proceed in the presence of C present in the coke bed (Reaction 2-24).^[74] The metallization of Mn starts at approximately 1250 °C and is a strongly endothermic reaction thereby consuming around two-thirds of the provided electric energy.^[74]



Considering Reactions 2-20, 2-21, and 2-23, it would be ideal if higher Mn-oxides are reduced in solid-state to MnO before a temperature of 800 °C is reached. Hence, a pre-treatment unit (excluding coke) can be added to the SAF where higher Mn-oxides are reduced to MnO before entering the furnace. The absence of coke eliminates the occurrence of reactions 2-20, 2-21, and 2-23, preventing elevated energy and C consumption.

2.8.3. Governing reaction mechanism

According to Szekely (2012)^[79] and Gustum (2018)^[80], all the reactions taking place in the pre-reduction zone of the FeMn process are topochemical gas-solid reactions. Reaction 2-25 applies to all gas-solid reactions.



Where b, c, and d are stoichiometric coefficients. Here solid reactant A represents the oxide that is reduced by the gaseous reactant B to form the lower oxide solid/metal C and the produced gaseous by-product D.^[79,80]

The shrinking-core model is commonly used to describe the process of gas-solid reactions. This model only considers one zone where the gas-solid reaction proceeds, initially, the zone is located at the surface of the particle. The reaction interface then recedes towards the center of the particle as the gas-solid reaction continues to convert the reactant solid A. Hence, a solid C layer is formed in the outer part of the particle while a gaseous gas D is also formed. The model was explained in five steps by Levenspiel (1998): i) B diffuses through the gas-film (surrounding the particle) to the surface of A, ii) B penetrates the solid product layer (consist out of C) and continues diffusing towards the interface between the solid product layer and unreacted center of the particle, iii) B reacts with A present at the reaction interface, iv) D diffuses through the solid product layer towards the exterior surface of solid A, v) further diffusion of D through the gas film.^[81]

The kinetics of solid-state reduction of various ores reveals that the reduction rate of Mn-ore is determined by the diffusion of solid A in and gas D out of the reaction zone.^[80] Hence, the stepwise shrinking core model can be applied to the reduction of Mn-ore by CO and H₂ gasses.^[74,82] Figure 2-9 shows the reduction of a spherical MnO₂ particle to lower oxides. The outer layer reduces first and subsequently grows inward as the gas diffuses through the layers of MnO, Mn₂O₃, and Mn₃O₄ causing the core to shrink.^[83]

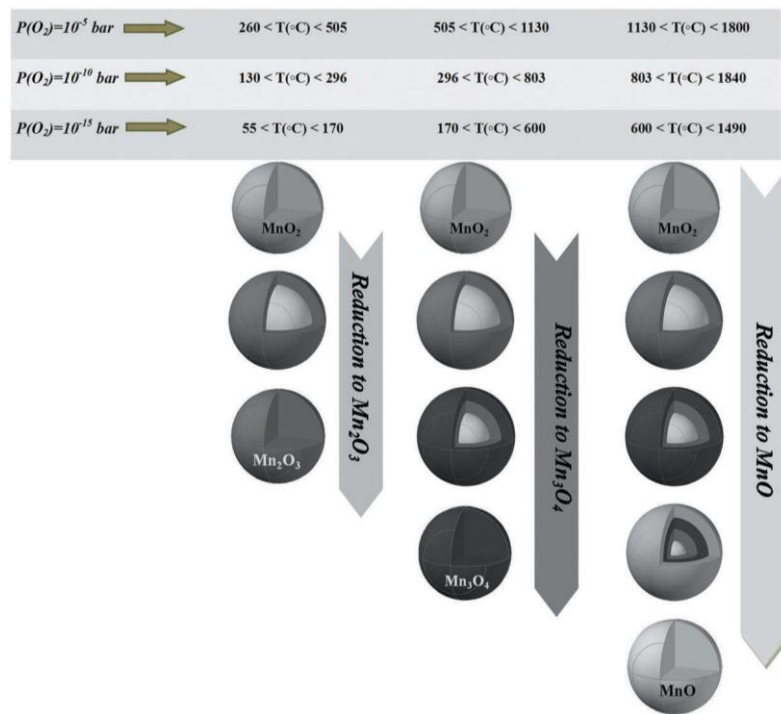


Figure 2-9 Proposed reduction model of MnO₂ to lower oxides with related temperature ranges for given pO₂.^[83]

The shrinking core model is controlled by chemical reaction, pore diffusion, or a mixture thereof. It is assumed that the reduction rate is controlled by the chemical reaction when the ore is in the temperature range of 250 – 300 °C, while at elevated temperatures of 700 – 1100 °C, the reaction rate is controlled by the gaseous diffusion.^[74] However, Kumar et al. stated that the transformation of Mn₃O₄ to MnO in the reduction process is controlled by chemical reactions.^[84]

To achieve a rapid reduction rate, the ore should have a small particle size and consist of numerous pores. A higher porosity will allow faster gas diffusion through the particle, resulting in accelerated reduction rates. The smaller size particles make the reduction of higher oxides at lower temperatures and the availability of reactant gas at elevated temperatures more feasible.^[82] It is worth mentioning that the shrinking core model can be discontinued due to solid-state diffusional limitations caused by the crystallization or sintering of the solid product.^[74,82]

2.8.4. Mn-ores from the Mamatwan environment

The most common commercial Mn-ores, originating from South Africa, are UMK, Gloria, and Mamatwan ores. The chemical composition and mineralogy of UMK ore are similar to other commercial ores, i.e., Gloria and Mamatwan from the Mamatwan environment (Table 2-1). The UMK, Gloria, and Mamatwan mines are in the Mamatwan region of the Kalahari basin (Figure 2-10). The UMK and Mamatwan mines are in the Southern part of the Kalahari basin, while the Gloria mine is more up North in the basin. The lower Mn-ore bed of the UMK, Gloria, and Mamatwan mines have an average thickness of 15 m, 13 m, and 47 m, respectively. The UMK and Mamatwan mines are both open-pit mines, meaning some of the ore could be exposed to supergene alteration due to the predominance of descending meteoric fluids (i.e. water derived from precipitation). However, Gloria is an underground mine and would probably not be subjected to any effects from the Kalahari unconformity.^[85]

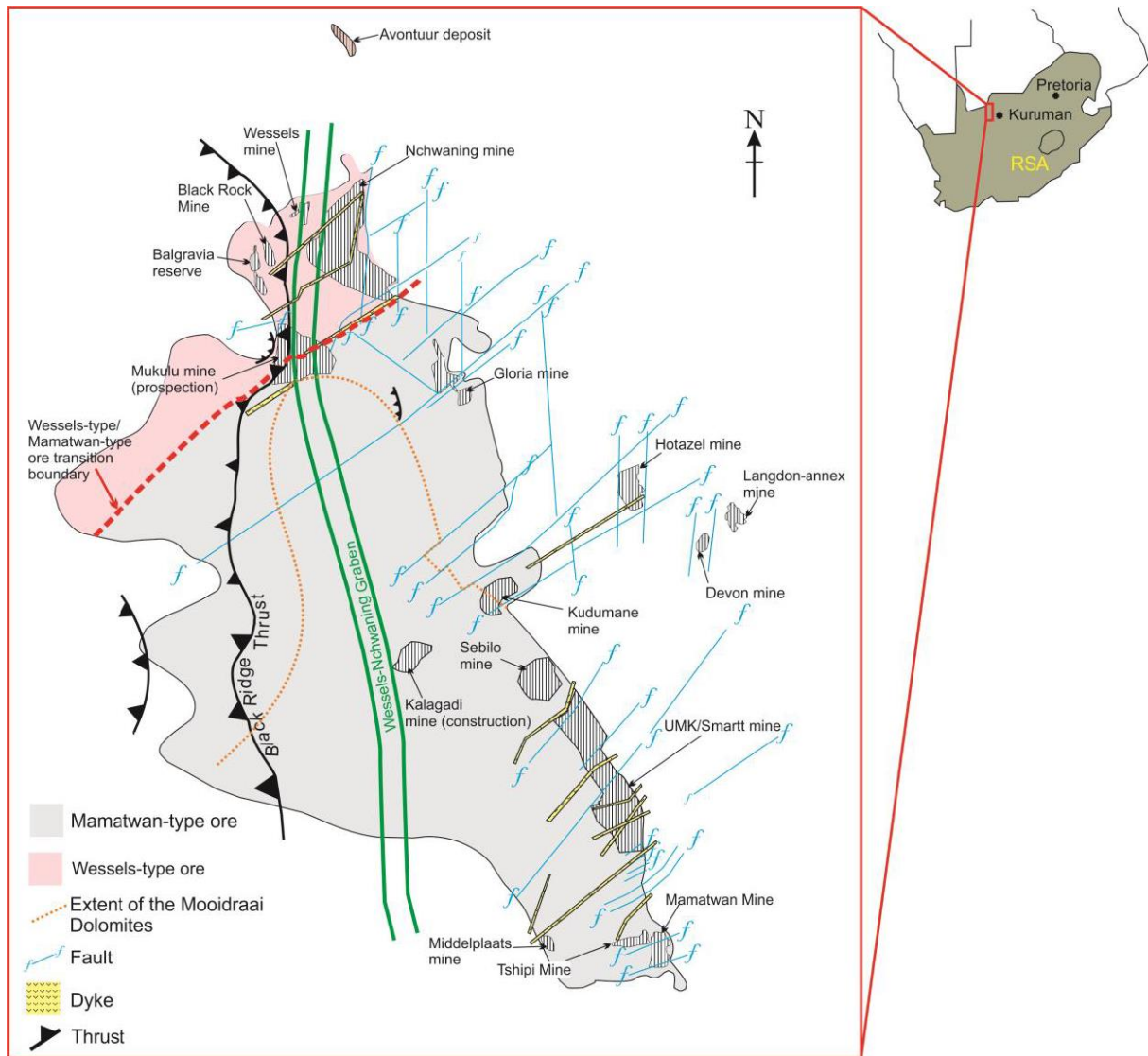


Figure 2-10 Geographical positioning of several mines located in the Kalahari manganese basin in South Africa. Also indicated are the mines of interest, i.e., UMK, Mamatwan (South), and Gloria (North) mines.^[85] The image was reused, without alterations, from <https://ujcontent.uj.ac.za/vital/access/services/Download/uj:31822/SOURCE1?view=true> (date of access: 30/05/2022).

Table 2-1: A summary of the mineralogy (given in wt%), Mn/Fe ratios, and LOI of UMK, Gloria, and Mamatwan Mn-ores originating from the Kalahari Basin.

Compound	Mn-ore from the Mamatwan environment									
	UMK				Gloria			Mamatwan		
BaO	0.02	0.05	0.06	0.07	0.34	-	0.1	-	0	0.1
CaO	16.08	13.29	15.3	13.29	14.9	12.3	12.7	13.9	14.7	13.9
MgO	2.98	3.17	2.73	3.17	4.1	3.6	3.80	2.4	3.50	4.0
CO ₂	15.00	14.00	15.9	-	17.8	-	15.4	-	17.0	-
K ₂ O	0.25	0.08	0.04	0.08	0.02	0.03	0	0.04	0	0.01
Fe	3.86	4.67	4.63	4.67	5.3	5.20	-	4.7	-	4.9
Mn	37.04	38.22	37.0	38.22	35.2	38.5	39.1	37.6	37.8	38.5
P	<0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
S	0.018	-	0.01	0.01	0.08	0.02	-	0.01	-	0.03
Al ₂ O ₃	0.38	0.74	0.47	0.74	0.3	0.20	0.30	0.2	0.50	0.20
SiO ₂	5.59	6.54	5.87	6.54	6.3	5.90	5.70	4.5	4.0	6.1
TiO ₂	<0.03	-	0.01	0.01	<0.05	-	-	-	-	-
MnO ₂	26.38	26.52	-	26.52	24.8	-	23.6	-	23.4	-
Mn/Fe	9.6	8.2	8.0	8.2	6.6	7.4	7.8	8.0	8.2	7.9
LOI 950	16.77	-	-	15.67	17.10	-	-	-	-	15.9
Reference	[86]	[87]	[88]	[89]	[90]	[91]	[74]	[91]	[74]	[92]

Table 2-1 shows that the ores from the Mamatwan region, i.e., UMK, Gloria, and Mamatwan, have relatively similar compositions. It can however be seen that there is a certain degree of variation in the composition of the ores from similar origins. The mineralogy of the ores in the Mamatwan environment, i.e., UMK, Gloria, and Mamatwan ores, is dominated by Mn silicates, i.e., braunite, carbonates (calcite (CaCO₃), dolomite (CaMg(CO₃)₂), and hausmannite (Mn₃O₄). Kutnahorite ((Ca, Mn, Mg, Fe)(CO₃)₂), manganite (MnOOH), bixbyite ((Mn, Fe)₂O₃), and hematite (Fe₂O₃) are also found in these ores but to a lesser extent.^[90] Braunite can be found in three forms, regular braunite (3(Mn, Fe)₂O₃.MnSiO₃), braunite II (7(Mn, Fe)₂O₃.CaSiO₃), and braunite new (which is similar to braunite II but contains less calcium and silicon).^[82]

The Mn-ores in the Mamatwan environment mainly contain braunite I, while the ores in the Wessel environment usually consist of braunite I and braunite II. Hence, the ores from the Mamatwan environment have a higher Mn/Fe ratio, due to braunite I containing less Fe

than braunite II. The braunite can be spotted as the fine-grained matrix between the white and/or light-brown carbonate ooids (<2 mm in diameter) grains with a core that is coated by a carbonate-rich external cortex of concentric laminae)^[93,94] inside the dark brown ores from the Mamatwan environment ore.^[75]

2.9. Previous studies on Mn-ores

2.9.1 Mn-ores originating from the UMK region

Several studies investigated the pre-reduction of Mn-ores such as Comilog, Nchwaning, and Mamatwan ore, however, little research has been done on the pre-reduction behavior of UMK ore.

Reiersen (2021) dissertation recently and extensively studied the pre-reduction behavior of UMK ores. TG experiments were performed in a vertical tube furnace. The UMK charge (10 – 12.5 mm) was exposed to three different heating rates, i.e., 3, 6, and 9 °C/min. The ore samples were pre-reduced to a peak temperature of 1000 °C in a 70% C/30% CO₂ gas atmosphere. After the pre-reduction of UMK ore, the total weight loss caused by carbonate decomposition was 14 wt%. The weight loss rate curves for UMK showed two rate peaks and the crucible temperature dropped at each peak indicating an endothermic reaction. Hence, it was assumed that pre-reduction and decomposition of carbonates proceeded in parallel. However, the decomposition of calcite occurred at a lower temperature than the expected 900 °C. The chemical analysis revealed that UMK ore contained 3 wt% MgO, likely in the form of dolomite which decomposes in two distinct steps. Reiersen (2021) further revealed that the decomposition of carbonates caused a rapid and high porosity increase in UMK ore. After a peak porosity was reached at 800 – 900 °C the porosity decreased, likely due to the sintering of the particles. It was also determined that UMK ore would rather decrepitate into large particles than into fines and that the decrepitation was not influenced by the heating rate.^[86]

Biørnstad (2020) investigated the pre-reduction of UMK ores. Pre-reduction experiments were performed on ores in the size fractions of 3.4 – 6.7 mm and 10.0 – 13.2 mm at a heating rate of 3 °C/min until the sample reached target temperatures of 400, 600, and 800 °C. The UMK ore was reduced in synthetic air in a TG furnace. The O/Mn ratio for the raw material of UMK was calculated as 1.45. No significant change in the weight of UMK ore was observed at temperatures <600 °C. The weight loss during the pre-reduction of Mn-ore is caused by the elimination of oxygen during the pre-reduction of higher oxides and carbonate decomposition. Hence the calculated weight loss percentage was used to determine the degree and rate of pre-reduction and carbonate decomposition. The theoretical weight loss was 19.5 wt%. For the 10.0 – 13.2 mm UMK size fraction the weight loss increased from 4.3 – 13.5 wt.% as the temperature increased from 600 – 800 °C. The porosity of the UMK ore was detected as 3.22%. Biørnstad (2020) further concluded that the UMK ore weakened as it was heated, possibly due to an increase in porosity or cracking caused by thermal shock.^[89]

Hamuyuni et al. (2021) studied the pre-reduction behavior of UMK ore in a TG furnace. The charge (300 – 400 g) was heated up to 800 °C at a rate of 10 °C/min in a CO gas mixture atmosphere. No weight loss in UMK ores was observed before 600 °C, while a significant weight loss was observed between 650 – 800 °C. The author concluded that the weight loss was caused by the thermal decomposition of carbonate and silicate (braunite) minerals.^[95]

Sukhomlinov et al. (2021) conducted a non-isothermal TG analysis on UMK ore in a vertical tube furnace. Three ore size fractions, i.e., 3.15 – 4.0, 6.3 – 8.0, and 12.5 – 16.0 mm were subjected to various CO/CO₂ gas mixtures (20, 50, and 80 vol% CO) at a heating rate of 6 °C/min. The samples (100 g) were heated to different temperatures, i.e., 700, 900, and 1100 °C. XRD analysis revealed that UMK ore mainly consisted of braunite, hausmannite, various Mn-containing carbonates, e.g., kutnohorite, and other more complex carbonates, e.g., calcite and dolomite. It was also detected that the UMK ore had a porosity of 3.3±3.4%.

Furthermore, two distinctive peaks were observed in the reduction rate curve. It was concluded that the first peak was caused by the reduction of Mn_3O_4 to MnO in the temperature range of 600 – 800 °C, while the second peak was due to the decomposition of calcite proceeding at higher temperatures. The reduction rate of higher Mn-oxides was affected by the particle size, while the decomposition of CaCO_3 was not.^[88]

Mukono et al. (2021) performed pilot-smelting experiments on an electric furnace to get a better understanding of energy requirements and CO_2 emissions during the production of high C FeMn alloys. UMK ore was mixed with sinter, flux, and coke before reduction. The initial O/Mn ratio of the UMK ore was 1.44. UMK showed a high increase in porosity as it was heated. It is assumed that the increase was caused by the high carbonate content decomposing with elevated temperature, and this promoted the extent of pre-reduction for UMK ore. The pilot experiments revealed that the degree of pre-reduction, C consumption, and energy consumption for the UMK charge mix was 68%, 292 kg C/t alloy, and 2000 kWh/t alloy, respectively. It was also noted that the extent of reduction was higher near the electrodes of the furnace. Usually, a high degree of pre-reduction will result in a low C consumption, however, this was not the case with the UMK charge. In the investigation, UMK had the highest degree of pre-reduction and energy consumption due to the high energy demand for carbonate decomposition.^[87]

2.9.2 The use of hydrogen gas atmospheres

The atmosphere in the industrial furnace consists of CO/CO_2 , hence many studies performed on the pre-reduction of Mn-ore utilize a CO/CO_2 gas mixture. Only a few studies have focused on the influence of hydrogen and water vapor on the pre-reduction of Mn-ore. This section discusses the results of these studies.

Bhalla and Eric (2015) investigated the influence of CH_4 on the pre-reduction of Mamatwan ore. The pre-reduction experiments were performed in a TG furnace. The ore was

subjected to different CH₄-Ar gas mixtures (10% and 30% CH₄ in Ar) at 1100 and 1200 °C. During the pre-reduction process, CH₄ cracking (CH₄ conversion into CO and H₂) was initiated at approximately 550 °C enabling the rapid reaction and formation of the reductants CO and H₂. The authors concluded that the reduction rate of the ore increased with an increase in CH₄ concentration and temperature.^[96]

A study conducted by Schanche and Tangstad (2021) explored the influence of hydrogen on the rate and extent of pre-reduction of Nchwaning ores within the size range of 9.5 – 15.0 mm. The isothermal experiments were performed in a TG furnace at 600, 700, and 800 °C. Hydrogen was included (without changing the thermodynamic driving force) in two of the four gas mixtures that were used, i.e., 16% CO 68% CO₂ 16% H₂ and 37% CO 26% CO₂ 37% H₂, and the samples were reduced at two different pO₂'s. The authors concluded that the rate and extent of reduction increased with an increase in temperature and a decrease in pO₂. In addition, the incorporation of hydrogen caused the reduction rate to increase by a factor of 1.3. and 2.6 for low and high pO₂, respectively. It was assumed that the increased reduction rate was due to the improved diffusion characteristics of hydrogen. Hence, the authors concluded that incorporating hydrogen into the pre-reduction gas mixture would be beneficial as it lowers the pO₂ and improves the kinetics of the pre-reduction process.^[97]

Ngoy et al. (2020) studied the influence of hydrogen on the pre-reduction of Nchwaning and Comilog ores (9.5 – 16.0 mm size fraction) by incorporating hydrogen into the CO/CO₂ mixtures, i.e., 41% CO 18% H₂ 41% CO₂ and 41% CO 41% H₂ 18% CO₂. Experiments were conducted in a TG tube furnace with a heating rate of 6.8 °C/min to 1000 °C. The authors found that the inclusion of H₂ in the gas mixture elevated the reduction rate by approximately 20 – 30%. The results also revealed that the reduction rate increased as the pO₂ decreased.^[98]

Summary

Chapter 2 is comprised of a detailed literature review of chromite and Mn-ore smelting. Though the ores differ from each other, the smelting thereof is similar, i.e., energy and material-intensive carbothermic smelting of stable metal-oxide ores using SAFs. General information on both the target metals, Cr and Mn, as well as details regarding their production were given separately. From the literature, hydrogen is currently not truly considered a reductant in the smelting industry. However, it has received more and more attention in recent years as it is a carbonless reductant, i.e., hydrogen-based reduction only yields water when reacted with metal oxides. Hence, to potentially curb the demand for C and possibly energy consumption during primary chromite and Mn-ore smelting, the use of hydrogen as the reductant is proposed. Selected aspects applicable to the investigation and development of a more environmentally friendly method of chromite and Mn-ore smelting, together with its preparation method and applications, were studied in detail in this dissertation, specifically:

- 1) Evaluate thermodynamically and experimentally if hydrogen is a potential chromite reductant. Results are shown in Chapter 3.
- 2) Investigated the effect of pre-oxidation on the reducibility of chromite ore where hydrogen is employed as the reductant. Results are shown in Chapter 4.
- 3) Studied the effect of hydrogen as a reductant on the pre-reduction of Mn-ore containing a high % of carbonates. Furthermore, determine the effect of temperature on the pre-reduction behavior. Results are shown in Chapter 5.

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Reprint from: Jamey Davies, Dogan Paktunc, José Juan Ramos-Hernandez, Merete Tangstad, Eli Ringdalen, Johan P. Beukes, Dmitri G. Bessarabov and Stephanus P. Du Preez. The Use of Hydrogen as a Potential Reductant in the Chromite Smelting Industry. *Minerals*, 2022, 12, 534. <https://doi.org/10.3390/min12050534>

CHAPTER 3: THE USE OF HYDROGEN AS A POTENTIAL REDUCTANT IN THE CHROMITE SMELTING INDUSTRY

The article presented in Chapter 3 was published by *Minerals* in 2022, Vol. 12, 534 (24 pages). (DOI: <https://doi.org/10.3390/min12050534>), and no permission from the copyright holder is required. Journal details can be found at <https://www.mdpi.com/journal/minerals> (date of access 25/05/2022). The article is published under an open-access license. The material published in the article can be re-used by any person if proper accreditation/citation of the original publication is given. For more information on open access publications, please visit <https://www.mdpi.com/openaccess>. The front page of the published article is presented in Appendix A.

3.1. Author list and contributions

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Contributions

The authors are presented as acronyms of the first-, middle names, and surnames. For instance, the candidate, Jamey Davies, is resented as J.D. The contributions of the various co-authors were as follows:

Author Contributions: The majority of the work, i.e., experimental, data processing and interpretation, research, and writing of the scientific paper, was performed by the candidate, J.D. Some investigations were performed by D.P., J.J.R.-H. S.P.D.P. (supervisor) assisted by providing conceptual ideas and recommendations regarding experimental work and writing of the article. D.P., M.T., E.R., and S.P.D.P contributed to the reviewing and editing of the article. Financial support was provided by M.T. and D.G.B.

Abstract: The chromium (Cr) content of stainless steel originates from recycled scrap and/or ferrochrome (FeCr), which is mainly produced by the carbothermic reduction of chromite ore. Ever-increasing pressure on FeCr producers to curtail carbon emissions justifies migration from traditional FeCr production routes. The interaction between hydrogen and chromite only yields water, foregoing the generation of significant volumes of CO-rich off-gas during traditional smelting procedures. For this reason, the use of hydrogen as a chromite reductant is proposed. In addition to thermodynamic modeling, the influence of temperature, time, and particle size on the reduction of chromite by hydrogen was investigated. It was determined that, at the explored reduction parameters, the iron (Fe)-oxides presented in chromite could be metalized and subsequently removed by hot-acid leaching. The Cr-oxide constituency of chromite did not undergo appreciable metallization. However, the removal of Fe from the chromite spinel allowed the formation of eskolaite with the composition of $(\text{Cr}_{1.4}\text{Al}_{0.6})\text{O}_3$ in the

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form of an exsolved phase, which may adversely affect the reducibility of chromite. The study included the limitations of incorporating hydrogen as a reductant into existing FeCr production infrastructure and proposed possible approaches and considerations.

Keywords: Chromite; hydrogen; ferrochrome/ferrochromium; pre-reduction

3.2. Introduction

Chromite ore is characterized by the unit formula, $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Cr}, \text{Fe}^{3+})_2\text{O}_4$ and serves as the only economically viable source of virgin Cr units.^[1,2] The energy-intensive carbothermic smelting of chromite ore yields ferrochrome (FeCr) – a crude alloy of Cr and Fe.^[3-5] Approximately 80 to 90% of produced FeCr is consumed by the stainless steel industry and is therefore considered equally important.^[4,6,7] The significance of FeCr production is highlighted by the Cr constituency thereof, as the inclusion of Cr in stainless steel is the reason for the corrosion resistance thereof under standard ambient conditions.^[4]

Chromite smelting is typically performed in semi-closed or closed submerged arc furnaces (SAFs) and, to a lesser extent, closed direct current (DC) arc furnaces.^[6,8,9] The energy consumption of a specific furnace is affected by factors such as material screening, chromite pre-heating, and pre-reduction.^[6] For instance, the energy consumption of a semi-closed SAF operating on unscreened feed materials can be as high as 4500 kWh/t FeCr produced, whereas a closed SAF operating on hot-fed pre-reduced chromite can be as low as 2000 kWh/t FeCr produced.^[6] In addition to this, produced FeCr contains a certain amount of Si, which originates from the unintended reduction of silica in the slag phase, which increases energy consumption.^[10,11]

During chromite smelting, various types of carbon sources are used as reductants, e.g., coke, coal, and charcoal. The Cr- and Fe-oxide constituencies of chromite are reduced to their metallic states or carbide form.^[3,12] For all these reduction reactions, CO(g) is formed and

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present in significant quantities in the off-gas. Due to the highly toxic nature of CO, the CO-rich off-gas has to be oxidized before its release into the atmosphere. For semi-closed SAFs, this oxidation occurs above the furnace bed concurrently with smelting operations while closed SAFs and DC furnaces oxidize CO-rich off-gas on a furnace stack.^[13-15]

Due to the nature of semi-closed SAFs, relatively significant quantities of air enter the space above the furnace bed and off-gas duct, and these SAFs produce between 10 000 to 15 000 Nm³/t FeCr off-gas. Closed SAFs generate the lowest volumes of off-gas during smelting (i.e., 650 to 850 Nm³/t FeCr), which are cleaned in venturi scrubbers before being flared or employed as fuel elsewhere on-site. The volume and CO-content of off-gas during closed SAF operations are however dependent on the leakage air.^[13, 16] Nevertheless, significant quantities of CO₂ are produced during chromite smelting, regardless of the furnace type and smelting regime employed.

Increasing pressure on the FeCr industry to curb C-emissions calls for the development of alternative smelting processes. Such processes should achieve high levels (preferably near-complete) of chromite reduction while reducing C-emissions (when compared to traditional smelting processes). A recent patent by Winters (2016) proposed a process to produce Cr-containing alloy without employing SAFs.^[17] This process utilizes a vertical moving reactor bed with external burners that consume pre-heated reformed natural gas (CO and hydrogen) to supply heat to the reactor, while concurrently injecting reformed natural gas into the bottom of the reactor. By doing so, the chromite is reduced in a solid-state. Thereafter, the Cr-containing alloy is recovered through physical separation based on differences in density and magnetic properties of the alloy. This smelting process consumes approximately a third of the electrical energy required during conventional chromite smelting. Water and CO₂ are generated during this smelting process, of which the CO₂ is captured, compressed, and supplied to various

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industries. Significant quantities of naturally occurring natural gas are however a pre-requisite for this smelting method.^[17]

A patent by Pheiffer and Cookson (2015) suggested that SiC can be employed as a reductant during the FeCr production process. SiC composites can be incorporated during the generation of chromite agglomerates (e.g., briquettes or pellets) destined for oxidative sintering or pre-reductive pellet curing. The proposed SiC composite comprises mainly SiC, C, and ash (various fractions of CaO, MgO, SiO₂, Al₂O₃, and FeO). The reaction of SiC with chromite yielded SiO₂ and CO as by-products; SiO₂ suggests that CO formation was partially diminished.^[18] However, Pheiffer and Cookson (2015) did not perform a techno-economical study, and due to the cost of SiC, the running operational cost of a furnace operating on SiC-based reductants will likely be higher than traditional smelting operations.^[5]

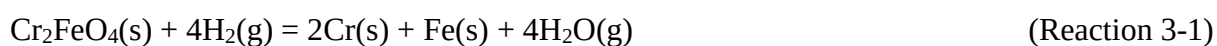
A solid-state chromite reduction process was investigated by Yu and Paktunc (2018) where segregation reduction was implemented. During the process graphite, petroleum coke, and charcoal were used as reductants and calcium chloride (CaCl₂) as the segregation catalyst. This flux-assisted process achieved high degrees of Cr metallization at 1300 °C after 2 hours of reduction in a rotary kiln or rotating hearth furnace. The CaCl₂ initiated the chlorination system that enabled the reducible Cr and Fe species from the chromite particles to segregate before the reduction and metallization by carbon. Subsequently, individual alloy particles were formed which made the separation during ferrochrome recovery easier.^[19] The CaCl₂ also provided a liquid media for the incongruent dissolution of chromite and migration of the reducible ions (e.g., Fe²⁺, Fe³⁺, Cr³⁺). It was also possible to recover CaCl₂ in the reduced product through water-leaching, the catalyst could then be re-used and possibly save on material cost.^[20] However, CaCl₂ could react with the siliceous gangue (e.g., clinocllore), causing the formation of Ca-bearing chromite, wadalite, and gaseous chlorides (MgCl₂, FeCl₂,

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and/or HCl). In the CaCl₂-assisted segregation reduction process the ferrochrome alloy particles needed to be separated from the unwanted gangue present in the reduced products. Separation could likely succeed through conventional gravity or magnetic concentration techniques; however further process development was proposed. ^[19, 21]

A patent by Sokhanvaran and Paktunc (2019) provided a method where the addition of cryolite (Na₃AlF₆) in chromite direct reduction was advantageous. The cryolite dissolved several oxides from the chromite spinel which diminished slag growth. The forming molten cryolite layer enabled the migration of Cr and Fe ions. Impure mixtures containing cryolite (e.g., a by-product of aluminum smelting processes and bath material produced as waste) were used in the chromite reduction. Using cryolite as an additive in chromite reduction involves several embodiments as well as many options for achieving these embodiments, enhancing the necessity for further research. ^[22] It is however noted that the use of F-containing reductants (as well as Cl-containing) are considered environmentally hazardous.

It has also been shown that the use of hydrocarbon gas for chromite reduction achieved higher degrees of reduction at lower temperatures when compared to traditional carbothermic smelting procedures. ^[23] To alleviate some C-dependence of chromite smelting, and to avoid the use of Cl- and F-containing compounds, the use of hydrogen as the reductant is proposed. Theoretically, the complete reduction of pure chromite by hydrogen is given as follows: ^[24]



It is noted that Reaction 3-1 requires temperatures greatly exceeding the typical temperatures associated with SAF smelting. In addition, the reduction of naturally occurring chromite does however proceed differently as the chromite spinel contains stabilizing Mg²⁺ and Al³⁺. ^[25] Reaction 3-1 shows that the only by-product when employing hydrogen as a reductant is water. Therefore, considering the occlusion of C-based by-products, the use of hydrogen to reduce

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chromite was explored in this study. More importantly, the reduction of Cr- and Fe-oxides was of importance, and the metallization mechanisms thereof were elucidated. It is proposed that by employing hydrogen to metalized chromite, or at least partially, the electrical and C consumption of a chromite smelter can be reduced.

3.3. Materials and Methods

3.3.1. Materials

Kleynhans et al. (2016) stated that in 2012 approximately 28% of globally smelted chromite originated from South Africa. Thus, a significant fraction of globally produced FeCr, which is estimated to be approximately 32%, originated from South African chromite.^[26, 27] Considering this, the results presented in this study are of international relevance.

Metallurgical-grade chromite ore was obtained from a large South African FeCr producer and was used as the case study ore. A homogeneous and representative sample collection campaign was undertaken at the South African FeCr smelter and sample selection for experimentation was applied here as described by Du Preez et al. (2019).^[2] A thorough characterization of this case study ore was conducted by Glastonbury et al. (2015),^[28] therefore characterization was not repeated here. Table 3-1 summarized the chemical, and crystalline characteristics of chromite ore used here. Bulk chemical characteristics were determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES) and bulk mineralogical composition by X-ray diffraction (XRD) analysis.

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Table 3-1: Characterization of the case study chromite ore in terms of the chemical composition (ICP-OES, wt.%)^[28], and mineralogical composition (XRD, wt.%).

ICP-OES		XRD	
Compound	Metgrade	Compound	Metgrade
Cr ₂ O ₃	44.19	Chromite	93.4
FeO	24.68	Enstatite	6.6
SiO ₂	2.96		
Al ₂ O ₃	14.71		
MgO	10.31		
CaO	0.16		
P	0.001		
Cr/Fe	1.58		

Of particular importance here were the Cr- and Fe-contents, and the Cr/Fe ratio. It is worth noting that South African chromite has relatively low Cr-contents. For instance, Ringdalen and Olsen (1998) indicated that Turkish, Kazak and Brazilian chromite ore contains 0.70 – 0.77 mol Cr in the octahedral sites, whereas South African ore contains between 0.59 – 0.62 mol Cr. As a result, octahedral sites are occupied by Al³⁺ and a relatively low amount of Fe³⁺ (around 0.06 mol).^[29] As stated earlier, the presence of Mg²⁺ (in tetrahedral sites) and Al³⁺ adversely affect the reducibility of chromite.

Hydrogen, which was the investigated reductant in this study, can be produced from numerous processes, e.g., thermochemical,^[30, 31] photocatalytic,^[32, 33] photochemical,^[34, 35] photo-electrochemical,^[36, 37] metal, and metal hydride hydrolysis,^[38-44] electrochemical,^[45-50] ammonia and formic acid decomposition,^[51-53] and various biological processes.^[54-56] The hydrogen used throughout this study as the reductant was generated on-site at Hydrogen South Africa Infrastructure, South Africa, by proton exchange membrane water electrolysis (PEMWE). A PEMWE stack was powered by photovoltaic energy and the generated hydrogen was stored as a pressurized gas. Therefore, the hydrogen used here is defined as green hydrogen as it is produced from renewable energy and a renewable source. Nitrogen (99% purity) was obtained from Afrox, South Africa.

3.3.2. Sizing of chromite

Size partitioning of as-received chromite ore was performed by screening it into the following size fractions, i.e., <106, 106 to 250, 250 to 500, and 500 to 1000 μm . Chromite screening was performed using a Haver EML Digital Plus sieve shaker and stainless steel Haver and Boecker sieves.

Particle size distribution of the screened chromite fractions was performed by laser diffraction particle sizing using a Malvern Mastersizer 3000. Samples were ultra-sonicated before measurements and continuously agitated by mechanical stirring at 2400 rpm during analyses. Laser obscuration was maintained between 10 to 20%. The d_{90} , d_{50} , and d_{10} values of as-received and size fractioned are presented in Table 3-2.

Table 3-2: D_{90} , d_{50} , and d_{10} (μm) of as-received and size fractioned chromite.

Size equivalent	As-received	Sieve sizes (μm)			
		<106	106 to 250	250 to 500	500 to 1000
d_{90}	415,0	140,2	282,1	464,2	924,1
d_{50}	182,3	87,4	186,3	347,4	667,7
d_{10}	71,7	51,8	120,7	260,0	487,6

3.3.3. Reduction procedure

Reduction procedures were performed in a Carbolite vertical tube furnace; the furnace had a maximum operating and maintainable temperature of 1200 and 1100 $^{\circ}\text{C}$, respectively. Ceramic heat shields were placed within the tube at both ends to increase the stability of the heated zone. Stainless steel caps were fitted to seal the tube ends and acted as a gas inlet and outlet. The thermocouple used to measure temperature was located at the center of the heating zone, immediately adjacent to the tube. The furnace was heated by a series of electrodes which were located adjacent to the tube.

The reduction was performed by placing 50 g of chromite in a crucible in the center of the furnace hot zone. The samples were then heated from room temperature at the maximum

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allowable heating rate for the specifically fitted tube, i.e., 5 °C/min, until the predetermined temperature was reached. The tube was continuously purged with N₂ at a flow rate of 75 mL/min. It was of importance to ensure no oxygen was present within the furnace seeing that hydrogen has a self-ignition temperature of approximately 572 – 585 °C and an explosive range of 4 – 75 vol.% in the air at standard ambient conditions.^[57-59] A 1 L/min hydrogen flow, in conjunction with the N₂ flow, was introduced at 600 °C to obtain an approximate 93 vol.% hydrogen atmosphere within the furnace tube. This atmosphere was maintained until a predetermined reduction temperature was reached/maintained. Thereafter, the hydrogen flow was discontinued, and the reduced samples were allowed to cool to room temperature in an N₂ atmosphere.

3.3.4. Analytical techniques

Temperature programmed reduction (TPR) was performed using an automated chemisorption analyzer AutoChem II 2920 (Micrometrics, USA). Approximately 0.25 g of sample was placed in a quartz U-tube fitted with quartz wool which was fixed to the bottom of the tube. TPR analyses were performed using 10 vol.% H₂/Ar at a flow rate of 50 mL/min. Before analysis, the sample containing tube was purged at room temperature for 30 min using the latter mentioned gas. Thereafter, the furnace was heated at a rate of 10 °C/min to 1000 °C while continuously recording hydrogen consumption with a thermal conductivity detector. This instrument had a maximum maintainable temperature of 1000 °C.

Scanning electron microscopy (SEM) equipped with an energy dispersive x-ray spectrometer (EDX) was used to perform surface and subsurface characterization of unreduced/reduced chromite particles in backscattered electron mode. An FEI Quanta 250 FEG SEM incorporating an Oxford X-map EDX system operating at 15 kV and a working distance of 10 mm was used. For subsurface analysis, treated chromite particles were set in resin, cross-

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sectioned, and polished using an SS20 Spectrum System Grinder polisher before being mounted on Al stubs using carbon adhesive tape. All samples considered for SEM analysis were coated with carbon using an Emscope TB 500 carbon coater.

Crystalline phase analysis of bulk samples was performed by X-ray diffraction (XRD) utilizing a Rigaku D/MAX 2500 rotating-anode powder diffractometer with Cu K α radiation at 50 kV, 260 mA, a step-scan of 0.02°, and a scan rate at 1/min in 2h from 5° to 70°. Phase identification was performed using JADE v.3.9 with the ICDD and ICSD diffraction databases. Further analysis was done by mounting cross-sectioned polished pellets on glass slides and carbon-coating them before characterization by electron probe microanalysis (EPMA). EPMA analyses were done to determine the oxidation states of the transformation products. Analysis was done using a JEOL JXA-8900 electron microprobe fitted with five wavelength dispersive spectrometers at an accelerating voltage of 20 kV and a beam current of 26 nA.

The extent of Cr and Fe metallization was determined after the reduction of chromite by solubilizing Cr and Fe through hot-acid leaching. The treated chromite was leached using a 50 vol.% H₂SO₄ solution at 90 °C for 60 min. Thereafter, the solubilized Cr and Fe contents were determined using ICP-OES

ICP-OES was performed by using a 5110 ICP-OES Instrument coupled with a VistaChip II CCD detector. The instrument was calibrated using Ultraspec aqueous certified single element reference standards (Fe, Cr) obtained from De Bruyn Spectroscopic Solutions (South Africa).

Considering that during size fractioning, gangue mineral (i.e., non-chromite, siliceous particles) particles could collect within a certain size range, the total Cr and Fe content of the respective size fraction were determined, and the extent of Cr and Fe metallization calculated as a function of the total Cr and Fe contents present in each size fraction.

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A Siebtechnik pulverizer was used to mill each size fraction. All parts of the pulverizer that made contact with the chromite during milling were made of SiC to prevent Fe contamination during the milling procedure. A sample was milled for 2 min to obtain a particle size distribution of which 90% of the particles were below 75 μm . Total Cr and Fe were determined for each size fraction by high-temperature alkaline fusion using Na_2O_2 . Alkaline fusion was performed on all size fractions by reacting 0.2 g of the milled chromite with 2 g Na_2O_2 and 0.5 g Na_2CO_3 , respectively, in a zirconium crucible. The fused material was then solubilized using a 20% mixture of 1:1 water: HNO_3 and the Cr and Fe contents were determined by ICP-OES.

3.3.5. Expressing the extent of metallization

Two terms are generally used to express the extent of Cr and Fe reduction; either in terms of lowering the oxidation state (e.g., $\text{Fe}_2\text{O}_3 (\text{Fe}^{3+})$ reduced to $\text{FeO} (\text{Fe}^{2+})$) or metallization (e.g., Cr_2O_3 reduced to Cr^0).^[12] Barnes et al. (1983) defined Reduction (%R) and Metallization (%M) as the following:^[12]

The removal of oxygen is associated with %R and is defined in terms of the oxygen mass loss expressed in Equation 3-1:

$$\%R = \frac{\text{Mass of oxygen removed}}{\text{Original removable oxygen}} \times 100 \quad (\text{Equation 3-1})$$

In a case where solid carbon is used as a reductant, CO will form as a product in the reduction process of chromite and for this reason, the reduction can also be described as:^[12]

$$\%R = \frac{\text{Mass of CO evolved}}{28/16 \times \text{original removable oxygen}} \times 100 \quad (\text{Equation 3-2})$$

$$\%M = \frac{\text{Cr}^0 + \text{Fe}^0}{\text{Cr}_{\text{tot}} + \text{Fe}_{\text{tot}}} \times 100 \quad (\text{Equation 3-3})$$

Where Cr^0 and Fe^0 are the total amounts of metalized Cr and Fe, and Cr_{tot} and Fe_{tot} are the total Cr and Fe contents of the original chromite. Furthermore, Barnes et al. (1983) proposed that

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due to the possible concurrence of the reduction of Fe_2O_3 to FeO and metallization of FeO to Fe and Cr_2O_3 to Cr , there is no linear relationship between chromite's reduction and its metallization.^[12]

However, there is a close resemblance between the complete removal of oxygen and complete metallization, as 100% reduction corresponds to 100% metallization.^[12] The factors explained by Barnes et al. (1983) have contributed to the statement given by Algie and Finn (1984) which explains the three stages of chromite reduction: At first, the Fe^{3+} is reduced to Fe^{2+} followed by its metallization. The metallization of Cr^{3+} is only initiated after approximately 50% of the Fe^{2+} is metalized. After the completion of Fe reduction, 60% of the Cr reduction could be achieved.^[60, 61]

However, the reduction of chromite by C is relatively well understood and more descriptive expressions have been formulated. In this study, the %Fe and Cr metallization was of importance and expressed individually according to Equation 3-4:

$$\% \text{Fe or Cr metallization} = \frac{\text{Solubilized Fe or Cr}}{\text{Total Fe or Cr content}} \times 100 \quad (\text{Equation 3-4})$$

Where the metalized Fe and Cr fractions of the treated chromite (defined as the fractions of leached Cr and Fe, as determined by ICP-OES analysis) are represented by the solubilized Fe or Cr value, which is divided by the total amount of Fe or Cr present in the untreated chromite ore. The metallization of Fe and Cr are presented individually.

3.4. Results and discussion

3.4.1. Thermodynamic considerations

When kinetic data is not available to characterize a process at elevated temperature, an alternative is to understand the thermochemical aspects that govern the behavior of the chemical species that are in reaction. Thermodynamic considerations are however required to understand what can be achieved, as well as the driving force for reduction to occur. The

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predominant area phase stability diagrams are a tool that allows us to graphically represent the conditions of thermochemical equilibrium of compounds in reaction. The diagrams presented in this section were generated using the methodology proposed by Ramos-Hernandez et. al.^[62], using recently updated thermochemical data that were selected from various sources, both old and recent.^[63-67]

To graphically evaluate the thermochemical conditions of the Cr and Fe reduction processes from chromite (Cr_2FeO_4) using C or hydrogen as a reducing agent, it is necessary to identify the reduction regions of interest (where the Cr and Fe species predominate) for each of the processes in a (Cr, Fe)-C-H-O diagram like Figure 3-1, where the chemical activity of Cr and Fe are represented on the X and Y axes respectively.

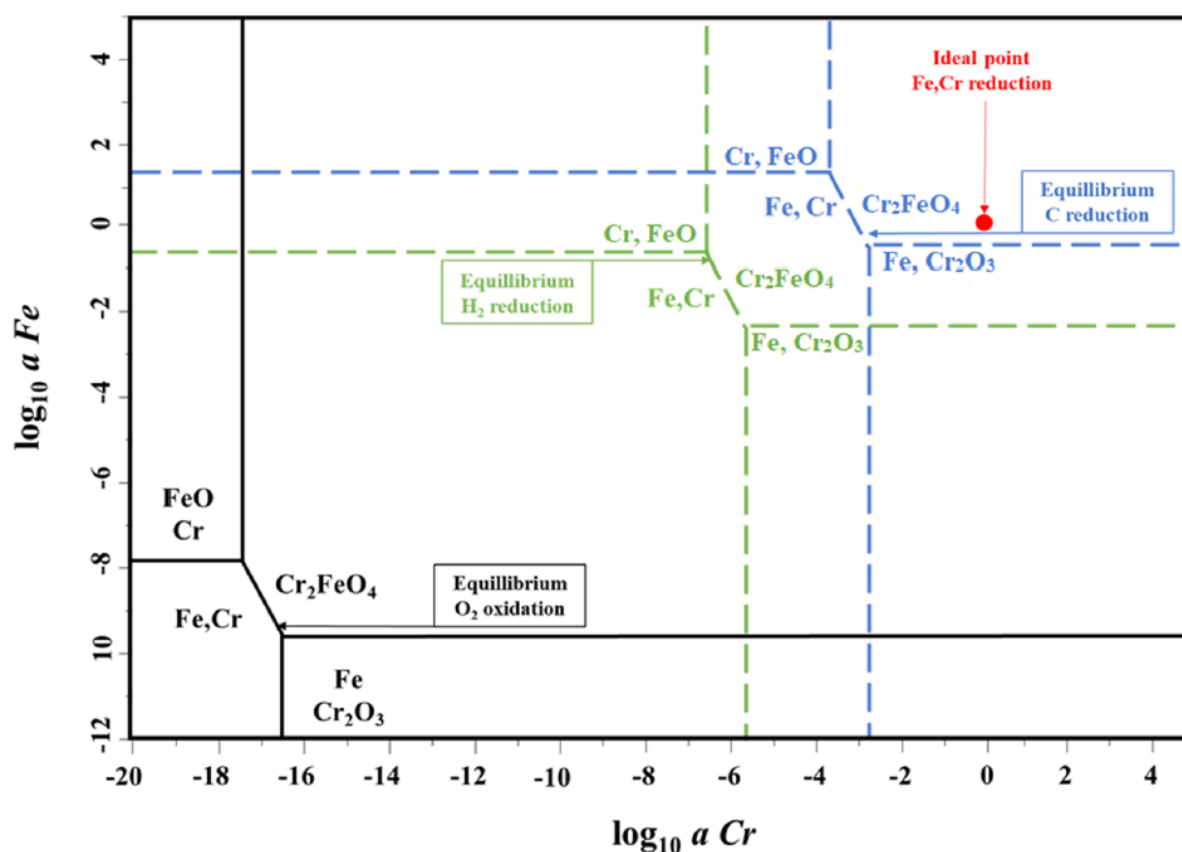
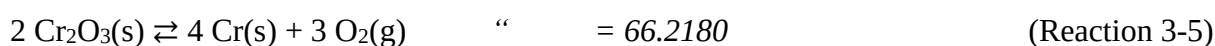
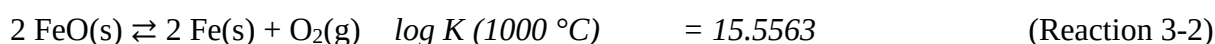
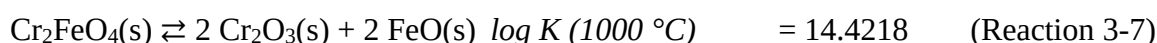


Figure 3-1 Phase stability diagrams of the (Cr, Fe)-C-H-O system as a function of partial pressure of H_2 and H_2O at a temperature of 1000 °C.

As references, the ideal point for the reduction of Cr and Fe is presented in red, considering that the chemical activity of each reduced metallic element takes the value of the unit ($\log a_M = 1$). Furthermore, the equilibrium lines in black correspond to the Cr_2FeO_4 reduction reactions in an environment containing O_2 . In this environment four regions of stability are defined where Cr_2FeO_4 predominates and where the following pairs of species: Fe-Cr, FeO-Cr, and Fe- Cr_2O_3 decomposition reactions have been considered:



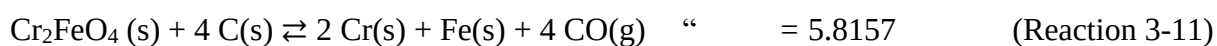
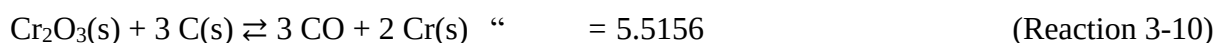
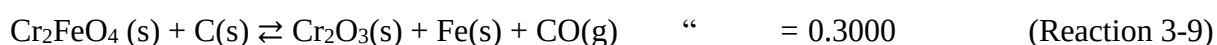
It is worth mentioning that there is a decomposition Reaction 3-7 that cannot be drawn on the diagram because it is independent of the variables being evaluated; however, its thermochemical viability can be evaluated as indicated below.



Each chemical reaction presents its corresponding value of the equilibrium constant ($\log K$) at 1000°C which is related to the value of the standard Gibbs free energy as $\Delta G^\circ = -RT \log K$. Each set of reactions was written considering this value in descending order to carry out a numerical evaluation of the thermochemical conditions of each one of them since the thermochemical viability of a reaction can be evaluated numerically considering it inversely proportional to the absolute value of $\log K$; however, when the $\log K$ value is zero, it is established that the reaction is in thermochemical equilibrium. Also, a positive value for $\log K$ indicates the thermochemical viability of the forward reaction (as written), while a negative value implies viability for the reverse reaction.

Based on the criteria described in the previous paragraph, all reduction reactions (Reactions 3-2 to 3-6) are not viable, considering the negative value of $\log K$ and the magnitude of its absolute values; that is why these reactions were considered an extreme case of comparison. However, relatively, it can be identified that the reduction of Cr and Fe from Cr_2FeO_4 (Reaction 3-4) is more viable than the reduction of Cr from Cr_2O_3 (Reaction 3-5) by 23.6 orders of magnitude. Although Reactions 3-4 and 3-5 have lower viabilities than Reactions 3-2 and 3-3, where the reduction of Fe from FeO (Reaction 3-2) is relatively more viable than from Cr_2FeO_4 (Reaction 3-2) by 3.5 orders of magnitude. Reaction 6 is the reaction with the lowest thermochemical viability and its interpretation in the case study of this work is meaningless; however, it is imperative to define the area of stability for Cr_2FeO_4 on the phase stability diagram. Reaction 3-7 is practically more viable, even more so than Reaction 3-2; this is the reason why the reduction of Fe and Cr is typically evaluated from Reactions 3-2 and 3-4.

The equilibrium lines in blue correspond to reduction reactions using C as a reducing agent and considering only CO as a byproduct (normally employed in carbothermic processes):



It is well understood that during the carbothermic reduction of chromite, Fe-oxide reduction initiates before the Cr_2O_3 constituency.^[61, 68] Considering this, the reaction kinetics of pure Fe-oxides and Cr_2O_3 and with carbon and hydrogen was considered separately to gain insight into their expected reactivity. The carbothermic reduction of Fe- and Cr-oxides of

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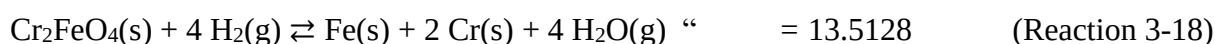
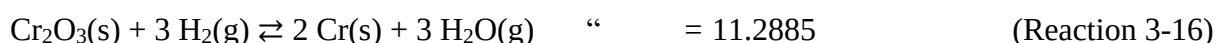
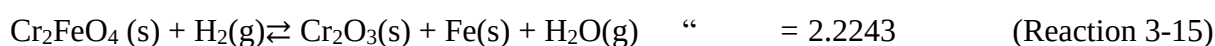
chromite proceeds according to the following reactions (for naturally occurring chromite, both Fe^{3+} and Fe^{2+} are present).^[12]

In the first stages of reduction, Fe_2O_3 (Fe^{3+}) is reduced to FeO (Fe^{2+}) without any metallization,



Subsequently, metallization occurs as FeO (Fe^{2+}) is reduced to Fe^0 (Reaction 3-8) and lastly, Cr_2O_3 (Cr^{3+}) is metallization to Cr^0 (Reaction 3-10). Considering Reactions 3-3 and 3-4, the reduction and metallization of Fe-oxides should occur at 552 and 694 °C, respectively. Considering Reaction 3-10, the reduction of Cr_2O_3 proceeds at 1263 °C. It is worth noting that during Reactions 3-8 to 3-13, hot CO gas is continuously generated which permeates from the smelting zone upwards through the furnace bed. The hot CO gas acts as a reductant, partially reducing chromite.^[69] The effect of $\text{CO}(\text{g})$ partial pressure was however not considered here.

The reduction reactions of Fe- and Cr-oxides by hydrogen, in terms of oxidation state changes, will likely follow similar routes as Reactions 3-8 to 3-13. The equilibrium lines in green color correspond to reduction reactions and considers H_2O as byproduct:



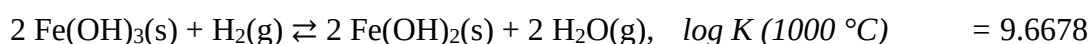
The presence of *in-situ* formed H_2O affects Reaction 3-14 to 3-18, and it has to be taken into account that these reactions proceed as a function of the partial pressure of both H_2 and H_2O .^[70,71]

In the diagram shown in Figure 3-1, the reduction region of the processes that use C and hydrogen as reductants, tend to be closer to the ideal reduction point, than to the reduction

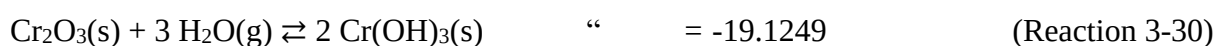
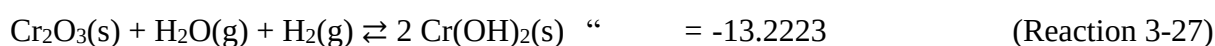
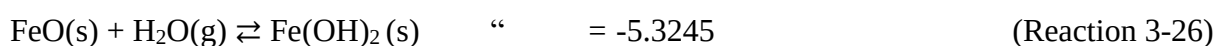
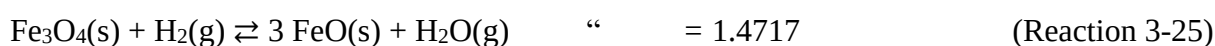
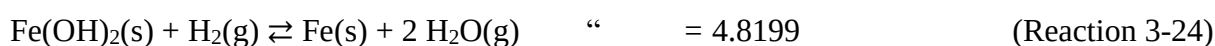
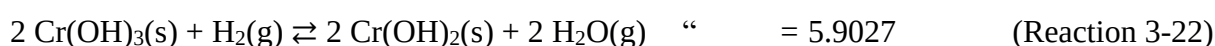
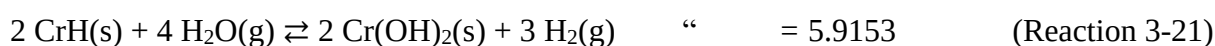
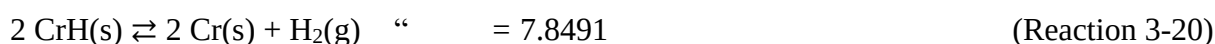
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region of the process in an environment rich in O₂; this indicates that the use of hydrogen as a reducing agent is a thermodynamically good alternative. Furthermore, the main advantage of using hydrogen as a reducing agent is that the main by-product of the process is H₂O, which means that it is a green alternative that contrasts with the greenhouse gases generated in the process that uses C as a reducing agent.

Figure 3-2 shows a full predominant area phase stability diagram for the (Cr, Fe)-H₂-H₂O system, where the Y-axis represents the partial pressure of hydrogen, and the X-axis represents the partial pressure of H₂O. Considering the chemical activity of each of the condensed species of interest (which can be formed from the elements Cr, Fe, H, and O) as a unit, in such a way that the equilibrium lines that establish the stability region of each species correspond to the reduction Reactions 3-14 and 3-16 and another listed below:



(Reaction 3-19)



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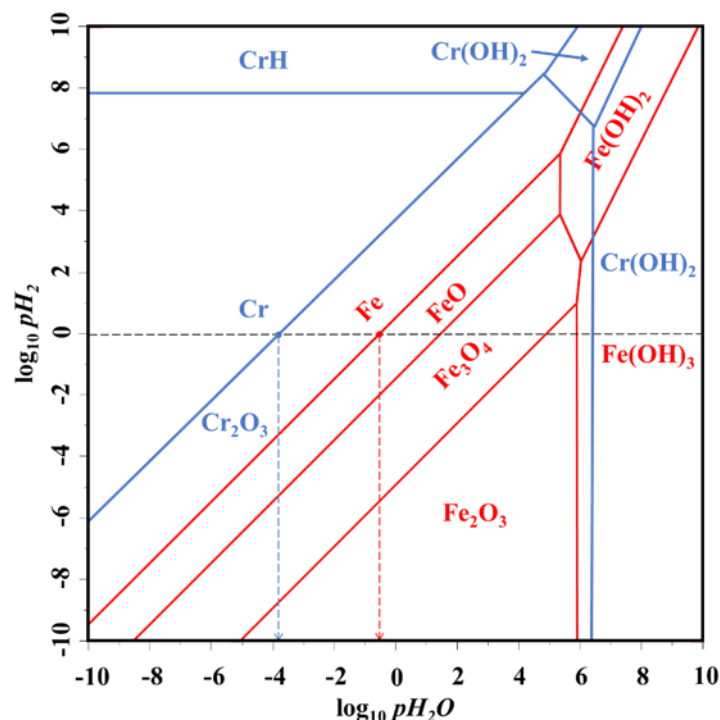
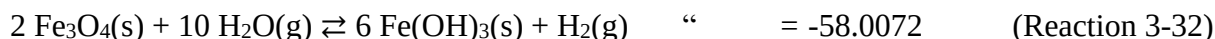
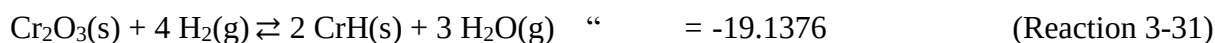


Figure 3-2 Phase stability diagrams of the (Fe, Cr)-H₂-H₂O system as a function of partial pressure of H₂ and H₂O at a temperature of 1000 °C.

The equilibrium lines in blue color correspond to the reactions involving Cr, while the equilibrium lines in red involve Fe. Also, the diagram shows a black dotted horizontal line that corresponds to the value of $\log \text{pH}_2=0$ (that is, $\text{pH}_2 = 1 \text{ atm}$), where two points are also located from which the conditions of $\log \text{pH}_2\text{O}$ of equilibrium for the reduction reactions of Fe (reaction H, $\log \text{pH}_2\text{O} \approx -0.5$) and Cr (reaction K, $\log \text{pH}_2\text{O} \approx -4$). The above indicates that to exclusively reduce Fe and Cr in the system, there must be a partial pressure of H₂O less than or equal to 0.0001 atm; when this partial pressure is between 0.0001 and 0.3162 atm, the Fe and Cr₂O₃ species will predominate and if the partial pressure it is even greater, species such as Fe₃O₄, Fe₂O₃, Fe(OH)₃, Cr(OH)₂ will also predominate. Słowiński and Smoliński (2016)

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showed that the introduction of Fe to an H₂O-rich atmosphere will result in its oxidation to Fe_{0.947}O (shown as FeO here).^[70] It can be seen from Figure 3-2 that Fe is stable in a relatively wide range of H₂/H₂O partial pressure ratios at 1000 °C, with decreasing stability as the partial pressure of H₂O increases. Cr is stable in a relatively small area, which corresponds to a high H₂/H₂O ratio (dry, H₂-rich atmosphere). Chu and Rahmel stated that the reduction of Cr₂O₃ is only possible in oxygen-free and dry hydrogen, assuming that the in-situ generated H₂O is continuously removed from reaction sites.^[71]

Most of the reactions with a log K value greater than zero are found in the region where the partial pressure of hydrogen is greater than 1 atm, while the reduction reactions with a log K value less than zero are found in the region of partial pressure less than 1 atm, which corresponds to the experimental conditions of this study.

It is important to note that the oxides considered in this study form part of the chromite spinel, i.e., [(Mg²⁺, Fe²⁺)(Al³⁺, Cr³⁺, Fe³⁺)₂O₄].^[1, 72] Chromite is considered isomorphic, with Mg²⁺ and/or Fe²⁺ occupying tetrahedral sites and Al³⁺, Cr³⁺, and/or Fe³⁺ occupying octahedral sites at standard ambient conditions.^[73] The presence of Mg²⁺ and Al³⁺ greatly decreases the reducibility of the chromite because these cations form highly stable oxides. It is noted that a magnesium-containing chromite spinel, i.e., (Fe²⁺, Mg²⁺)Cr₂O₄, has a greater resistance to reduction when compared to an Al-containing spinel, i.e., Fe(Cr³⁺, Al³⁺)₂O₄.^[23] Nevertheless, although the reductions reactions (Reactions 3-2 to 3-32) are for pure Cr₂FeO₄, Fe- and Cr-oxides, the conclusions reached from the phase stability diagrams presented are consistent with the results of this work.

3.4.2. Reactivity of chromite with hydrogen

Though thermodynamic explanations of a reaction are a useful tool, it ignores kinetic effects. To determine the actual interaction between the case-study chromite and hydrogen,

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TPR analysis was performed on as-received chromite (Figure 3-3). The initiation of Fe-oxidation state reduction was included in Figure 3-3.

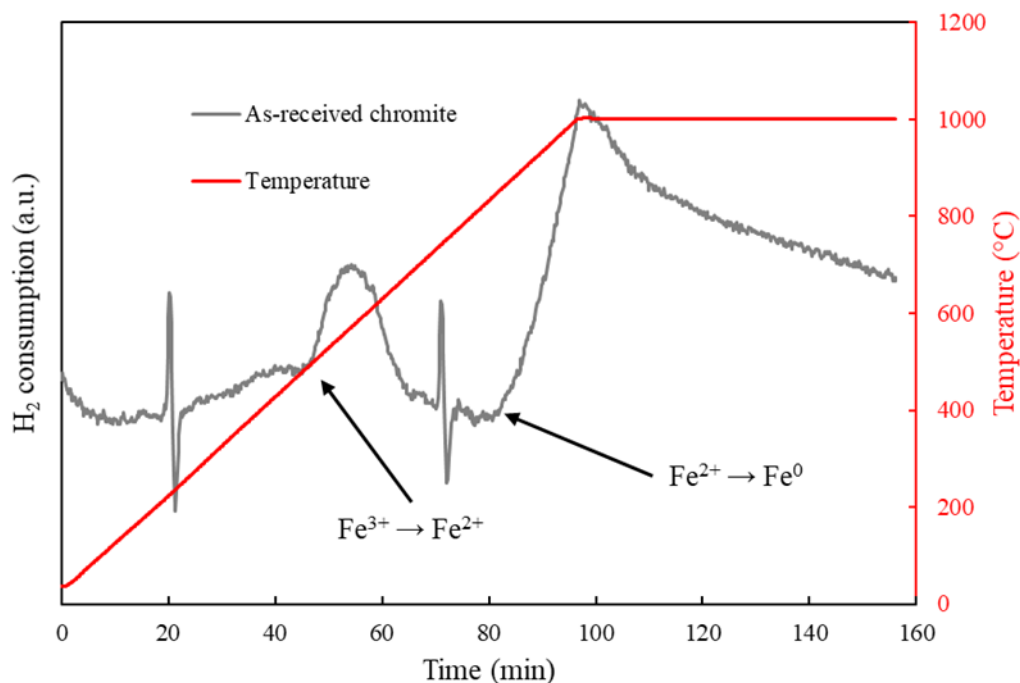


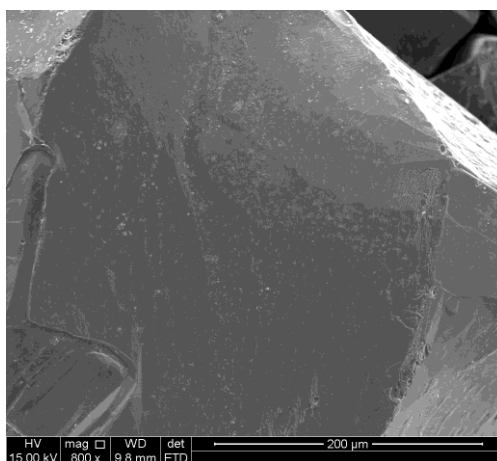
Figure 3-3 Temperature programmed reduction (TPR) profile of as-received chromite reduced in a 10 vol.% H₂/N₂ atmosphere at 1000 °C for 60 min.

Figure.3-3 presents the interaction between hydrogen and chromite as a function of temperature. When considering Figure 3-3, the following deductions may be made: i) the reduction of Fe₂O₃ to FeO (Fe³⁺ to Fe²⁺) initiated at approximately 500 °C, ii) the peak observed at approximately 846 °C is likely the reduction of FeO to Fe (Fe²⁺ to Fe⁰), iii) no magnetite (expressible as Fe(Fe³⁺)₂O₄ or FeOFe₂O₃) to FeO reduction peak is observed likely indicating that the intermediate step proceeds rapidly during the reduction of Fe₂O₃ → FeO, iv) the reaction rate peaked after reaching 1000 °C and proceeded at a slower rate thereafter; suggesting hydrogen diffusion was likely limited by the formation of a surficial metallic layer and restricted hydrogen-chromite reaction surface, or that the reduction reaction rate decreased as a function of decreasing FeO concentration, or that mass transfer was limited due to a build-

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up of H_2O in the atmosphere surrounding the crucible, and v) the absence of addition peaks suggests that Cr_2O_3 did not undergo observable reduction, which was expected considering thermodynamic calculations.

During thermal treatment of chromite, the constituents present in the chromite spinel migrate as a function of the atmosphere. For instance, Fe_2O_3 -rich sesquioxide phases form at the rim of chromite particles as well as the cleavage planes during calcination in air,^[2] whereas metalized Fe forms at the rims during carbon-based solid-state reduction.^[74] To evaluate the constituency mobility of chromite during reduction using hydrogen, the surface of as-received, reduced, and acid-leached chromite particles were explored by SEM (Figure 3-4) and EDX (Table 3-3). Reduced particles presented here were exposed to hydrogen at 1100 °C for 30 min. The acid-leached sample was imaged at a higher magnification than the as-received and treated samples to better illustrate the surface morphology.



(a)

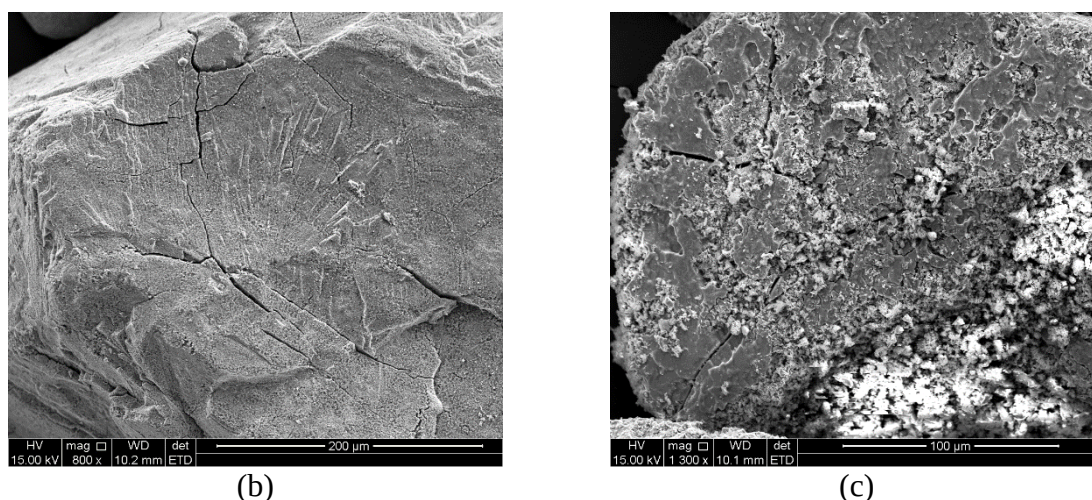


Figure 3-4 Backscattered electron SEM micrographs of the surface of as-received chromite (a, 800 times magnification), hydrogen-treated chromite (b, 800 times magnification), and acid-leached hydrogen-treated chromite (c, 1300 times magnification).

Table 3-3: Microanalyses of chromite particles by SEM-EDX (wt.%). A minimum of eight randomly selected particles were considered and between three to five areas were analyzed with the averages and standard deviations indicated. The Cr/Fe ratio is also indicated.

Sample surface	Detected element (wt.%)						Cr/Fe ratio
	O	Mg	Al	Si	Cr	Fe	
As-received	36.68	6.29	8.45	0.29	30.85	17.44	1.77
	±1.41	±0.30	±0.23	±0.01	±1.49	±0.52	
Treated	26.32	2.12	13.69	0.42	13.94	43.53	0.32
	±3.69	±0.49	±0.48	±0.04	±1.35	±5.4	
Leached	28.98	2.43	14.93	0.66	49.98	3.01	16.60
	±0.68	±0.23	±0.63	±0.18	±0.74	±0.37	

Considering Figure 3-4, it is clear that morphological changes occurred during the reduction and acid leaching procedures of chromite. Table 3-3 indicated that the Cr/Fe ratio of as-received (Figure 3-4a) and treated (Figure 3-4b) chromite particles were 1.77 and 0.32, respectively, suggesting that the surface was enriched with Fe after reduction. The acid-leached chromite particles (Figure 3-4c) had a Cr/Fe ratio of 16.60. This increase in Cr/Fe ratio suggests that the Fe enriched surficial layer was removed during the acid leaching procedure. Hazar-

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Yoruc (2007) found that cracks, dislocations, and cavities/spaces of the spinal are ideal locations for the nucleation of Fe.^[61] Therefore, the cavities observed on the surface of acid-leached particles (Figure 3-4c) may be ascribed to the dissolution of Fe. Table 3-3 further suggests that only Fe was mobile and that Cr likely remained immobile. To gain further insight into the mobility of chromite constituents, treated particles were cross-sectioned and investigated by SEM (Figure 3-5) and SEM-EDX (Table 3-4).

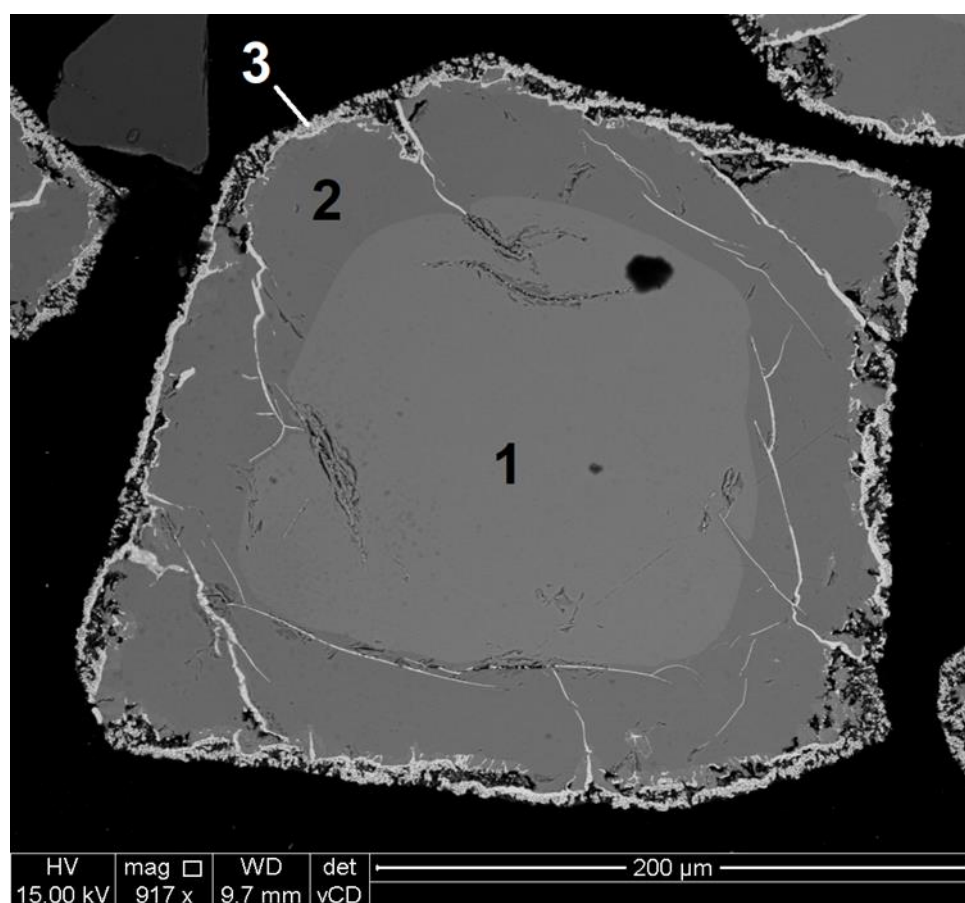


Figure 3-5 Backscattered electron SEM micrograph of a representative polished cross-sectioned chromite particle thermally treated at 1100 °C for 30 min.

Table 3-4: SEM-EDX (wt.%) of the centre (Area 1), transition phase (Area 2), and rim (Area 3) of a representative particle thermally treated at 1100 °C for 30 min, as well as the respective Cr/Fe, Mg/Fe, and Al/Fe ratio for each of the areas. A minimum of eight randomly selected

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particles were considered for EDX analysis and between three to five areas were analyzed with the averages and standard deviations indicated.

Cross-sectioned particle	Detected element (wt.%)						Cr/Fe ratio	Mg/Fe ratio	Al/Fe ratio
	O	Mg	Al	Si	Cr	Fe			
Area 1	31.64	6.19	8.24	0.47	33.41	20.07	1.66	0.31	0.41
	±0.39	±0.07	±0.04	±0.06	±0.04	±0.31			
Area 2	32.42	8.86	8.79	0.38	40.29	9.27	4.35	0.96	0.95
	±0.30	±0.08	±0.13	±0.02	±0.10	±0.33			
Area 3	3.44	0.22	1.53	0	4.05	90.38	0.04	0.002	0.017
	±0.13	±0.30	±0.04		±0.51	±0.35			

Area 1 (center) represents the chromite particle core, Area 2 (transition phase) represents the Fe-deprived area, and Area 3 (rim) represents the surficial Fe-enriched layer. The detected O and Cr in Area 3 may be ascribed to the nearby Area 2.

Figure 3-5 shows that the metallization occurred at the rim (Area 3) of chromite particles. EDX analysis indicates that the rim with a composition of 90.4 wt.% Fe and 4.1 wt.% Cr, which corresponds to a Cr/Fe ratio of 0.04. The O content of 3.4 wt.% indicates that some of the Fe, Cr, Al, and Mg concentrations may not be elemental, which may partially be ascribed to the presence of unreduced oxides. However, EDX is a semi-quantitative analytical technique, with O determined by difference. Area 2 had a relatively low Fe content of 9.3 wt.%, which is ascribed to the migration of Fe towards the particle surface. The Cr/Fe ratio for Area 2 was 4.35, which is significantly higher than the 1.66 Cr/Fe ratio of the particle core (Area 1). A non-related study utilizing the same ore had a similar Cr/Fe ratio (i.e., 1.65) at the particle core,^[58] which suggests that the total Fe content at the particle center was unaffected.

The migration of Fe (as Fe²⁺ and Fe³⁺) towards the rim of chromite particle creates vacancies in the octahedral and tetrahedral sites of the chromite spinel.^[58] The removal of Fe²⁺ from tetrahedral sites increased the Mg/Fe ratio from 0.31 for Area 1 to 0.96 for Area 2, whereas the removal of Fe³⁺ from octahedral sites increased the Al/Fe ratio from 0.45 for Area

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1 to 0.95 for Area 2. More so, the low Mg/Fe and Al/Fe ratios of Area 3 indicate that Mg and Al did not undergo any migration.

As opposed to the significant decrease in Fe observed in Areas 1 and 2 (Table 3-4), the Cr content remained relatively unchanged. Additionally, the observed increase in the Cr/Fe ratio of 1.66 to 4.35 for Areas 1 and 2 supports the migration of Fe towards the particle rim. This is made evident when considering the Cr/Fe ratio of 0.04 of Area 3.

Soykan et al. (1991) proposed the reduction mechanism of chromite as well as the subsequent formation of Cr- and Fe-carbides during carbothermic smelting where carbon is used as the reductant. The reduction mechanism proceeds according to the following four steps:^[68] (i) the surface of the chromite particle serves as the location for the chemical reduction reaction where Fe^{2+} is metalized to Fe. (ii) Cr^{2+} ions migrate from the rim to the transition phase (Area 3 to Area 2) via solid-state diffusion, (iii) at the outer edge of the center (Area 1), Fe^{3+} ions are reduced to Fe^{2+} ions as presented in the following reaction:^[68]



The round and square brackets refer to the tetrahedral and octahedral sites of the spinel lattice, respectively. The formed Fe^{2+} ions migrate from the center to the rim of the particle via solid-state diffusion. After the complete reduction of Fe, the remaining Cr^{2+} ions together with the Cr^{3+} ions are reduced to their metallic state (Cr^0), creating Fe-and Cr depleted spinel of MgAl_2O_4 .^[68]

Though the reaction mechanism proposed by Soykan et al. (1991) is for carbothermic smelting, it is likely true for the employment of hydrogen as a reductant during solid-gas reduction. The use of hydrogen is however limited to the reduction mechanism of Fe-oxides as Cr_2O_3 reduction was not evident when considering Tables 3-3 and 3-4.

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EPMA analysis was employed to determine the chemical compositions of the center (Area 1) and transition phase (Area 2) of treated chromite. The rim (Area 3) was not considered for EPMA as it mainly comprised of metallic Fe. The results obtained from EPMA analysis are represented in Table 3-5.

Table 3-5: EPMA of particle Areas 1 and 2 (as indicated in Figure 3-4) of ore particles reduced by hydrogen at 1100 °C for 30 min. Table 3-5 presents 90 spot analyses from Area 1 (center) and 21 spot analyses from Area 2 (transition phase).

Grain area	Detected phase (wt,%)						
	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO [#]	MnO	MgO	NiO
Untreated*	0.97	11.97	44.45	32.14	0.36	4.45	0.12
	±0.04	±0.18	±0.34	±0.22	±0.02	±0.09	±0.02
Area 1	0.59	16.69	56.14	12.28	0.34	13.71	0.01
	±0.07	±0.25	±0.75	±0.28	±0.06	±0.17	±0.02
Area 2	3.31	21.47	71.82	0.62	0.04	0.67	0.01
	±0.15	±0.28	±0.86	±0.08	±0.03	±0.04	±0.02

* average values of six microanalyses, Paktunc and Cabri (1995)^[72]

[#]total iron

It is evident from Table 3-5 that the total Fe content decreased systematically from Untreated to Area 2, and that the total Fe in Area 2 was <1 wt.%. The decrease in total Fe indicates its migration towards the rim (Figure 3-5), where it occurs as a metallic Fe layer.

The Cr₂O₃ content of Area 1 and 2 increased from 56.1 to 71.8 wt.%, respectively, which may be ascribed to the migration of Fe²⁺ from Area 2 to Area 3. This observation suggests that Cr remained immobile at the investigated reduction conditions. The migration of Fe towards the rim of the particle further leads to changes in the MgO content within the different grain areas. The presence of MgO in Area 2 is non-appreciable and according to EPMA calculations, Area 2 is dominated by eskolaite with the composition of Cr_{1.4}Al_{0.6}O₃. This further suggests that tetrahedral vacancies created in Area 1 were occupied by Mg⁺² originating from Area 2.

Changes in the composition of chromite resulting from reduction by hydrogen are shown in Figure 3-6 in terms of Mg fraction among the tetrahedral cations and Cr fraction

among the octahedral cations in chromite. Increases in the Cr fraction from the original unreacted chromite to Area 1 shown as groups of A and B are resulting from the reduction of Fe^{3+} . With the continued reduction and migration of Fe from the chromite structure, $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio increases from A to B in Figure 3-6. The highest observed $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ratio is 0.87 indicating the extent of Fe reduction under the experimental conditions.

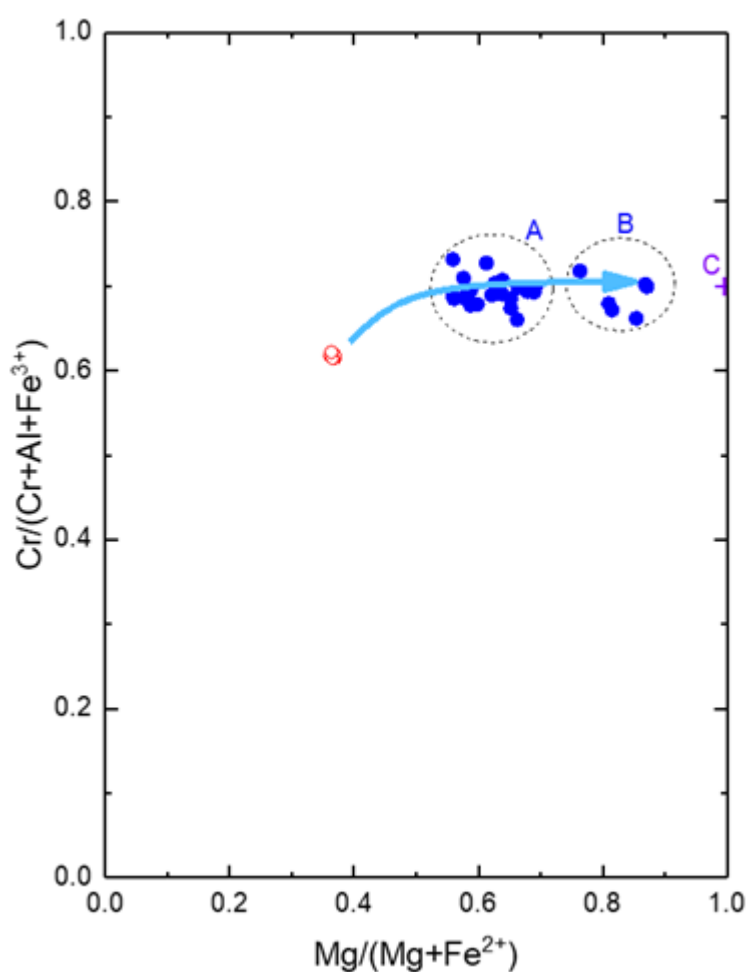
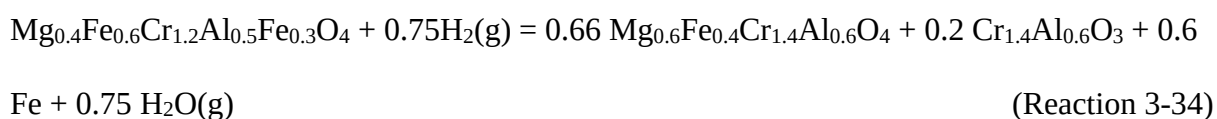


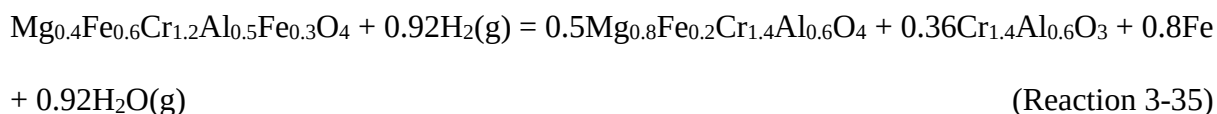
Figure 3-6 Changes in the composition of chromite resulting from reduction by hydrogen (blue symbols grouped as A and B with average chromite formulas of $\text{Mg}_{0.6}\text{Fe}_{0.4}\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_4$ and, $\text{Mg}_{0.8}\text{Fe}_{0.2}\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_4$, respectively. Original untreated chromite compositions are shown by red circles with an average starting composition of $(\text{Mg}_{0.4}\text{Fe}_{0.6})(\text{Cr}_{1.2}\text{Al}_{0.5}\text{Fe}_{0.3})\text{O}_4$.

According to Figure 3-6, the removal of Fe from the chromite spinel yields a partially Fe-depleted chromite phase, and eskolaite with the composition $\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_3$ (as determined by EPMA). The extent of reduction is determined by the amount of Fe removed from the chromite spinel. To illustrate this, the following reactions were compiled based on the results presented in Figure 3-6.

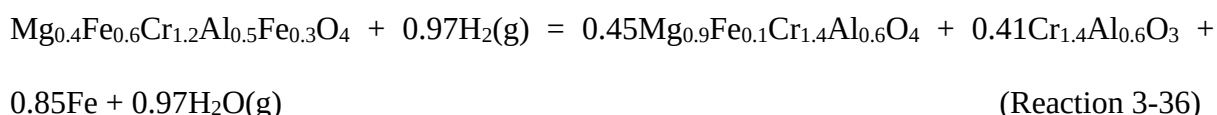
The lowest extent of reduction is indicated as Group A (circled in Figure 3-6) and is expressed as follow:



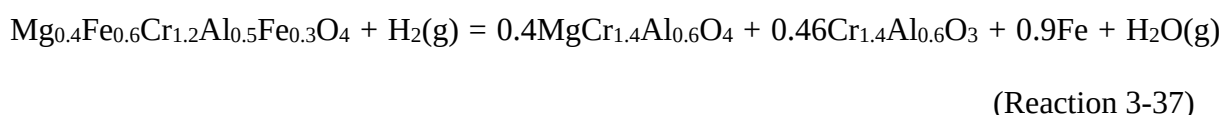
Chromite which has undergone a higher extent of reduction than the chromite shown in Reaction 3-9 is indicated as Group B (circled in Figure 3-6) and is expressed as follow:



Chromite which has undergone near-complete removal of Fe from the spinel is indicated with the arrow as part of Group B and is expressed as follow:



Lastly, chromite which has undergone complete removal of Fe is indicated as C in Figure 3-6 and is expressed as follow:



Considering Reactions 3-34 – 3-37, it is evident that the reduction of the Fe-oxides present in the chromite spinel proceeded systematically and was kinetically limited under parameters considered in this study, i.e., complete removal of Fe was not achieved.

Nevertheless, it is theoretically possible to metalize chromite's total Fe-oxide content by selective metallization using hydrogen (Reaction 3-37).

3.4.3. XRD characterization of pre-reduced chromite fines

To determine the mineralogical changes occurring within the chromite spinel during reduction, quantitative Rietveld refined XRD analysis was performed on as-received, treated, and leached chromite particles (Figure 3-7). The treated particles were reduced at 1100 °C for 30 min. The peaks of importance, i.e., eskolaite and metallic Fe, were indicated. The remained of unmarked peaks are ascribed to chromite and were not labelled.

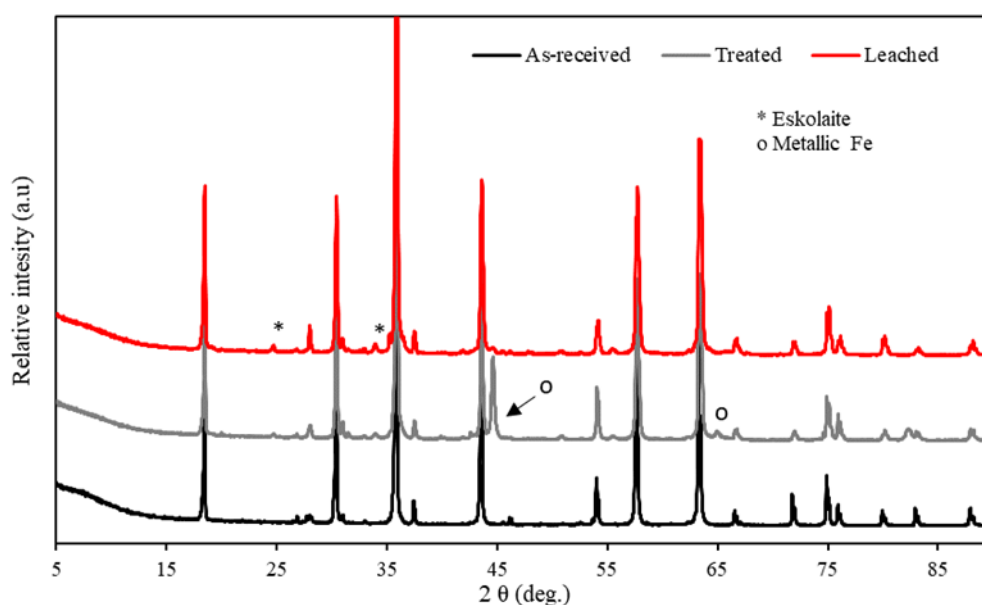


Figure 3-7 XRD patterns of as-received, treated, and acid-leached chromite.

Figure 3-7 shows the formation of metallic Fe and eskolaite phase after the thermal treatment of as-received chromite with hydrogen. During the reduction process, Fe is released from the chromite spinel and afford the formation of eskolaite from the spinel structure in the form of exsolution. It was further clear that the applied acid-leaching procedure effectively removed the metalized Fe from the treated chromite and any remaining Fe may be ascribed to

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its encapsulation (the confinement of an individual molecule within a larger molecule in the host chromite in the form of fine and minor inclusion).

Considering the formation of the eskolaite phase, it is important to determine the effect thereof on the reducibility of hydrogen-treated chromite. An Ellingham diagram was compiled with the HSC thermodynamics program to indicate the change in the reduction ΔG° of pure chromite (Cr_2FeO_4) and eskolaite (shown as Cr_2O_3) by C (Figure 3-8).

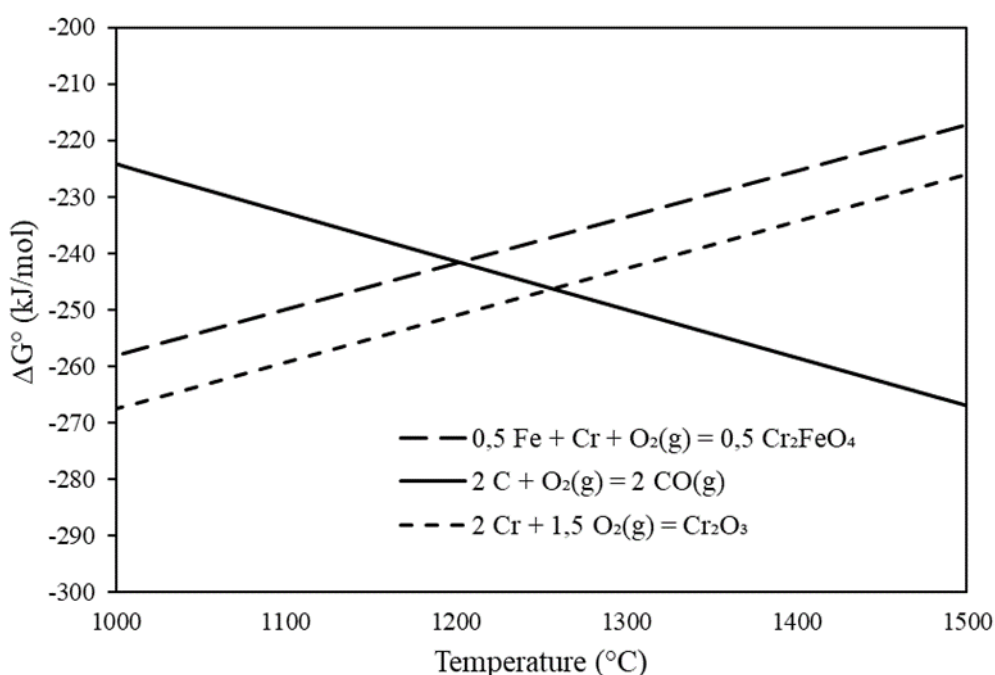


Figure 3-8 Ellingham diagram (ΔG° as a function of temperature) indicating standard ΔG° of the reduction of Cr_2O_3 and Cr_2FeO_4 with solid C (constructed with HSC thermochemical software).^[75]

Figure 3-8 indicates that synthetic chromite Cr_2FeO_4 is reduced at approximately 1200 °C, whereas Cr_2O_3 reduces at a slightly higher temperature of 1250 °C.^[13] The reason is that a sesquioxide solid solution forms between $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 that stabilizes eskolaite (i.e., $\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_3$) against reduction. Both Al_2O_3 and Cr_2O_3 are sesquioxide with a similar corundum crystal structure that could form a range of substitutional corundum-eskolaite-type

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compounds, e.g., $\alpha\text{-(Al}^{3+}, \text{Cr}^{3+})_2\text{O}_3$, at high temperatures.^[76] It is however noted that in practice, the $\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_3$ phase will have a higher degree of resistance to reduction when compared to Cr_2O_3 due to the stabilizing effect of Al.

According to Kleynhans et al. (2016), the formation of Cr_2O_3 may not necessarily be beneficial, as according to thermodynamical calculations, eskolaite reduces at a slightly higher temperature when compared to pure chromite. Kleynhans et al. (2016) proposed that it is crucial to identify the maximum temperature for Fe-oxide reduction while minimizing the extent of eskolaite-phase formation.^[27] From this study, it is evident that eskolaite-phase formation is ascribed to the removal of Fe from the chromite spinel.

3.4.4. Effects of reduction time and particle size on metallization

To evaluate the effect of particle size on the extent of Fe and Cr metallization, size partitioned chromite (refer to d_{90} values, Table 3-1) was reduced at 1100 °C for 30 min (Figure 3-9). It is evident from Figure 3-9 that the degree of Fe and Cr metallization increased as the particle size decreased. The smallest size partition (d_{90} of 140 μm) had the highest %Fe and %Cr metallization, i.e., 57% Fe and 7.5% Cr metallization. The lowest percentage of metallization was observed for the largest size partition (d_{90} of 941 μm), i.e., 18% Fe and 0.25% Cr metallization.

The observed effect of particle size on chromite metallization was however expected, considering that the larger particle surface area is present for the smallest size partition (d_{90} of 140 μm), affording a greater chromite/hydrogen contact boundary when compared to the largest size partition (d_{90} of 941 μm). More so, during the initial phase of the reduction reaction, the reaction occurs at the surface and sub-surface of the chromite particles, which suggests a relatively short diffusion path for both Fe-movement and hydrogen penetration.^[61, 68]

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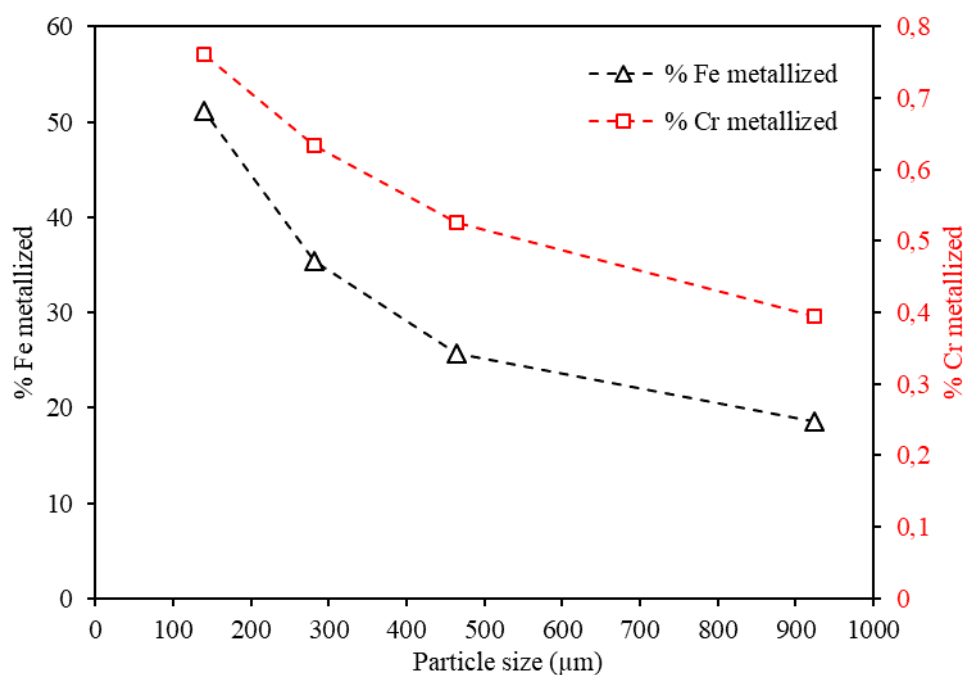
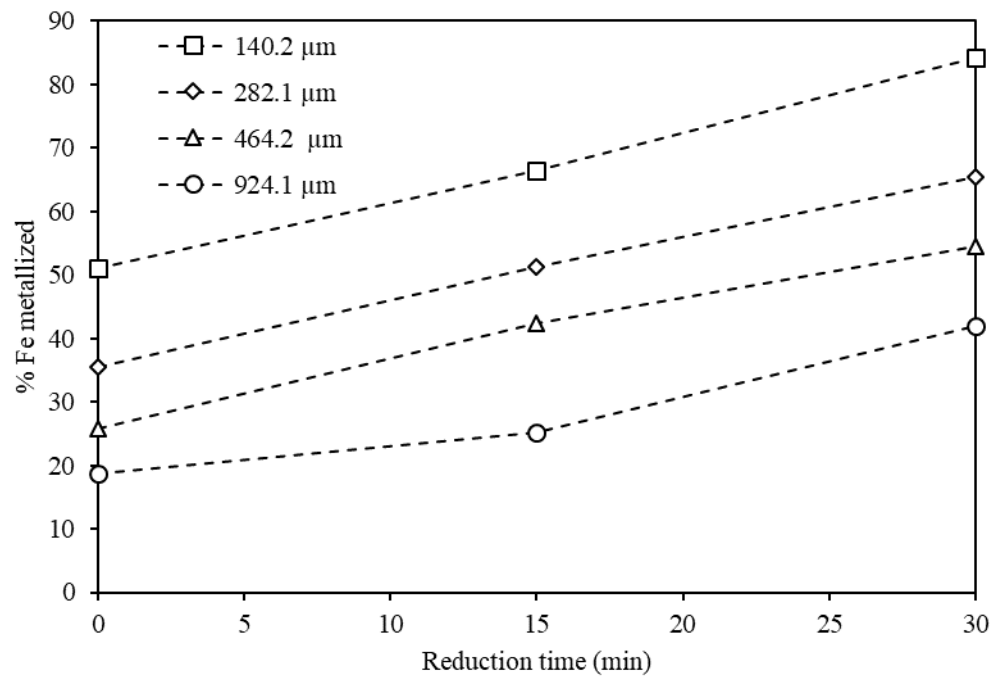
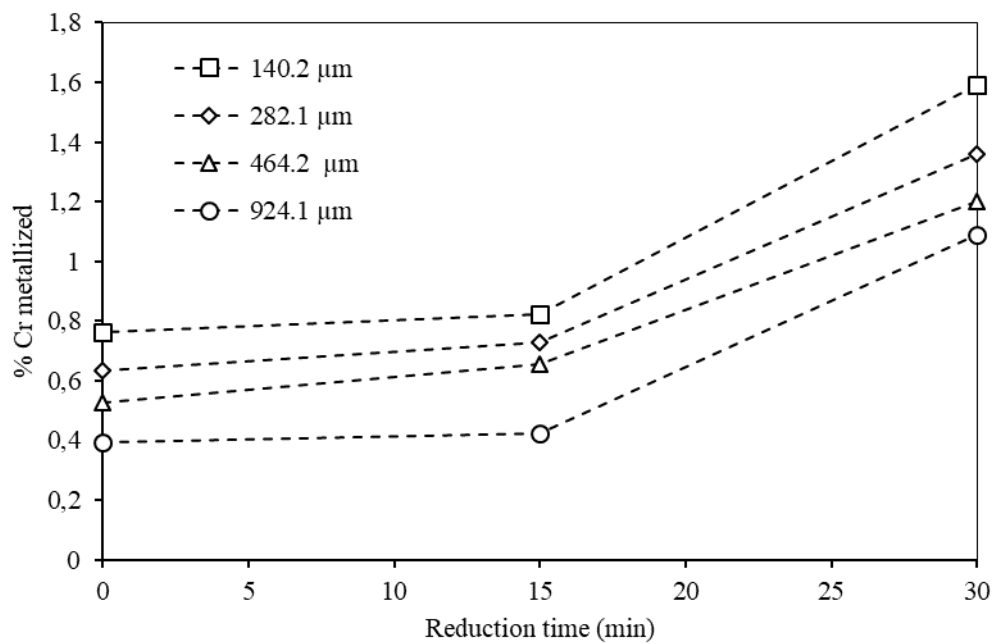


Figure 3-9 The effect of particle size on Cr and Fe metallization. Thermal treatment was performed at 1100 °C for 30 min.

To evaluate the effect of reduction time on the extent of Cr and Fe metallization, the size partitioned chromite was reduced isothermally at 1100 °C for between 0 and 30 min (Figure 3-10).



(a)



(b)

Figure 3-10 The effects of reduction time on Fe (a) and Cr (b) metallization during isothermal treatment at 1100 °C.

Figure 3-10a further shows that the %Fe reduction had a near-linear trend. The %Fe metallization increased systematically from 51 to 84% for the smallest size fraction (d_{90} of 140.2 μm) as the isothermal reduction time increased from 0 to 30 min. A similar trend was

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observed for all other size fractions (d_{90} of 282.1 to 924.1 μm). Considering the relatively linear %Fe, it is likely that the formation of the surficial Fe layer did not curtail hydrogen's accessibility to the underlying Fe-oxides present in the bulk material.

For all four particle size fractions, Figure 3-10b indicated very little Cr metallization during the first fifteen minutes of the reduction process, followed by a relatively significant increase in metallization. This can likely be explained by the ionic diffusion mechanism proposed by Soykan et al. that suggested reduced Cr^{2+} is metalized to Cr^0 after the complete reduction of Fe.^[68] However, considering that the highest %Cr metallization did not exceed 1.52%, it is evident that the reduction of Cr-oxide present in the chromite spinel was insignificant under the investigated conditions.

It can therefore be concluded that the metallization of Fe-oxides present in chromite occurs readily, whereas Cr-oxide metallization was insignificant.

3.4.5. Practical implementation

This study was mainly dedicated to exploring the fundamentals of incorporating hydrogen as a reductant during chromite smelting. To guide further development, it is worth mentioning the limitations of the current study and aspects that need to be considered in the future. It is further important to consider the existing infrastructure of FeCr smelters, and the chemical properties of hydrogen, when developing an approach to incorporate hydrogen as a reductant.

Firstly, existing industrial processes employing high temperatures before smelting are considered. A significant fraction of chromite is beneficiated and pelletized via two high-temperature processes.^[28] The existing pellet curing processes are summarized: i) oxidative sintered pellets are generated by batching chromite, 1 to 2 wt.% carbonaceous reductant fines such as (coke, gas coke, char, and anthracite), and 1 wt.% refined clay (usually bentonite).

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Green pellets are then generated in a pelletization drum and cured/sintered between 1400 to 1500 °C,^[6, 77] ii) pre-reduced pellets are generated by batching chromite ore, 12 to 14 wt.% carbonaceous reductant, and 3 to 4.5 wt.% clay binder.^[6] The green pellets are then cured/pre-reduced between 1300 to 1400 °C.^[3, 6] The hot pre-reduced green pellets are fed directly without being screened to a closed SAFs.^[78, 79]

In both pellet curing processes, green pellets are directly exposed to thermal energy sources. The incorporation of hydrogen directly into the pellet curing kilns as part of the kiln atmosphere is perplexed by the combustion properties of hydrogen. For instance, hydrogen has a flammability range (in air) of 4–75 vol.%, an auto-ignition temperature of approximately 570 °C, and minimum ignition energy of 0.02 mJ.^[57, 59, 80-82] Therefore, hydrogen ignition would be a certainty within its combustion range if the required amount of oxygen is present within the furnace atmosphere. Nevertheless, the addition of hydrogen outside its 4–75 vol.% flammability range is possible but would be a major safety concern and operational perplexity. Considering the latter, the incorporation of hydrogen as a reductant will require a designated process as its incorporation into existing infrastructure is unlikely. Selecting a suitable furnace is critical, and the employment of an enclosed and externally heated furnace is the evident choice. Though, internal heating using hot gas could also be considered.

The stage at which the hydrogen treatment is incorporated in the overall chromite smelting process is another critical consideration. Two scenarios are considered here; i) run-off-mine ore (ore as recovered from mines) is treated before beneficiation and a Fe-separation step (magnetic, chemical, or density) is included as part of the beneficiation circuit, ii) cured pelletized chromite is subjected to hydrogen treatment. Considering the two pellet types (oxidative sintered and pre-reduced), the effects of hydrogen treatment on oxidized and pre-reduced chromite should be determined. Though, it is likely that the hydrogen treatment of pre-

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reduced pellets would not be beneficial, as a significant fraction of Fe would already be in a metallic state.^[83]

Considering this section, it is clear that further research is required on the use of hydrogen and its real-world application. It is proposed that further fundamental research be conducted to quantify kinetic parameters for the different reactions as a basis for process design. Hereafter, a comprehensive techno-economic study be performed.

3.5. Conclusions

In this paper, we present the reduction of naturally occurring chromite using hydrogen. It was shown that the reduction of $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} \rightarrow \text{Fe}^0$ for as-received chromite, initiates at 500 and 846 °C, respectively. It was found that three distinct areas were present within chromite particles after hydrogen reduction, i.e., a rim area enriched by metallic Fe, a Fe-deprived transition phase, and a centre phase representative of untreated chromite. The Cr/Fe ratios of the rim, transition phase, and centre were 0.04, 4.35, and 1.66, respectively.

Removal of the Fe layer by hot-acid leaching revealed an underlying eskolaite-phase ($\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_3$) phase, which suggests the exsolution of at least a fraction of chromite's Cr-oxide content. Preliminary tests showed that particle size had a relatively significant effect on the %Fe and Cr metallization. Also, the %Fe metallization increased near-linearly with increasing reduction time, while the %Cr metallization showed a relatively appreciable increase as the %Fe metallization increased. The highest %Fe metallization was achieved for chromite with a d_{90} value of 140.2 μm , treated with hydrogen at 1100 °C for 30 min, while the %Cr metalized was approximately 1.52%. This suggests that, under the considered experimental parameters, the Cr-oxide content of chromite was essentially unaffected.

Lastly, we indicate the limitations of employing hydrogen as a chromite reductant and indicate that its incorporation into existing infrastructure is unlikely. Specialized alterations to

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existing infrastructure are required to prevent unwanted hydrogen ignition during operations.

We further propose that significant research and development are required before hydrogen can be employed as a real-world chromite reductant.

Acknowledgments: This study was funded by the Research Council of Norway (RCN) as the Thanos project (INPART Project 309475) and is acknowledged. The Department of Science and Innovation, South Africa, and HySA Infrastructure Centre of Competence, South Africa, are also acknowledged for financial support through the KP5 program. The authors thank Nico Lemmer, Kosie Oosthuizen, Sarel Naude, and Thabo Diobe at the North-West University for the assistance provided during sample preparation and analysis. Thanks, are also given to Derek Smith and Dominique Duguay at CANMET for XRD and electron microprobe analyses, respectively.

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CHAPTER 4: THE EFFECT OF PRE-OXIDATION ON THE REDUCIBILITY OF CHROMITE BY HYDROGEN: A PRELIMINARY STUDY

The article presented in Chapter 4 was published by *Minerals* in 2022, Vol. 12, 911 (25 pages). (DOI: <https://doi.org/10.3390/min12070911>), and no permission from the copyright holder is required. Journal details can be found at <https://www.mdpi.com/journal/minerals> (date of access 31/07/2022). The article is published under an open-access license. The material published in the article can be re-used by any person if proper accreditation/citation of the original publication is given. For more information on open access publications, please visit <https://www.mdpi.com/openaccess>. The front page of the published article is presented in Appendix B.

4.1. Author list and contributions

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Contributions

The contributions of the various co-authors were as follows:

Author Contributions: The majority of the work, i.e., experimental, data processing and interpretation, research, and writing of the scientific paper, was performed by the candidate, J.D. S.P.D.P. (supervisor) assisted by providing conceptual ideas and recommendations regarding experimental work and writing of the article. M.T., E.R., and S.P.D.P contributed to the reviewing and editing of the article. Financial support was provided by M.T. and D.G.B.

Abstract: The majority of ferrochrome (FeCr) is produced through the carbothermic reduction of chromite ore. In recent years, FeCr producers have been pressured to curb carbon emissions, necessitating the exploration of alternative smelting methods. The use of hydrogen as a chromite reductant only yields water as a by-product, preventing the formation of carbon monoxide (CO)-rich off-gas. It is however understood that only the Fe-oxide constituency of chromite can be metalized by hydrogen, whereas the chromium (Cr)-oxide constituency requires significantly higher temperatures to be metalized. Considering the alternation of chromite's spinel structure when oxidized before traditional smelting procedures, the effects on its reducibility using hydrogen were investigated. Firstly, the effect of hydrogen availability was considered and shown to have a significant effect on Fe metallization. Subsequently, spinel alternation induced by pre-oxidation promoted the hydrogen-based reducibility of the Fe-oxide constituency, and up to 88.4% of the Fe-oxide constituency was metallized. The Cr-oxide constituency showed little to no reduction. The increase in Fe-oxide reducibility was ascribed to the formation of an exsolved Fe₂O₃-enriched sesquioxide phase, which was more susceptible to reduction when compared to Fe-oxides present in the chromite spinel. The extent of Fe

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metallization of the pre-oxidized chromite was comparable to that of unoxidized chromite under significantly milder reduction conditions.

Keywords: pre-oxidation; metallization; hydrogen; reduction; chromite; ferrochrome/ferrochromium

4.2. Introduction

Chromite ore, unit formula of $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Cr}, \text{Fe}^{3+})_2\text{O}_4$, is the only commercially exploited source of new chromium (Cr) units.^[1-3] Approximately 90 to 95% of chromite ore is utilized to produce several grades of ferrochrome (FeCr).^[3-5] FeCr, a crude alloy between Cr and iron (Fe), is produced through the energy-intensive carbothermic smelting of chromite ore.^[4,5] Temperatures of 1600–1700 °C within the smelting zone are required to allow metallization and separation of the metal and slag phases.^[6] Semi-closed and closed submerged arc furnaces (SAFs) are mainly used during the production of FeCr in South Africa. Direct current (DC) arc furnaces are also used but to a lesser extent.^[3] During smelting, the specific energy consumption of a furnace is affected by a variety of factors, e.g., feed material pre-screening, if a fraction of the Cr- and Fe-oxide content has been pre-reduced, and if the chromite charge is pre-heated. For instance, the energy consumption of a semi-closed SAF operating on unscreened feed materials can be as high as 4500 kWh/t FeCr produced, whereas a closed SAF operating on hot-fed pre-reduced chromite can be as low as 2000 kWh/t of FeCr. The pre-reduction of chromite ore before smelting is an effective technique to lower the energy consumption during chromite smelting, but requires a higher capital investment/operational costs.^[7]

Carbon-based reductants (e.g., coke, coal, or charcoal) are currently used as reductants during chromite smelting, depending on availability and furnace type.^[4,8] For instance, coke is no longer a cost-effective reductant in South Africa as it has become expensive and difficult to

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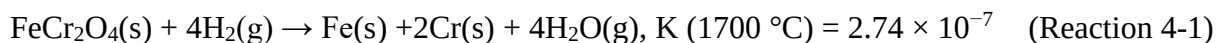
source.^[9] Due to increases in the cost of reductants and scarcity of high-carbon-content reductants, the incorporation of hydrogen as a reductant is becoming more and more attractive. This is especially true for developed countries, where renewable energy is relatively available. For instance, Norway has an abundance of renewable hydro-energy (which accounts for approximately 94% of its energy production).^[10] which is not perplexed by supply–demand intermittence associated with solar and wind energy. Therefore, hydrogen can be produced on site from water, and consumed where needed. In this case, hydrogen does not necessarily need to be stored in large quantities and/or for extended periods. A cost–benefit study has yet to be conducted on the economic implications of partial replacement of C-reductants with hydrogen. From an environmental perspective, however, the use of hydrogen is preferred.

The carbothermic smelting of chromite produces a significant amount of carbon monoxide (CO) in the off-gas. The CO-rich off-gas is flared on the top of furnace stacks to oxidize CO to carbon dioxide (CO₂) before being released into the atmosphere.^[11,12] The significant quantities of released CO₂ is of an environmental concern. In closed SAFs, the volume of off-gas ranges from 2500 to 4000 Nm³/h per MW consumed or from 10,000 to 15,000 Nm³/ton of alloy. The off-gas volume originating from semi-closed SAFs is significantly higher due to air dilution and ranges between 4000 to 13,000 Nm³/h per MW consumed or 15,000 to 55,000 Nm³/ton of alloy.^[13]

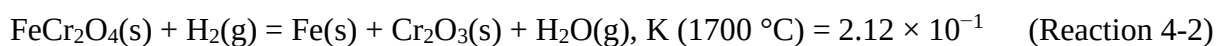
Hydrocarbons, e.g., methane (CH₄), and reformed natural gas (CO and H₂), have been proven as alternative reductants for the production of FeCr via a solid–gas process.^[14,15] In addition, the use of CaCl₂ and Na₃AlF₆ have also been demonstrated as reductants and/or reduction-enhancing additives during chromite smelting.^[16,17] The use of hydrogen was nevertheless considered here as a reductant to curve C-consumption and to avoid the use of

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Cl₂- and F-containing compounds. Theoretically, the complete reduction of pure chromite (FeCr₂O₄) with hydrogen is shown in Reaction 4-1:^[18]



Reaction 4-1 shows that only water is yielded as a by-product when hydrogen is used as a reductant. Though Reaction 4-1 is used for pure chromite, the reduction of naturally occurring chromite ore will proceed differently due to its isomorphic nature.^[19] It is further noted that, thermodynamically, Cr-oxide would require extremely high temperatures to be metallized by hydrogen.^[20] Considering that Reaction 4-1 includes both the metallization of Fe- and Cr-oxides, the equilibrium constant (K) at 1700 °C for Reaction 4-1 is very small and only approaches 0 at temperatures more than 3800 °C. The metallization of Fe- and Cr-oxides will not metallize simultaneously, and it is understood that Fe-oxides are less resistive to reduction when compared to Cr-oxide. Reaction 4-2 presents the metallization of the Fe-oxide fraction of chromite using hydrogen.



Reaction 4-2 shows the reaction if only the Fe-oxide constituency of chromite is metallized. This K value is significantly larger than that of Reaction 4-1, which suggests that Reaction 4-2 is thermodynamically more favorable than Reaction 4-1. It is therefore evident that Fe- and Cr-oxide changes during processing may be considered separately on a thermodynamic level.

Davies et al. (2022) performed a fundamental investigation to show the behavior of chromite when exposed to hydrogen at elevated temperatures. These temperatures were however significantly lower than the temperatures in the smelting zone of a SAF. The authors showed that the Fe-oxide constituency of chromite could be selectively reduced to metallic Fe using hydrogen under relatively mild thermal conditions.^[20] Up to 84% of the total Fe content

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was metalized (and subsequently removed via hot acid leaching) from the chromite spinel, while Cr metallization was insignificant. Fundamentally, it is possible to reduce chromite's entire Fe constituency using hydrogen under certain conditions. However, the Fe reduction process should be considered from an economical perspective too. For instance, employing unrealistic reduction conditions (e.g., extreme reduction temperatures, prolonged reduction periods, and excessive hydrogen utilization) will likely not be a feasible option for the FeCr industry.

In this study, it was considered to include a pre-oxidation step before reduction using hydrogen. It is relatively well understood that the phase decomposition reaction in spinels proceeds via various mechanisms and can be defined by Reaction 4-3.^[21]



The decomposition products of pure chromite, $FeCr_2O_4$, at elevated temperatures are FeO , i.e., (AO) , and Cr_2O_3 , i.e., $[B_2O_3]$. However, considering that chromite is a solid solution of pure spinel end members, the decomposition products are not only affected by the mineral composition, but also by the pO_2 . Exposure to air at high temperatures in an excess of oxygen will oxidize the Fe^{2+} to Fe^{3+} , resulting in a Fe_2O_3 phase.^[21]

Kapure et al. (2010) showed that the pre-oxidation of chromite increases the extent of Fe and Cr metallization during direct reduction using coal. The authors showed that Fe^{2+} present in the chromite spinel oxidized to Fe^{3+} during pre-oxidation, which then forms an exsolved sesquioxide Fe_2O_3 phase. In addition, the migration (and oxidation) of Fe^{2+} from tetrahedral to octahedral sites results in the formation of cation vacancies in the spinel structure. Both the Fe_2O_3 phase and cation vacancy formation promote the reducibility of the chromite ore while contributing to the formation of the slag phase during reduction.^[22] Zhao and Hayes (2010) reported similar observations when pre-oxidized chromite pellets before employing

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solid-state reduction using CO. During the pre-oxidation process at 1000–1200 °C, Fe^{2+} was oxidized to Fe^{3+} , which promoted the extent of subsequent Fe metallization.^[23] Borra et al. (2010) made a similar observation.^[24]

Kleynhans et al. (2016) showed that the pre-oxidation of chromite significantly improved the extent of pre-reduction of chromite during the pre-reduction of pelletized chromite. The optimal pre-oxidation temperature (defined as the temperature at which maximum sesquioxide Fe_2O_3 formation and minimal eskolaite-type phase formation occurred) was determined to be 1000 °C. It was also shown that pre-oxidizing the chromite ore can lower the specific electricity consumption (SEC) of a SAF from 2.4 to 2.2 MWh/t. Additionally, the carbonaceous reductant required during smelting was reduced from 99.5 to 85.5 kg/t pellets.^[25]

Biswas et al. (2018) investigated pre-oxidized Indian chromite and found that the Fe_2O_3 -enriched sesquioxide phase formation was controlled by the oxidation of Fe^{2+} to Fe^{3+} and that longer oxidation times (up to 120 min) and higher temperatures (up to 1000 °C) expedited Fe^{2+} oxidation.^[26] Tathavakar et al. (2015) indicated that South African chromite decomposes into two phases, i.e., $(\text{Mg}_{1-x}\text{Fe}_x)(\text{Cr}_{1-y}\text{Al}_y)_2\text{O}_4$ and $(\text{Fe}_{1-a}\text{Mg}_a)(\text{Cr}_{1-b}\text{Al}_b)_2\text{O}_4$.^[21] Du Preez et al. (2019) confirmed the presence of the two phases, as well as the presence of free Fe_2O_3 , in pre-oxidized chromite fines obtained from a large FeCr producer.^[27]

It is therefore relatively well understood that the reducibility of the Fe constituency of chromite by a C-based reductant can be expedited by chromite's pre-oxidation. However, as far as the authors could assess, the use of hydrogen as a reductant of pre-oxidized chromite has yet to be reported in the peer-reviewed public domain. Therefore, the primary objective was to investigate the effects of pre-oxidation on the reducibility of chromite using hydrogen as a reductant. The secondary objectives were to determine the mildest reaction conditions required for optimal metallization.

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4.3. Materials and Methods

4.3.1. Materials

A metallurgical-grade chromite ore sample was obtained from a large South Africa FeCr producer and was used as the case study ore. It is worth noting that China is classified as the largest stainless steel producer in the world, responsible for 54% of the world's stainless steel supply in 2017. Chromite ore is essential for stainless steel production and the majority of chromite consumed by China's stainless steel industry originated from South Africa (approximately 72% in 2017).^[28] Considering this, the results presented in this study are of international relevance.

A homogeneous and representative sample collection campaign was undertaken at a large South African FeCr smelter and sample collection for experimental work was applied here, as described by Du Preez et al. (2019).^[27] Previously, a detailed characterization of this case study ore was presented by Glastonbury et al. (2015) in a non-related study. Therefore, full characterization is not repeated here.^[29] Of interest here is the Cr₂O₃ content of 44.2 wt% and the FeO (total Fe expressed as FeO) of 24.7 wt%. These values equate to an approximate Cr/Fe ratio of 1.58. This ratio was calculated from the Cr₂O₃ and total Fe contents, which were determined using inductively coupled plasma optical emission spectrometry (ICP-OES).

X-ray diffraction (XRD) of the respective ore revealed that the ore mainly comprised chromite (93.4 wt%) and siliceous gangue (i.e., 6.6 wt% enstatite). It is further worth noting that South African chromite has a relatively low Cr content of approximately 0.59–0.62 mol Cr in the octahedral sites, whereas chromite ores from Brazil, Turkey, and Kazakhstan contain 0.70–0.77 mol Cr. Due to the relatively low Cr content of South African ores, the remainder of octahedral sites is occupied by Al³⁺, which stabilized the spinel against reduction. In addition to this, Fe³⁺, which also occupies the octahedral sites of chromite, is relatively low at

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approximately 0.06 mol.^[30] Similar to Al^{3+} , Mg^{2+} occupying tetrahedral sites stabilized chromite against reduction.^[19] Canaguier showed that Mg-containing chromite ((Fe, Mg) Cr_2O_4) was more resistant to reduction when compared to an Al-containing chromite ($\text{Fe}(\text{Cr},\text{Al})_2\text{O}_4$).^[15]

Hydrogen, the reductant considered in this study, is currently mainly produced from non-renewable sources, e.g., coal, oil, and natural gas, while water electrolysis accounts for approximately 4% of the globally produced hydrogen.^[31] Nevertheless, numerous processes can be employed for generating hydrogen, e.g., thermochemical^[32,33], photocatalytic^[34,35], photochemical^[36,37], photo-electrochemical^[38,39], metal and metal hydride hydrolysis^[40-48], electrochemical^[49-54], and ammonia and formic acid decomposition^[55-57] processes, as well as various biological processes^[58-60]. In this investigation, the hydrogen reductant was generated on-site at Hydrogen South Africa (HySA) Infrastructure, Potchefstroom, South Africa, through proton exchange membrane water electrolysis (PEMWE). A PEMWE stack was powered by photovoltaic energy and the produced hydrogen was stored as a pressurized gas. Therefore, the employed hydrogen is considered green hydrogen as it is generated from renewable energy and a renewable source. The generated hydrogen purity was >99.9%. The nitrogen (99% purity) used in this study was supplied by Afrox, South Africa. The chemicals Na_2O_2 (97%), Na_2CO_3 (99.5%), and HNO_3 (>99.999%) were obtained from Sigma-Aldrich, Johannesburg, South Africa.

4.3.2. Sizing of Chromite

As-received chromite ore was size-partitioned after being screened into the following size fractions, i.e., <106, 106 to 212, 212 to 425, and 425 to 850 μm . Chromite screening was performed using a Haver EML Digital Plus sieve shaker (Haver and Boecker, Oelde, Germany) and stainless steel Haver and Boecker sieves.

Particle size distribution of the screened chromite fractions was determined by laser diffraction particle sizing using a Malvern Mastersizer 3000 (ATA Scientific, Sydney, Australia). Samples were ultra-sonicated before measurements were taken and continuously agitated by mechanical stirring at 2400 rpm during analyses. Laser obscuration was maintained between 10 and 20%. Table 4-1 exhibits the d_{90} , d_{50} , and d_{10} values of as-received and size-fractionated chromite.

Table 4-1: D_{90} , d_{50} , and d_{10} (μm) of as-received and size-fractionated chromite.

Size Equivalent	As-Received	Sieve Sizes (μm)			
		<106	106 to 212	212 to 425	425 to 850
d_{90}	455	133	260	467	778
d_{50}	253	84	178	335	569
d_{10}	132	51	122	238	416

4.3.3. Reduction Procedure

A Carbolite CTF 12 vertical tube furnace (Carbolite Gero, Derbyshire, UK) with a maximum maintainable temperature of 1100 °C was used for all reduction procedures. This reduction temperature was selected as higher reduction temperatures could not be achieved using this furnace. It was however shown by Davies et al. (2022) that up to 84% Fe metallization was achieved at similar reduction temperatures.^[20] A stable heating zone was created within the tube by placing ceramic heat shields at each end of the tube. Both tube ends were sealed with stainless steel caps which acted as a gas inlet and outlet. The thermocouple used to measure temperature was placed at the center of the heating zone, directly adjacent to the tube. The furnace was heated by a series of electrodes which were located alongside the tube.

Reduction was performed by placing 5 or 30 g of size-fractionated metallurgical-grade chromite ore (d_{90} of 133 to 778 μm) in a ceramic (99.8% Al_2O_3) boat crucible in the center of

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the furnace hot zone. The samples were then heated from room temperature to the maximum maintainable temperature of 1100 °C. The samples were heated at a rate of 5 °C/min which was the maximum allowable heating rate for the specifically fitted tube. After the maximum maintainable temperature was achieved, the temperature was kept constant for a duration of 60 to 180 min. The tube was continuously purged with N₂ at a flow rate of 150 mL/min. It was necessary to avoid the presence of oxygen within the furnace considering that hydrogen has a self-ignition temperature of approximately 572–585 °C and a flammability range of 4–75 vol.% in the air at standard atmospheric conditions.^[27,61-63] A hydrogen flow of 150 or 750 mL/min, together with the N₂ flow, was introduced at 600 °C to obtain an approximate 50 and 83 vol.% hydrogen atmosphere, respectively, within the furnace tube. This atmosphere was maintained until 1100 °C was reached and maintained for up to 180 min. Thereafter, the hydrogen flow ceased, and the reduced samples were kept in the tube to cool to room temperature in a N₂ atmosphere.

4.3.4. Pre-Oxidation Procedure

During the industrial preparation of oxidative sintered chromite pellets, referred to as steel belt sintering (developed by Outokumpu, process also referred to as Outotec process), pellets are typically heated to a temperature of 1400–1500 °C before the air is pulled through the pellet bed. By doing so, the carbon content present in the pellets, typically between 1–2 wt% reductant (typically coke), is ignited to allow silicates present in the pellets, i.e., typically refined bentonite or attapulgite clays, to melt. The chromite particles are bound together by these molten silicates.^[4,7] This process affords pellets with the mechanical properties necessary for the ferrochrome smelting procedure, and the process is not implemented to maximize the pre-oxidation of chromite. Zhao and Hayes (2010) showed that the center of industrially produced pellets were un-oxidized, whereas chromite at the pellet boundary was oxidized.^[23]

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Du Preez et al. (2019) heated pellets at a rapid rate from 900 to 1200 °C; the produced pellets had a matching oxidation pattern when compared to the oxidation pattern presented by Zhao and Hayes (2010) and Biswas et al. (2021).^[23,26,27] Therefore, it is accepted that the oxidative sintering process used by industry is not dedicated to chromite's oxidation and is rather employed to produce mechanically strong pellets.

In order to prepare chromite that can be used for mono-variance investigation, pre-oxidized chromite is generated with a representative extent of pre-oxidation. Heat transfer within laboratory scale furnaces is significantly better than industrial-scale furnaces, ensuring that pre-oxidized samples can be representative (i.e., all particles present in the samples are oxidized equally). The oxidation mechanism pellets prepared by oxidative sintering, and the samples prepared in this study, are accepted to follow a similar mechanism, i.e., chromite spinel alteration as a result of heat treatment in an oxygen-containing atmosphere. The only difference was that chromite oxidized here was equally oxidized.

Kleynhans et al. (2016) showed that chromite pre-oxidized at >1000 °C started to be more resistive to pre-reduction. However, in the case of Kleynhans et al. (2016), pre-reduction was determined by considering the amount of metallized Cr and Fe. The authors reported that extensive pre-oxidation resulted in the formation of a Cr-oxide phase, which was more resistive to carbothermic reduction when compared to raw chromite.^[25] An oxidation temperature of 1100 °C was therefore considered for evaluation, as this was the border temperature where Cr-oxide may be stabilized against carbothermic reduction. It has been shown that Cr-oxide metallization using hydrogen is thermodynamically limiting and kinetically challenging.^[20] Therefore, the 1100 °C pre-oxidation temperature was mainly selected to ensure optimal Fe-oxidation.

The chromite ore was oxidized in an Elite BRF15/5 chamber furnace (UK) equipped with a programmable temperature controller. A ceramic (99.8% Al₂O₃) square crucible

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containing 20 g of the specific size-fractionated metallurgical-grade chromite ore (d₉₀ of 133 to 778 μm) was placed in the center of the furnace chamber. During oxidation, the sample was heated in the ambient atmosphere at a ramp rate of 5 $^{\circ}\text{C}/\text{min}$. Each particle size fraction was heated from room temperature to 1100 $^{\circ}\text{C}$. Oxidation times of 60, 120, and 240 min were considered here. Thereafter, the furnace was switched off and the sample was kept in the furnace and allowed to cool to room temperature.

4.3.5. Analytical Techniques

Scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray spectrometer (EDX) was employed to determine the surface and subsurface characterization of unreduced, reduced, and pre-oxidized/reduced chromite particles in backscattered and secondary electron mode. An FEI Quanta 250 FEG SEM (Thermo Fisher Scientific, Waltham, MA, USA), incorporating an Oxford X-map EDX system operating at 15 kV and a working distance of 10 mm, was used. For subsurface analysis, treated chromite particles were mounted in resin, cross-sectioned, and polished using an SS20 Spectrum System Grinder polisher before being placed on Al stubs using carbon adhesive tape. All samples considered for SEM analysis were covered with an Emscope TB 500 carbon coater (Hertfordshire, UK).

XRD was employed to determine the crystalline phase analysis of bulk samples. A Rigaku D/MAX 2500 (Japan) rotating anode powder diffractometer with Cu $K\alpha$ radiation ($\lambda_{K\alpha_1} = 1.5406 \text{ \AA}$) at 40 kV was used. Furthermore, a current of 40 mA, a step scan of 0.034° , and a scan rate at 0.5 sec/step from 0.5 to 130° were used for the analysis. Phase identification was achieved using JADE v.3.9 with the ICDD and ICSD diffraction databases.

The extent of Fe metallization was determined after the reduction of chromite by solubilizing Fe through hot acid leaching. The treated chromite was leached using a 50 vol.% H_2SO_4 (98%) solution at 90 $^{\circ}\text{C}$ for 60 min. Thereafter, the solubilized Fe contents were

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determined using ICP-OES. ICP-OES was performed using an Agilent 5110 ICP-OES Instrument (USA) coupled with a VistaChip II CCD detector. Ultraspec aqueous-certified single-element reference standards (Fe, Cr) obtained from De Bruyn Spectroscopic Solutions (South Africa) were employed to calibrate the instrument.

During size fractioning, gangue mineral (i.e., non-chromite, siliceous particles) particles could collect within a specific size range, and the total Cr and Fe contents of the respective size fraction were determined. Subsequently, the extent of Cr and Fe metallization was calculated as a function of the total Fe contents present in each size fraction. A Siebtechnik pulverizer was used to mill each size fraction. All parts of the pulverizer in contact with the chromite during milling were made of SiC to prevent Fe contamination during the milling procedure. Each sample was milled for 30 s to obtain a particle size distribution, of which 90% of the particles were below 75 μm . The total Cr and Fe contents were determined for each size fraction by high-temperature alkaline fusion using Na_2O_2 and Na_2CO_3 . Alkaline fusion was performed on all size fractions by reacting 0.2 g of the milled chromite with 2 g of Na_2O_2 and 0.5 g of Na_2CO_3 , respectively, in a zirconium crucible. The fused material was subsequently solubilized using a 20% mixture of 1:1 water: HNO_3 . The total Cr and Fe contents were then determined by ICP-OES.

4.3.6. Expressing the extent of metallization

Barnes et al. (1983) showed that the total % metallization (i.e., %M) can be determined using the following equation:^[8]

$$\% \text{ M} = \frac{\text{Cr}^0 + \text{Fe}^0}{\text{Cr}_{\text{tot}} + \text{Fe}_{\text{tot}}} \times 100 \quad (\text{Equation 4-1})$$

Here, Cr^0 and Fe^0 are the total amounts of metalized Cr and Fe, and Cr_{tot} and Fe_{tot} are the total Cr and Fe contents of the original chromite. In addition, Barnes et al. (1983) stated

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that the correlation between chromite's metallization and reduction is non-linear due to the simultaneity of chromite's metallization and reduction (e.g., $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ and $\text{Cr}^{3+} \rightarrow \text{Cr}^0$).^[8]

Nevertheless, 100% reduction corresponds to 100% metallization, justifying a close similarity between the complete removal of oxygen and complete metallization.^[8] The elements provided by Barnes et al. (1983) contributed to the knowledge obtained by Algie and Finn (1984) which proposed three stages of chromite reduction. Firstly, the Fe^{3+} is reduced to Fe^{2+} followed by its metallization. Then, after approximately 50% of the Fe^{2+} is metalized, metallization of Cr^{3+} is initiated. Finally, after the entire Fe-oxide content is reduced, about 60% of the Cr reduction is obtained.^[64,65]

The latter is only true for carbonaceous reduction of chromite and is attentively known and expressed in detail. In this investigation, focus was placed on the Fe and Cr metallization %, individually expressed through the following equation:

$$\% \text{ Fe or Cr metallization} = \frac{\text{Solubilized Fe or Cr}}{\text{Total Fe or Cr content}} \times 100 \quad (\text{Equation 4-2})$$

where the metalized Fe and Cr fraction of the treated chromite (as determined by ICP-OES analysis) is expressed as the solubilized Fe and Cr value, which is divided by the total amount of Fe and Cr present in the untreated chromite ore. During size fractioning, it is likely that certain gangue material can accumulate in a certain size reaction, or that the distribution of such gangue materials will not be uniform over the size fractions considered here. Therefore, the total amount of Fe and Cr (presented in grams, determined by ICP-OES) present in 1 g of as-received and size-fractioned chromite ore is given in Table 4-2. All of the Fe and Cr metallization percentages presented in this study were determined using the values presented in Table 4-2.

Table 4-2: Total amount of Fe and Cr present per in the as-received chromite and the size-fractioned chromite ores.

	As-Received	Size-Fractionated Chromite Ore			
Size equivalent d_{90} (μm)	455	778	467	260	133
g Fe/g chromite ore	0.186	0.189	0.184	0.196	0.199
g Cr/g chromite ore	0.302	0.313	0.295	0.313	0.289

4.4. Results and Discussion

4.4.1. The Effect of Hydrogen Availability

To minimize the hydrogen consumption, the effect of the ratio between hydrogen (given as mL/min) and the sample size (measured in g) on metallization was considered. A hydrogen flow rate of 150 mL/min was maintained and the chromite ore sample sizes of 5 and 30 g were considered. The reduction process was performed at 1100 °C for 180 min and the results are presented in Figure 4-1.

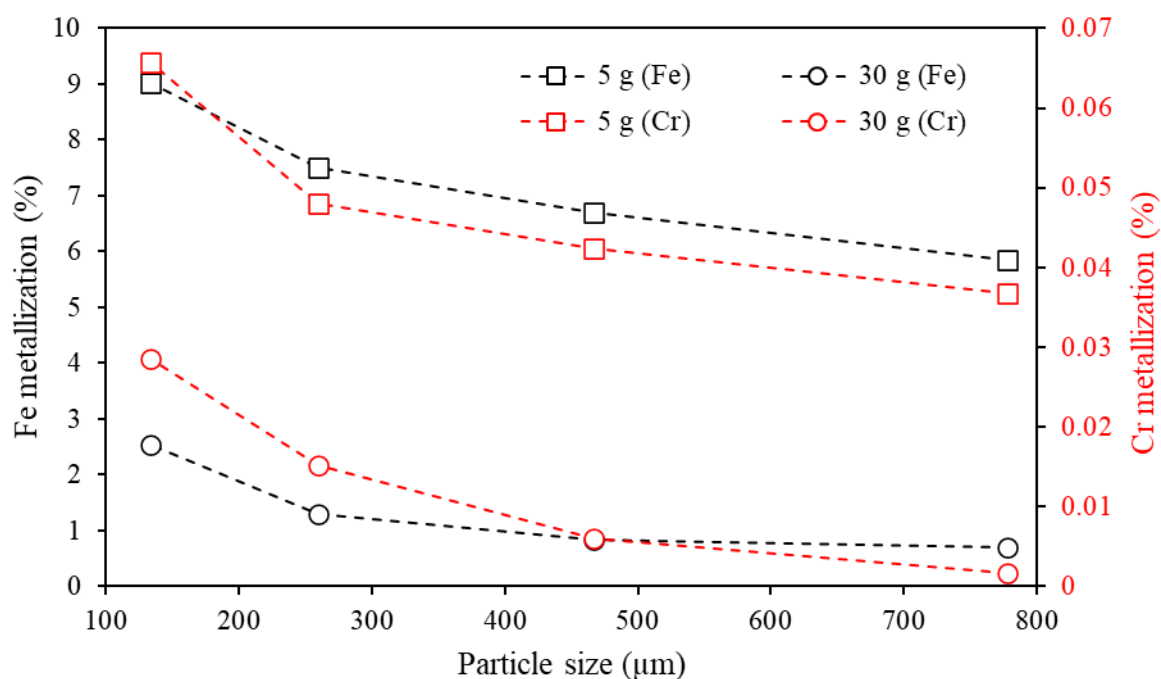


Figure 4-1 The effect of sample mass exposed to hydrogen on Fe and Cr metallization during reduction. Both chromite batches (5 g and 30 g) of all size-fractionated (d_{90} of 133 to 778 μm) samples were reduced at 1100 °C for 180 min at a hydrogen flow rate of 150 mL/min.

Figure 4-1 shows that for both the 5 and 30 g samples, the Fe and Cr metallization % increased with a decrease in particle size. This observation is ascribed to the increase in the sample surface area, as the particle size decreased for a fixed amount of particulate matter. In addition, smaller particles can provide a shorter diffusion path for Fe migration from the center to the rim of the particle.^[65] The unit cell parameter of chromite is 8.38 Å^[66], making it possible for hydrogen (kinetic diameter of 2.89 Å) to penetrate the chromite spinel with a relative degree of ease.^[67] It was however evident that the increase in particle size had an adverse effect on the reduction process.

Figure 4-1 further shows that the Cr metallization % was nearly unaffected by hydrogen and that the highest Cr metallization % (<0.07%) is significantly lower than the highest Fe metallization % (9.03%). Thus, considering the near-zero Cr metallization %, only the Fe-oxide constituency of chromite was reduced under the investigated conditions. This observation may be ascribed to the ionic diffusion mechanism proposed by Soykan et al. (1991), which suggested that Cr metallization only proceeds after the majority of Fe has metalized; this mechanism was however compiled for the carbothermic reduction of chromite.^[68] The same is likely true for the reduction of chromite using hydrogen, even though the extent of Cr metallization will be significantly less when compared to C-based reduction.

The Fe metallization % did not exceed 9.0 and 2.5% for the 5 and 30 g samples, respectively. The observed increase is ascribed to the availability of hydrogen for reduction given the hydrogen-to-chromite ratio (defined as the hydrogen flow rate per gram of chromite). Here, the use of this mass unit was considered due to the dissimilarities in the Fe and Cr content per size fraction of chromite. The effect of flow rate is conceptualized in the following text.

According to Boericke et al. (1945), the reduction of chromite using hydrogen proceeds slowly, even at >1300 °C. At temperatures <1300 °C, equilibrium could not be established with

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certainty. At low hydrogen flow, the measured water content was above the equilibrium value, possibly caused by the accumulation of water in colder locations in the reaction tube, causing the reduction reaction to slow down. Furthermore, at an elevated hydrogen flow, the water content was below the equilibrium value due to the low reaction rate.^[69]

A study by Chakraborty et al. (2010) showed that an increase in the flow rate of argon led to an increase in the carbonaceous reduction rate of chromite. The higher argon flow rate displaced evolved CO₂ (the gaseous reaction product) from their immediate reaction sites. By doing so, the carbonaceous reductant could freely react with the surface of chromite particles. Hence, an increase in the hydrogen flow rate could displace water vapor from the immediate hydrogen–chromite reaction site, accelerating the reduction reaction.^[70] In addition, Chu and Rahmel (1979) stated that Cr₂O₃ could only be reduced by dry hydrogen (above 1026 °C) in an oxygen-free atmosphere, assuming the continuous removal of in situ-generated water vapor from the reaction site.^[71]

The hydrogen flow rate was therefore increased from 150 to 750 mL/min to investigate the effect thereof on Fe and Cr metallization (Figure 4-2). The 150 mL/min results for the 5g chromite ore batch (shown in Figure 4-1) were included in Figure 4-2 as a reference.

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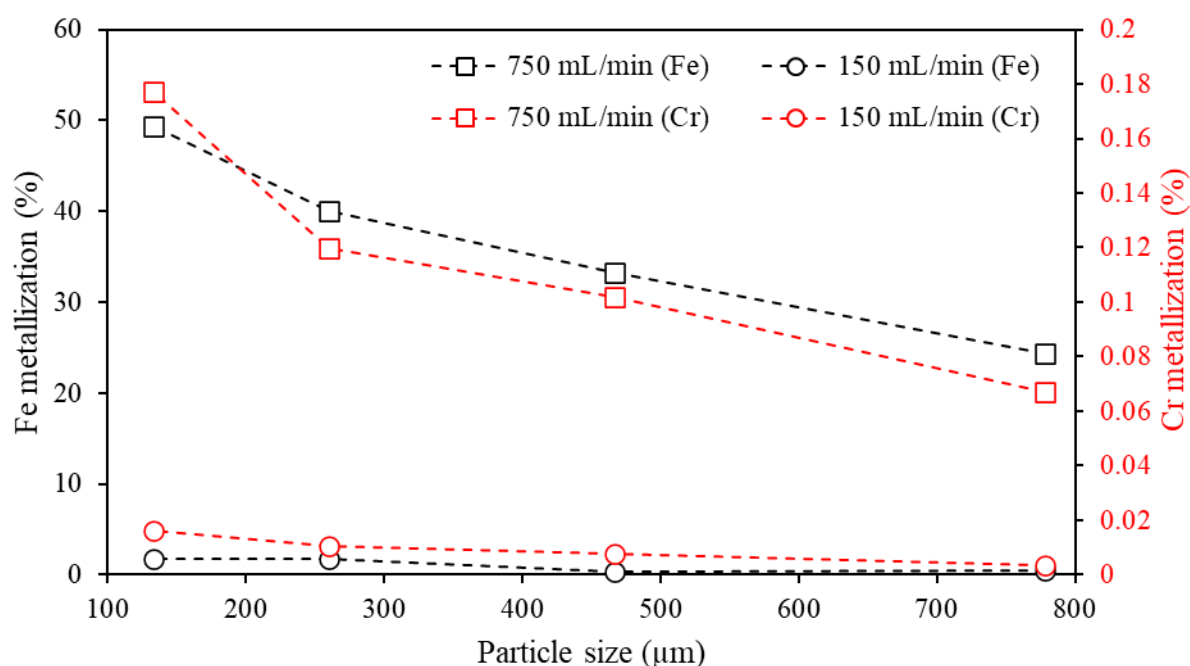


Figure 4-2 The effect of hydrogen flow rate on Fe and Cr metallization. Size-fractionated samples (d_{90} of 133 to 778 μm) were reduced at 1100 $^{\circ}\text{C}$ for 60 min.

Figure 4-2 shows that the Fe and Cr metallization of samples reduced at 150 mL/min did not exceed 1.8 and 0.016%, respectively. The Fe and Cr metallization of samples reduced at 750 mL/min increased from 24.3 to 49.3% and 0.067 to 0.18%, respectively, for samples with decreasing d_{90} values of 778 to 133 μm .

It can further be seen from Figure 4-2 that the extent of Fe and Cr metallization increased with a decrease in particle size. The smallest size fraction (d_{90} of 133 μm) reduced at an elevated hydrogen flow rate of 750 mL/min obtained the highest Fe and Cr metallization % of 49.3 and 0.18%, respectively. The lowest Fe and Cr metallization % was determined at the largest size fraction (d_{90} of 778 μm), i.e., 24.3 and 0.067%, respectively. The effect of the hydrogen flow rate on the reduction of chromite, specifically the Fe-oxide constituency, coincided with observations made by Boericke et al. (1945), Chu and Rahmel (1979), and Chakraborty et al. (2010).^[69-71]

XRD analysis was employed to characterize the mineralogical constituency of the samples reduced at 150 and 750 mL/min. Samples were reduced at 1100 °C for 60 min (Figure 4-3). The XRD pattern of as-received chromite was included in Figure 4-3 as a reference.

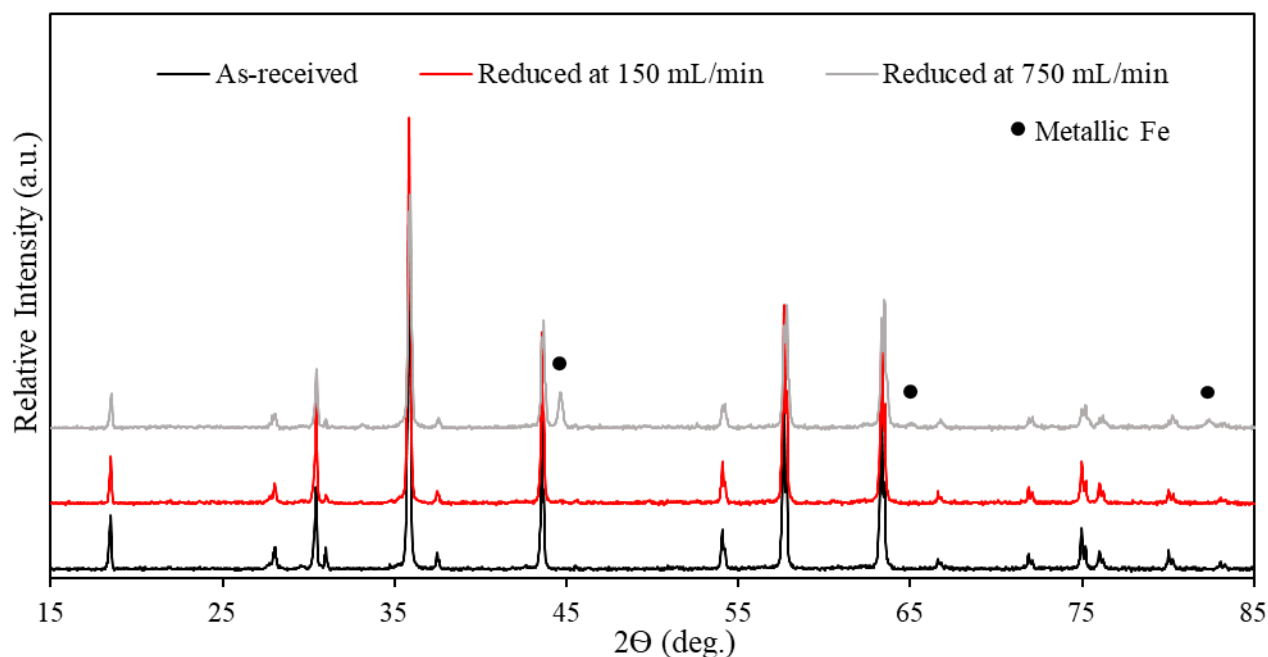


Figure 4-3 XRD patterns of the as-received chromite ore, and samples reduced at 150 and 750 mL/min hydrogen flow rates at 1100 °C for 60 min.

Figure 4-3 shows that the chromite reduced at 150 mL/min did not contain any prominent Fe peaks, which was anticipated considering the <1.9% Fe metallization (Figure 4-2). By increasing the flow rate from 150 to 750 mL/min, some Fe peaks were observed. Of particular interest was the absence of any other phases other than chromite and Fe. Similar results were obtained in a study conducted by Park et al. (2001). Only an Fe and Fe₃C peak was detected by XRD of the sample subjected to reduction using a gas mixture of 10 vol% Ar, 55 vol% H₂, and 35 vol% CH₄ at 925 °C for 60 min. The presence of Fe₃C was due to the presence of CH₄ in the gas mixture, while only Fe and water vapor formed during reduction in the presence of pure hydrogen.^[72]

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To further characterize the samples, SEM (Figure 4-4) and EDX analysis of the samples reduced at 150 and 750 mL/min provided a visual explanation of why the Fe metallization % increased with an increase in the hydrogen flow rate.

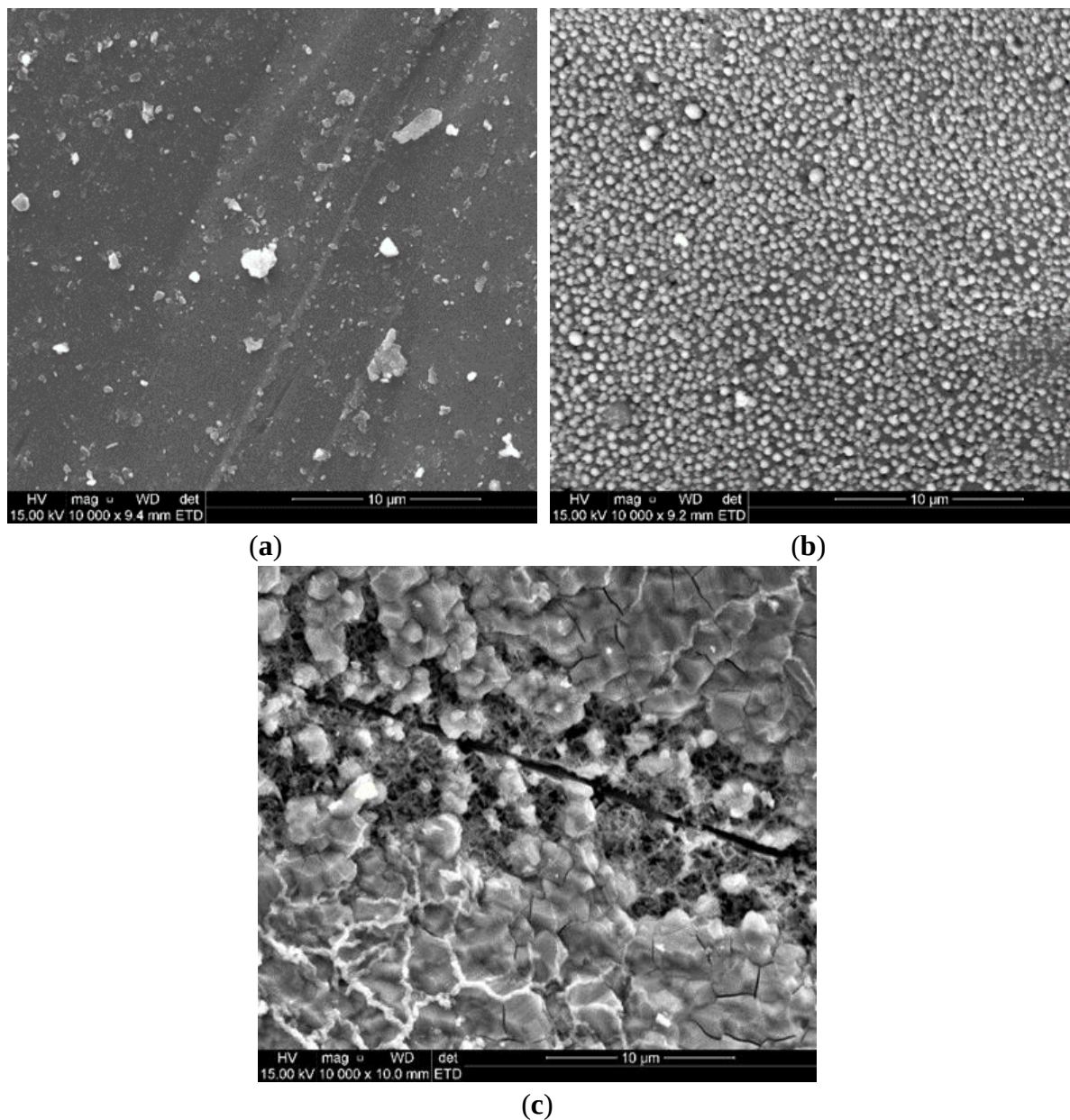


Figure 4-4 Secondary electron SEM micrographs of the surface of as-received chromite particles (a) reduced at a 150 mL/min (b) and 750 mL/min (c) hydrogen flow rate. Samples were reduced at 1100 °C for 60 min.

Compared to as-received chromite shown in Figure 4-4a, a remarkable change in the morphology of the chromite particles reduced at 150 (Figure 4-4b) and 750 mL/min (Figure 4-4c) hydrogen flow rates was observed. Furthermore, Figure 4-4b shows the presence of distinctive small globules on the surface of the chromite particle treated at 150 mL/min. Figure 4-4c shows that by increasing the flow rate from 150 to 750 mL/min, the globule count and intensity were expedited to the point where it forms a near-continuous layer.

To further characterize the surface of the hydrogen-treated chromite particles, the surface presented in Figure 4-4b was magnified and characterized by SEM-EDX. Hereafter, the particles were subjected to the acid leaching procedure and re-characterized. Figure 4-5 presents an enlarged view of the globules presented in Figure 4-4b before and after acid-leaching together with the points of interest considered for SEM-EDX analysis.

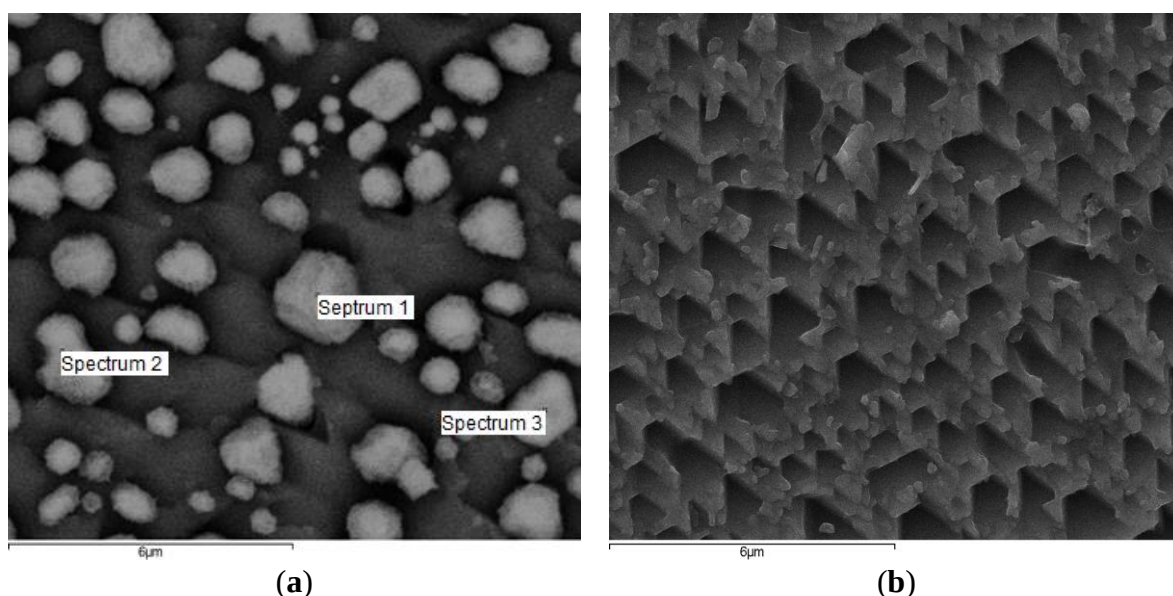


Figure 4-5 Backscattered electron SEM micrographs of the globules observed on the surface of a chromite particle reduced at a hydrogen flow rate of 150 mL/min **(a)** and a similar surface after acid leaching **(b)**.

EDX analyses of the points of interest (marked Spectrum 1–3 in Figure 4-5a) revealed a Cr and Fe wt% of 6.06 and 74.16, respectively. The globule formation is ascribed to the

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migration of Fe ions from the chromite spinel to the particle surface, where it is present in its metallic form. Figure 4-5b presents a similar surface as shown in Figure 4-5a after employing the hot acid leaching procedure. It is evident that the globules were solubilized by acid leaching, and that only a structured surface remained. The reasoning for the specific structure is unclear and future research is required.

To better understand the effect of elevated hydrogen flow on the migration of Fe ions in the chromite spinel, particles reduced at 150 and 750 mL/min were cross-sectioned and investigated by SEM (Figure 4-6) and SEM-EDX (Table 4-3).

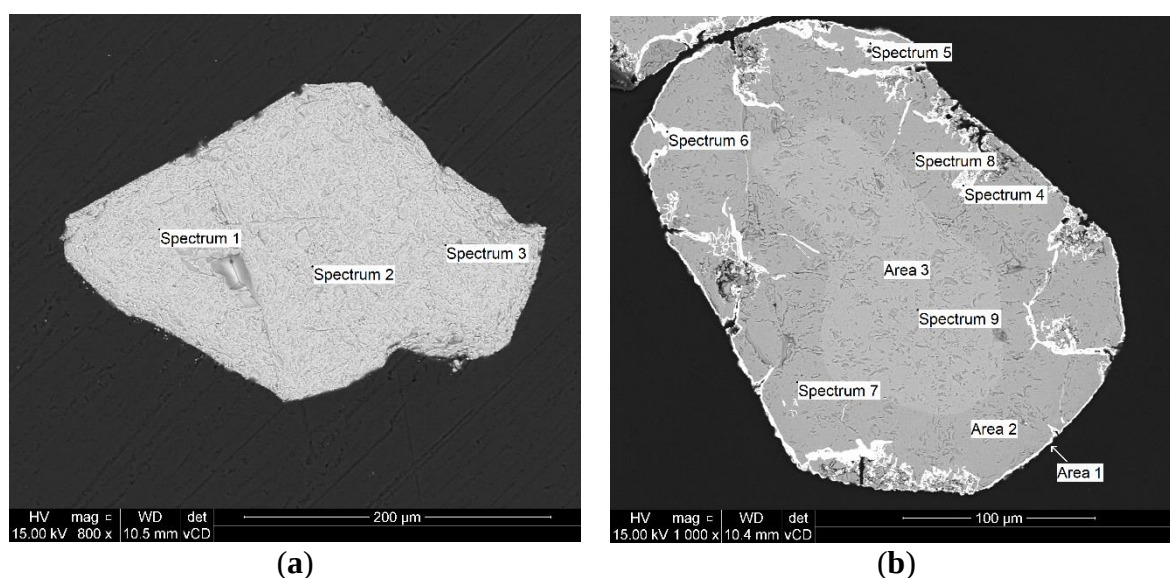


Figure 4-6 Backscattered electron SEM micrograph of chromite particles reduced at 1100 °C for 60 min at a 150 **(a)** and 750 mL/min **(b)** hydrogen flow rate.

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Table 4-3: Microanalyses by SEM-EDX (wt.%) of chromite particles are shown in Figure 4-

6. The samples were reduced at 1100 C for 60 min at a hydrogen flow rate of 150 or 750 mL/min. The Cr/Fe ratio and hydrogen flow rate are indicated.

Spectrum	Designation	Detected Element (wt.%)					Cr/Fe	Hydrogen Flow Rate (mL/min)
		O	Mg	Al	Cr	Fe		
1	n/a	38.60	6.01	7.76	30.06	17.57	1.71	150
2		38.39	6.02	7.63	30.30	17.66	1.72	
3		40.72	6.24	7.8	28.55	16.69	1.71	
4	Area 1	8.81	0.39	5.99	5.10	79.71	0.06	750
5		1.42	0.05	0.02	5.71	92.8	0.06	
6		16.78	2.94	3.4	11.06	65.83	0.17	
7	Area 2	41.25	7.85	7.93	34.15	8.82	3.87	
8		40.59	8.05	8.32	34.4	8.65	3.98	
9	Area 3	40.33	5.8	7.63	29.18	17.06	1.71	

Table 4-3 shows that the average Cr/Fe ratio of Spectra 1–3 prepared from the indicated areas shown in Figure 4-6a is approximately 1.71, which corresponded with a Cr/Fe ratio of 1.77 reported in a study by Davies et al. (2022) which utilized the same ore.^[20] Therefore, Spectra 1–3 represent chromite where no change in Fe is observed.

Unlike the chromite particle shown in Figure 4-6a, three distinctive layers formed within the chromite particle when reduced at 750 mL/min, as shown in Figure 4-6b. These layers were designated as the center (Area 1), transition phase (Area 2), and rim (Area 3). Spectra 4–6 are located in Area 1 and have a low Cr/ Fe ratio of between 0.06–0.17. The low Cr/Fe ratio of Area 1 shows that the rim of the particle is enriched in Fe. More so, considering the relatively low O content, the Fe likely occurred in a metallic state. Spectra 7 and 8 were prepared from Area 2 and have an average Cr/Fe ratio of 3.93, which is significantly higher than the ratio of Area 1. The higher Cr/Fe ratio of Area 2 is indicative of the absence of Fe. Spectrum 9 is located in Area 3 and has a similar Cr/Fe ratio to Spectra 1–3. Therefore, Area 1 is representative of chromite which is not reduced by hydrogen.

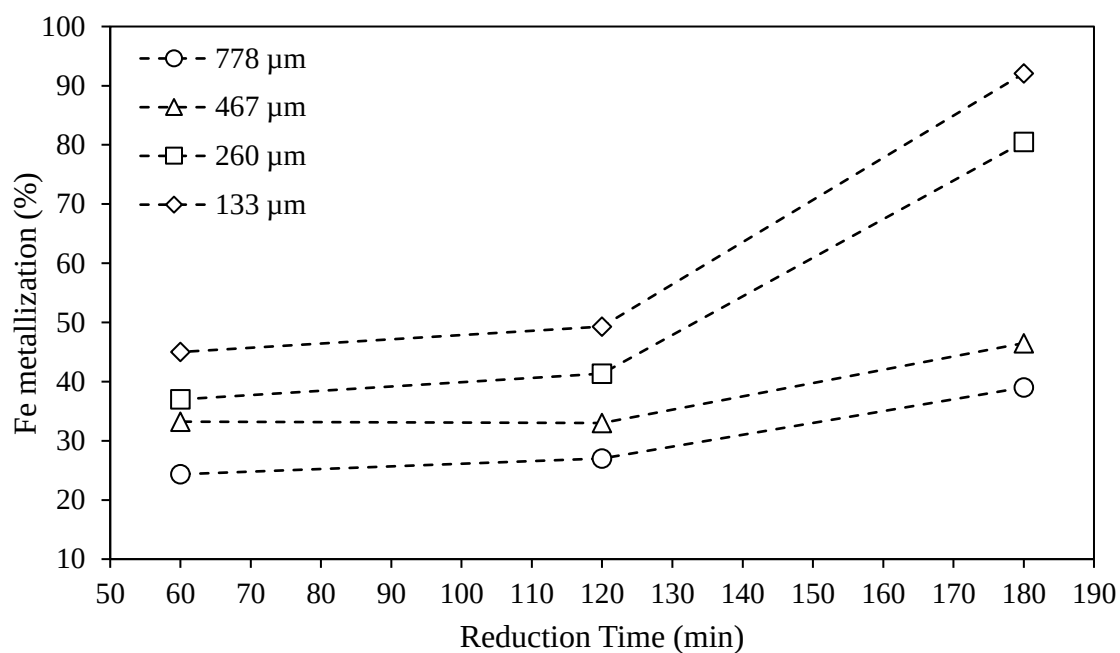
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Similar results were presented by Leikola et al. (2018) whereby chromite particles were reduced using 10:90 vol% CH₄:H₂ at 1100 °C for 20 min.^[73] Furthermore, an investigation carried out by Davies et al. (2022) described the migration of Fe present in chromite particles after being reduced at 1100 °C for 30 min at a hydrogen flow rate of 1 L/min.^[20] Davies et al. (2022) showed the formation of three distinctive layers similar to Figure 4-6b. Hence, no in-depth explanation regarding the Fe migration is given here. The migration of Fe is however summarized as Fe-oxides (presented as Fe²⁺ and Fe³⁺ occupying tetrahedral and octahedral sites, respectively) moving towards the particle grain where they occur as Fe⁰.

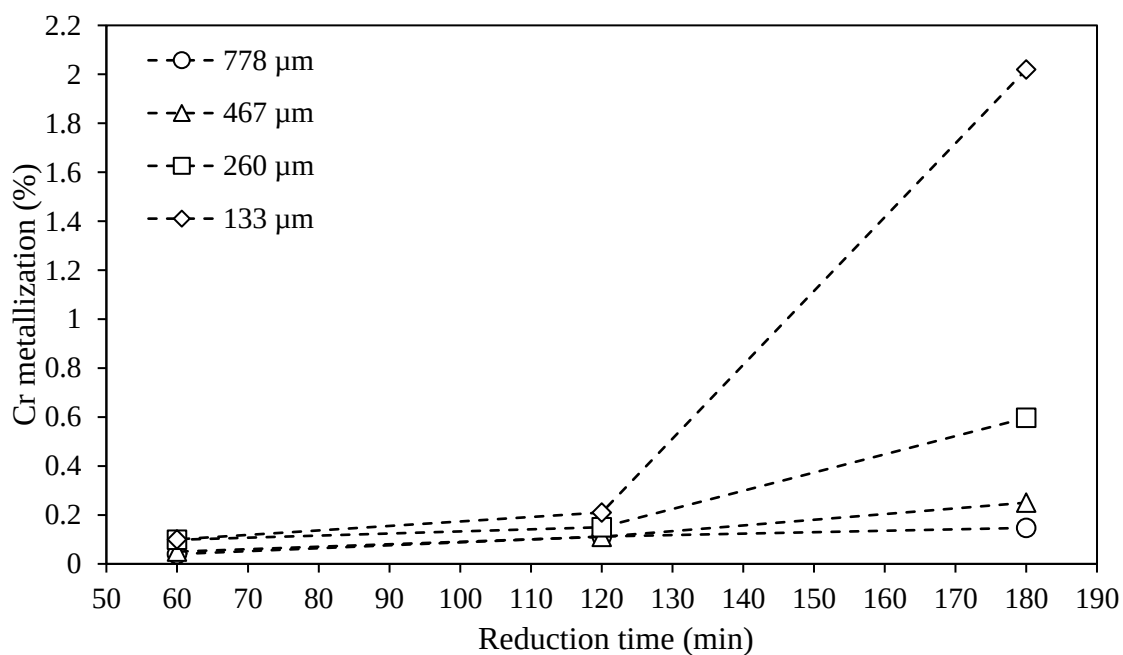
It is clear that the layer formation observed in Figure 4-6b is absent in Figure 4-6a, and the Cr/Fr ratio of approximately 1.71 indicates that the hydrogen flow rate of 150 mL/min did not reduce an appreciable amount of Fe-oxide. Hence, no metallic Fe layer was observed in Figure 4-6a. However, a metallic Fe layer was present on the surface of the chromite particle in Figure 4-6b because of surface and sub-surface Fe-oxide reduction and Fe migration.

4.4.2. Effect of Reduction Time

By increasing the hydrogen flow rate to 750 mL/min, an Fe metallization of 49.3% was achieved. However, the objective of the study was to achieve optimal Fe metallization. It was therefore considered to increase the reduction time, as metallization would likely increase if chromite particles were exposed to hydrogen for extended periods. To determine this, all size-fractionated chromite samples were reduced at 1100 °C for 60, 120, or 180 min (Figure 4-7).



(a)



(b)

Figure 4-7 Effect of reduction time on the Fe (a) and Cr (b) metallization. All size-fractioned chromite samples were reduced at 1100 °C for 60, 120, or 180 min at a 750 mL/min hydrogen flow rate.

According to Figure 4-7a,b a relatively insignificant change in the Fe and Cr metallization % was observed for the samples reduced for 60 and 120 min. However, samples

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reduced for 180 min showed a significant increase in metallization when compared to samples reduced for 120 min. The Fe and Cr metallization % for the smallest size fraction (d_{90} of 133 μm) increased from 39.0 to 92.1% and 0.1 to 2.0%, respectively, as the reduction time increased from 60 to 180 min. A similar trend was observed for all other size fractions (d_{90} of 160 to 778 μm). It is again worth noting the significant difference in the Fe and Cr metallization %.

It is also evident from Figure 4-7a,b that the increase in the Fe and Cr metallization % after 120 min was more significant for the size fractions with a d_{90} of 133 and 160 μm than for the size fractions with a d_{90} of 467 and 778 μm . As indicated earlier, the higher Fe and Cr metallization of smaller particles can be ascribed to the shorter diffusion path and larger surface area. This principle is made more evident as the effect of particle size is magnified here. To conclude, the reduction time has a significant effect on the Fe and Cr metallization after 120 min, while still not obtaining complete Fe metallization.

4.4.3. Effect of Pre-Oxidation

Relatively high Fe metallization was achieved in Section 3.2. It was however considered that 180 min of reduction would not be operationally or economically attractive on an industrial scale. Alternative means were therefore identified to promote Fe metallization and to minimize Cr metallization under milder conditions (i.e., shorter reduction periods) than the conditions considered thus far. Based on several studies^[22-27], the pre-oxidation of chromite to promote the reducibility of Fe-oxides was considered. To exemplify the effect of pre-oxidation on Fe metallization, size-fractioned chromite (refer to d_{90} values, Table 4-1) was oxidized at 1100 °C for 60 min and reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min. The Fe and Cr metallization percentages of pre-oxidized/reduced and reduced chromite particles are compared in Figure 4-8.

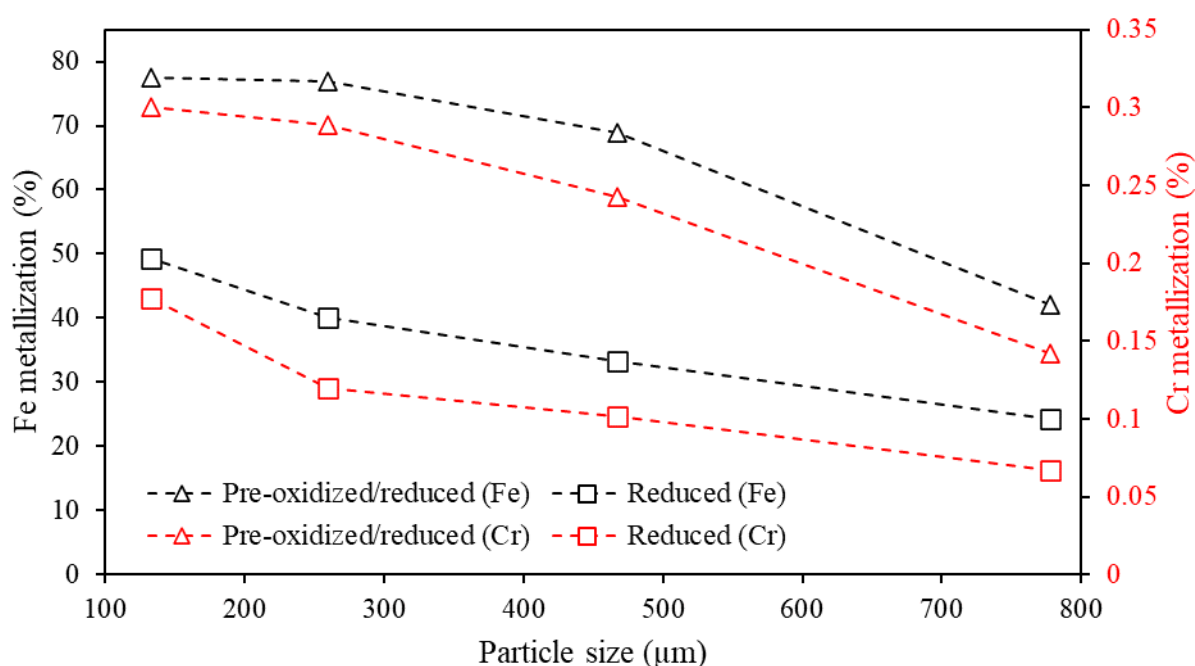


Figure 4-8 The effects of pre-oxidation (1100 °C for 60 min) on the Fe and Cr metallization of samples reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min.

It can be seen from Figure 4-8 that the pre-oxidation of chromite was advantageous for the subsequent reduction reaction. For the size-fractioned chromite with a d_{90} of 133 μm, a relatively significant increase in the Fe metallization was observed, i.e., 49.3 and 77.5% for reduced and pre-oxidized/reduced chromite, respectively. The increase in Fe metallization ranged between 17.7 and 37.0%. The lowest increase was observed for the d_{90} of 778 μm, which is ascribed to the low surface area of the specific size fraction. The size fractions with a d_{90} of 467 and 260 μm showed an increase in Fe metallization of 35.8 and 37.0%, respectively. These increases exceeded that of the size fraction with a d_{90} of 133 μm, i.e., 49.3%. This observation is however ascribed to the fact that the Fe metallization of the unoxidized chromite with a d_{90} of 133 μm was already relatively high. It can therefore be concluded that the increase in Fe metallization of pre-oxidized chromite is optimized within the size range of 260–467 μm for experimental conditions considered in this study. All pre-oxidized/reduced size-fractioned

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chromite showed significant increases in Fe metallization. A similar trend was observed for Cr metallization, e.g., the percentage Cr metalized increased from 0.18 to 0.30% for the smallest size fraction (d_{90} of 133 μm). In addition, the 0.30% Cr metallization was the highest Cr metallization achieved.

The observed increase in Fe metallization may be ascribed to the transformation of the chromite spinel during pre-oxidation. The oxidizing atmosphere provides a natural driving force for an Fe^{2+} to Fe^{3+} phase change. It is relatively well understood that during the oxidation of chromite, an exsolved Fe_2O_3 -rich sesquioxide phase forms in a Widmanstätten-like pattern.^[22] This Fe_2O_3 phase initially exists as a metastable $\gamma\text{-Fe}_2\text{O}_3$ (maghemite) exsolved precipitate and forms because of dislocations along the (111) chromite spinel plane. At temperatures greater than 600 °C and in the presence of oxygen, the $\gamma\text{-Fe}_2\text{O}_3$ phase changes to more stable hematite (Fe_2O_3).^[21,22,24,27,29,74] Additionally, cation vacancies form within the spinel during Fe^{3+} -enriched phase formation.^[22,24] Furthermore, the applied oxygen chemical potential also promotes the diffusion of Fe ions from the particle interior to the particle surface where the solid–gas interface is located. Ultimately, the formed Fe_2O_3 phase, together with the generated vacancies, improves the carbothermic reducibility of the chromite ore.^[22]

XRD was employed to characterize the mineralogical changes occurring during the pre-oxidation and/or reduction of chromite (Figure 4-9).

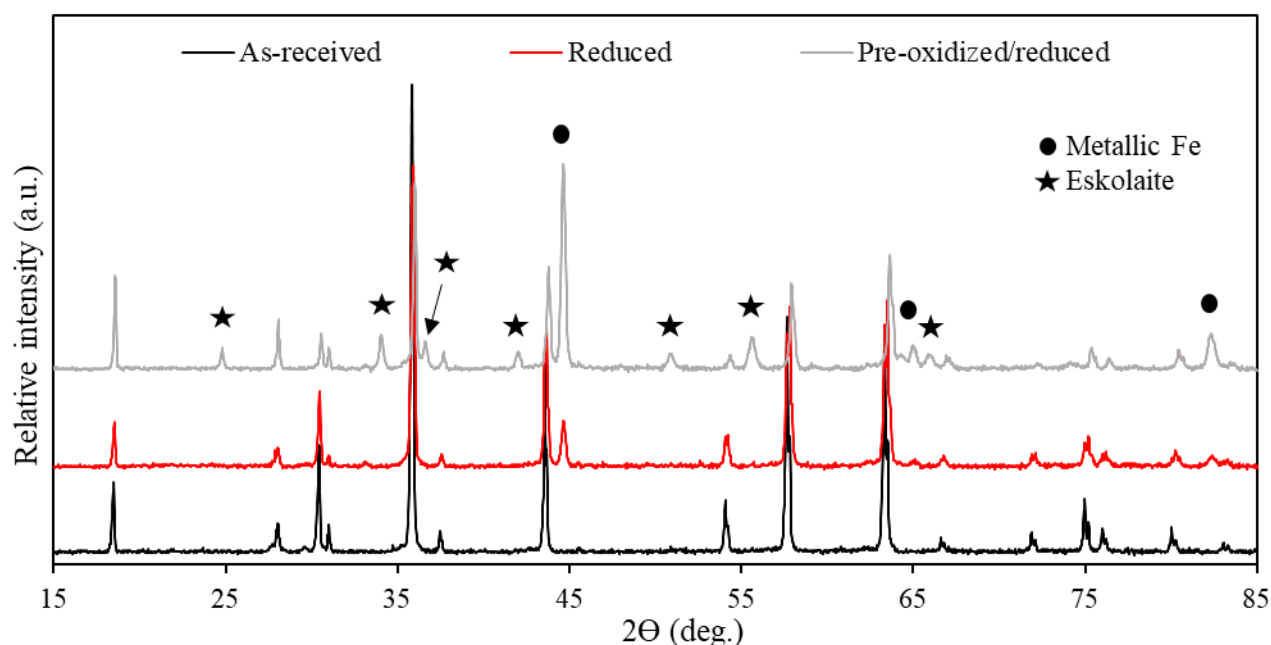


Figure 4-9 XRD patterns of the as-received chromite ore, samples reduced at 750 mL/min hydrogen flow rates, and samples pre-oxidized (1100 °C for 60 min) and reduced (1100 °C at a 750 mL/min hydrogen flow rate for 60 min).

As can be seen from Figure 4-9, pre-oxidation resulted in the formation of an eskolaite-type phase. This observation coincided with results presented by Kleynhans et al. (2016).^[25] Nevertheless, Figure 4-9 further shows that the Fe peak intensity of the pre-oxidized and reduced sample was significantly higher than that for the reduced sample. Here, the beneficial effect of pre-oxidation on Fe metallization is emphasized. Davies et al. (2022) showed that the presence of the eskolaite-type phase (eskolaite–corundum solid solution, $\text{Cr}_{1.4}\text{Al}_{0.6}\text{O}_3$) in hydrogen reduced chromite after hot acid leaching. The authors ascribed the presence of the eskolaite-type phase to the removal of the Fe from the chromite spinel.^[20]

To better understand the effect of pre-oxidation on the migration of Fe ions through the chromite particle, the pre-oxidized and pre-oxidized/reduced particles were cross-sectioned and investigated by SEM (Figure 4-10) and SEM-EDX (Table 4-4).

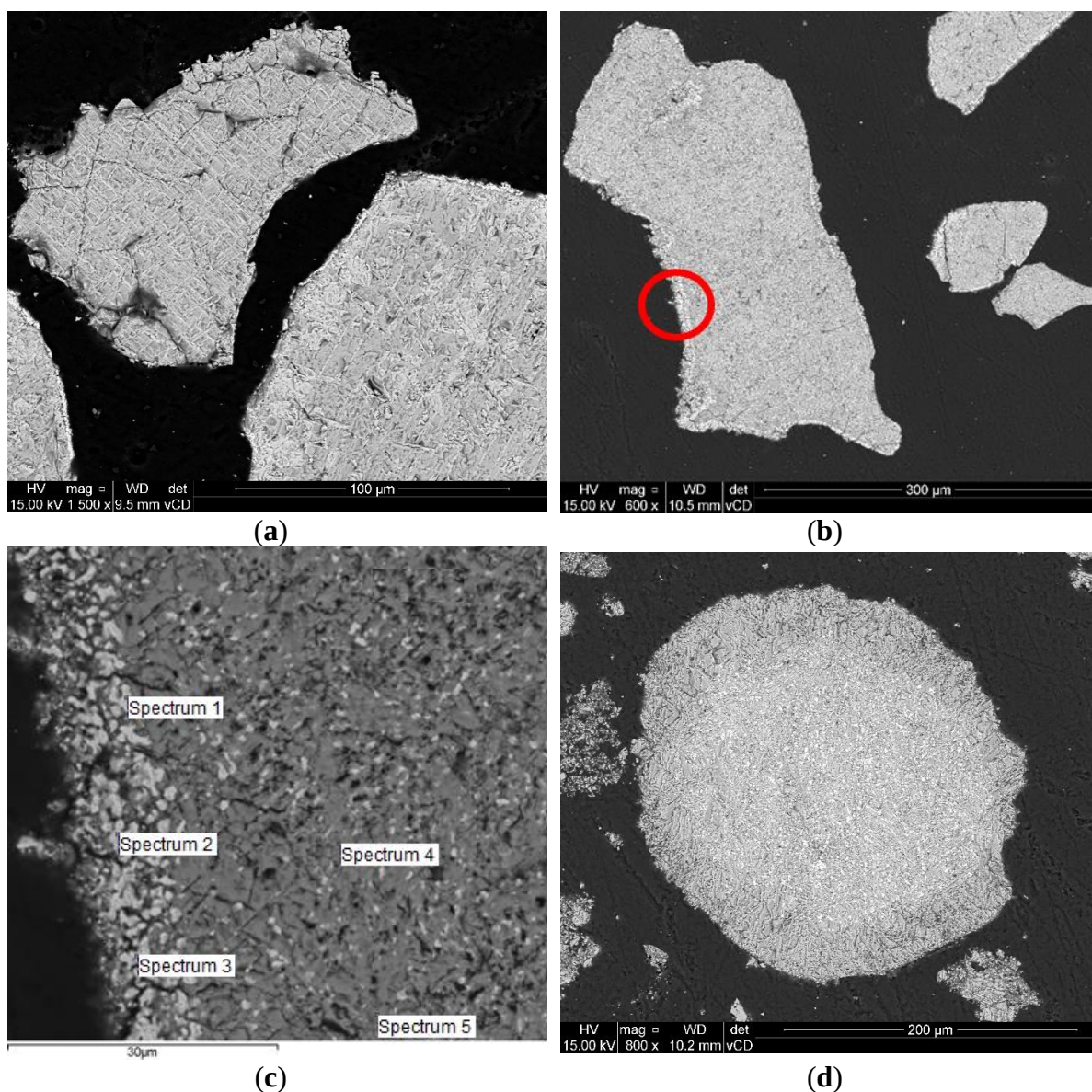


Figure 4-10 Backscattered electron SEM micrograph of chromite particles pre-oxidized at 1100 °C for 60 min (a) and subsequently reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min (b,c) presents a similar particle as shown in (b) at a higher magnification (encircled) and a pre-oxidized/reduced particle after leaching (d).

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Table 4-4: Microanalyses by SEM-EDX (wt.%) of chromite particle shown in Figure 4-10c.

The sample was pre-oxidized at 1100°C for 60 min and subsequently reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min.

Spectrum	Description	Detected Element (wt.%)						
		O	Mg	Al	Ti	Cr	Fe	Cr/Fe
1	White area	9.37	2.35	2.38	-	8.4	77.5	0.12
2		6.2	0.89	1.63	-	5.55	85.73	0.06
3		8.15	1.21	2.61	-	7.31	80.71	0.09
4	Grey area	42.28	4.09	12.46	1.04	34.36	5.77	5.95
5		42.08	10.21	9.71	-	30.66	7.34	4.18

It is evident from Figure 4-10a that the Widmanstätten pattern formed within the chromite particle after being pre-oxidized at 1100 °C for 60 min. The presence of the Widmanstätten pattern suggests the formation of an exsolved Fe_2O_3 phase. This was however expected based on results presented elsewhere.^[22,24,27] In Figure 4-10b, the Widmanstätten pattern is no longer visible after the particles were reduced. Rather, numerous randomly scattered white areas were observed within the particle.

An area close to the edge of the particle shown in Figure 4-10b (marked with a red circle) is shown in Figure 4-10c. According to EDX, the white areas (marked as Spectrum 1–3) were enriched in Fe. Table 4-4 shows that these areas had an average Cr/Fe ratio of 0.09, which was similar to the Cr/Fe of Area 3 in Table 4-3. Figure 4-10c further shows that the Fe-rich phase was more prominent when close to the particle edge, while the distribution of such phases within the particle interior was relatively less significant.

Considering the positioning and high Fe content of the white areas within the chromite particle, it could be ascribed to the formation of the Widmanstätten pattern. A similar observation was made by Zhao and Hayes (2010) while investigating the reducibility of pre-oxidized chromite pellets. The authors showed that metallization proceeded preferentially at sites where the Fe_2O_3 -enriched sesquioxide phase was present, allowing metallization to

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proceed over the whole interior of the particle (not only at the rim of the particle) following the Widmanstätten pattern. Hence, the surface area available for metallization increased, allowing a shorter migration path for the oxides by not migrating to the rim of the particle. The Fe_2O_3 -enriched sesquioxide phase, which cannot accommodate MgO , was the preferential nucleation and growth point for the metallic phase.^[23,74] Moreso, the relatively low Al content (Table 4-4, Spectra 1–3) suggests the absence of Al_2O_3 from the sesquioxide phase, which promoted reducibility. It is however noted that EDX is a semi-quantitative analytic technique, and that the detected Mg and Al contents may be ascribed to their nearby presence, i.e., from the bulk material.

Figure 4-10b further shows that the metallic phase did not only occur at the particle rim but was beleaguered throughout the particles. This was considered a relatively critical observation as the effectiveness of the applied leaching procedure can be affected by the occurrence of metallic Fe inside the particle. The applied leaching procedure was, however, maintained for the sake of consistency. It is however noted that future studies must consider this when determining experimental procedures for total Fe removal of similarly prepared samples.

Figure 4-10d shows that the leaching procedure removed Fe from the surface and near-surface area of the pre-oxidized/reduced particles, which is indicative of incomplete Fe removal. Figure 4-10c further shows that during the applied leaching procedure, Fe was solubilized up to $34.1 \pm 4.9 \mu\text{m}$ into the particle.

To evaluate this, XRD analysis was applied to leach the pre-oxidized/reduced chromite samples and the reduced chromite samples (Figure 4-10). The patterns for leached and unleached reduced samples (Figures 4 and 5) were included for comparative purposes.

Figure 4-11 shows that the leaching procedure removed the majority of Fe from the reduced chromite. Relatively significant metallic Fe peaks were observed for the leached pre-oxidized/reduced samples. This was however expected when considering Figure 4-10 and Table 4-4. Likely, prolonging the acid leaching method used in this study may not ensure the total removal of the metalized Fe content. As a prospect, size reduction (e.g., ball milling) of the hydrogen reduced chromite before acid leaching. It is further noted that the Fe (and Cr) metallization of pre-oxidized/reduced samples reported in this study is under-reported. The occurrence and extent of incomplete leaching are further conceptualized in the proceeding sections.

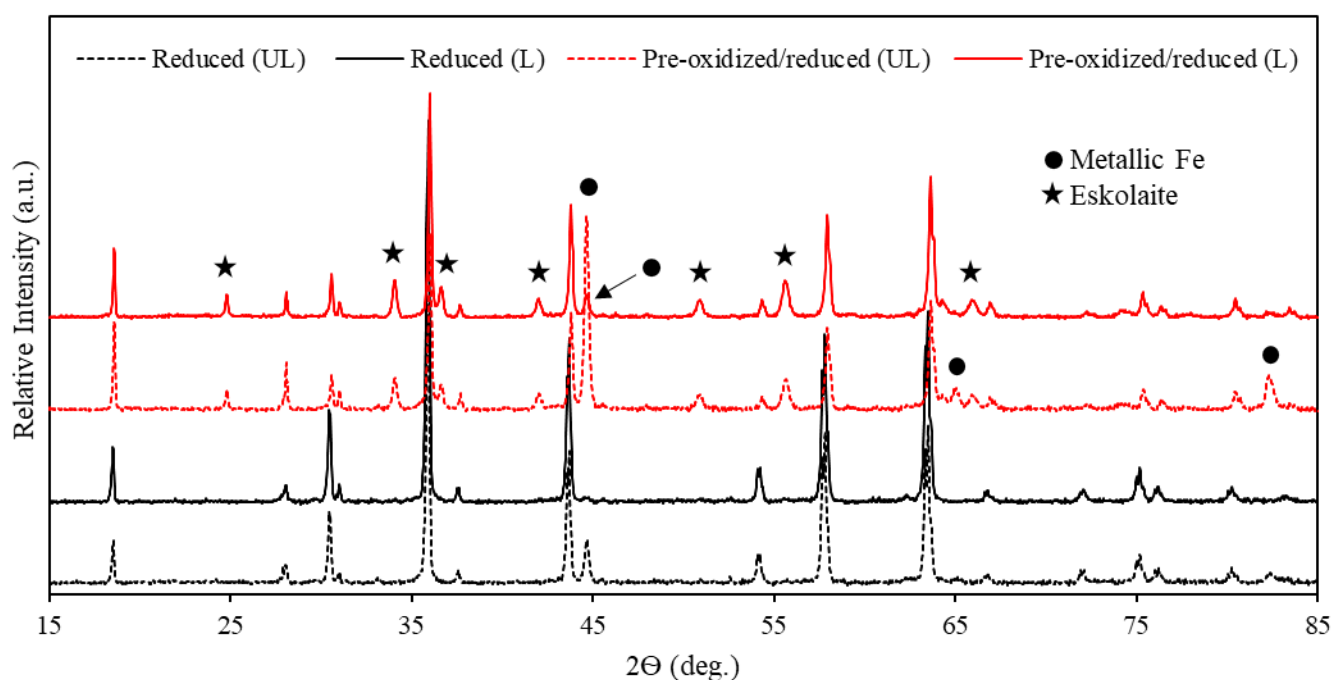


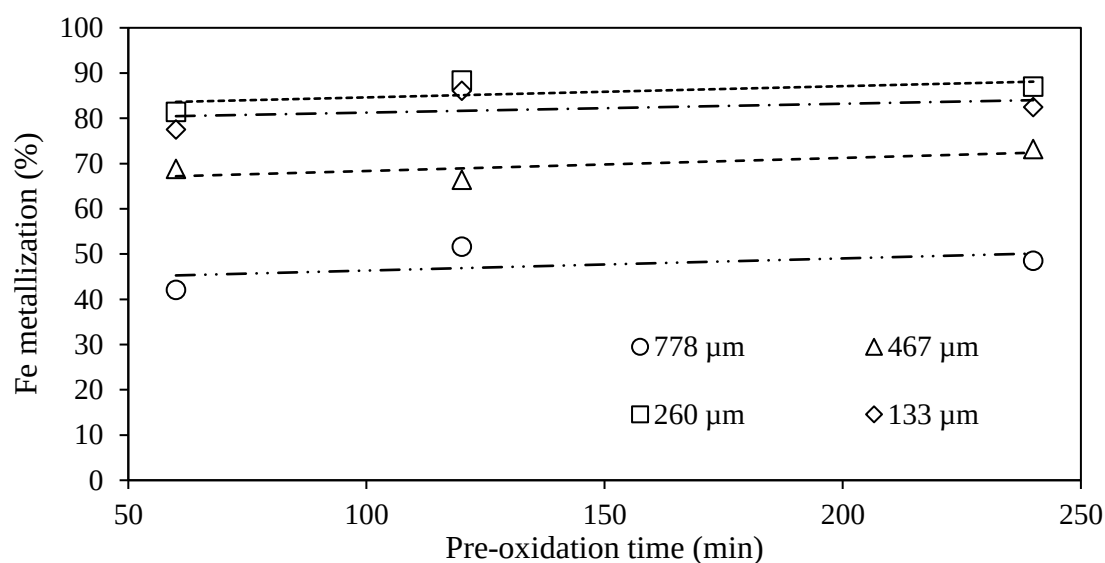
Figure 4-11 XRD patterns of leached (L) and unleached (UL) reduced and pre-oxidized/reduced samples. Pre-oxidation was performed at 1100 °C for 60 min and reduction was performed at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min.

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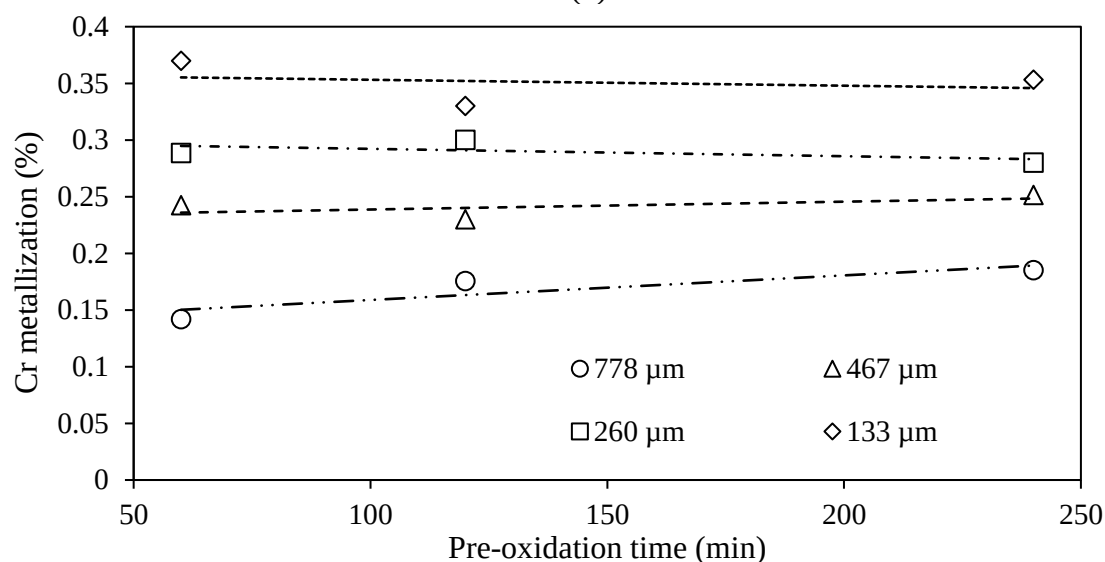
4.4.4. Effect of Pre-Oxidation Time

It is well known that the oxidation temperature has a significant influence on the reducibility of chromite.^[22-26] Kleynhans et al. (2016) indicated that lower levels of reduction were obtained at oxidation temperatures above 1100 °C. Pre-oxidation temperatures >1000 °C resulted in the formation of an eskolaite-type phase between Cr_2O_3 and $\alpha\text{-Al}_2\text{O}_3$.^[75] Thermodynamically, the eskolaite-type phase is more resistive to reduction than naturally occurring chromite and is reduced at a slightly higher temperature.^[25] Considering the stabilizing effect of the eskolaite-type phase on the reducibility of Cr, the effect of pre-oxidation parameters on Fe metallization was considered.

Size-fractionated chromite (refer to d_{90} values, Table 4-1) was subjected to pre-oxidation at 1100 °C for different durations (60, 120, and 240 min) and subsequently reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min (Figure 4-12).



(a)



(b)

Figure 4-12 The effect of pre-oxidation time on Fe (a) and Cr (b) metallization. Size-fractionated samples were pre-oxidized at 1100 °C for 60, 120, and 240 min and subsequently reduced at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min.

Figure 4-12 shows that pre-oxidation exceeding 60 min did not have an appreciable effect on the extent of Fe and Cr metallization; this was true for all size-fractionated chromite samples evaluated. The size fraction with a d_{90} of 133 and 266 μm had a comparable Fe metallization % and ranged between 77.5 (d_{90} of 133 μm , 60 min pre-oxidation) and 88.4%

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(d_{90} of 266 μm , 120 min pre-oxidation). The lowest Fe metallization % was achieved for the largest size fraction (d_{90} of 778 μm) which ranged between 42.1 and 51.7%.

It was however evident from Figure 4-12 that the Fe metallization % was not significantly affected by increasing the pre-oxidation time from 60 to 240 min. A study by Kapure et al. (2010) showed that exceeding 120 min of pre-oxidation at 900 °C did not have an appreciable effect on Fe and Cr metallization using a carbonaceous reductant.^[22] Considering the results presented in Figure 4-12, it is evident that pre-oxidation >60 min did not promote Fe metallization. Shorter pre-oxidation times should be considered in future research, as shorter processing times can benefit from an economic perspective.

4.4.5. Effect of Pre-Oxidation and Leaching on Particle Integrity

During the handling of the materials in this study, a change in the chromite particle size was visually observed after the leaching procedure—more so for the leached pre-oxidized/reduced samples than for the leached reduced samples. To investigate this, SEM images of leached and unleached reduced and/or pre-oxidized samples were prepared. Pre-oxidation and reduction were performed at 1100 °C for 60 min. A 750 mL/min hydrogen flow rate was used during reduction.

Figure 4-13 suggests that the leaching process applied resulted in the structural degradation of the reduced and pre-oxidized/reduced chromite particles. When comparing the surface of the reduced particles (Figure 4-13a) to the leached counterpart (Figure 4-13b), numerous cracks and structural flaws can be observed; this suggests that, at the very least, the surface of the leached reduced particles deteriorated during the applied process.

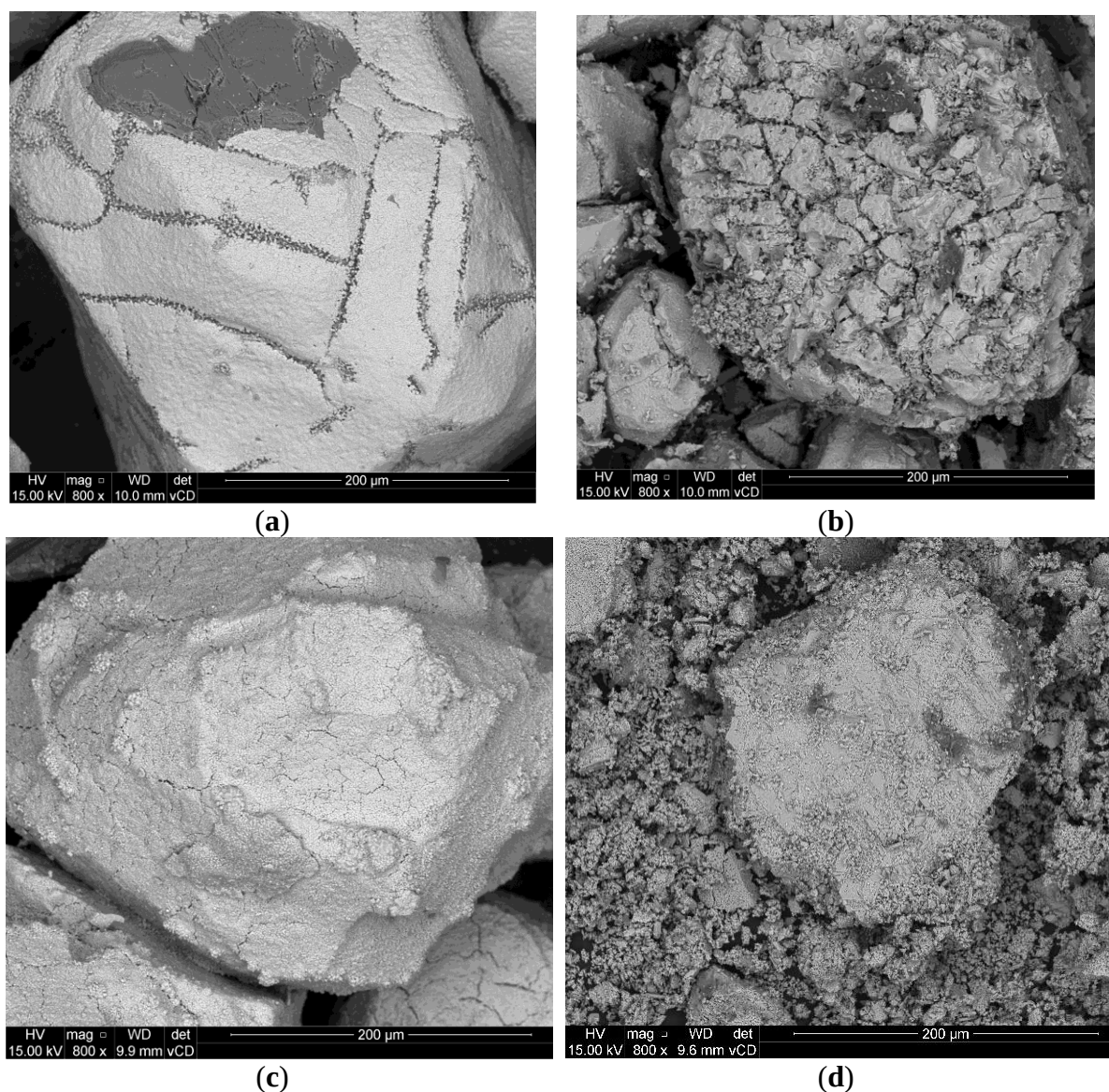


Figure 4-13 Backscattered SEM images of reduced chromite particles before (a) and after (b) leaching, and pre-oxidized/reduced chromite particles before (c) and after (d) leaching.

From Figure 4-13d, it is clear that the pre-oxidized/reduced particles underwent significant deterioration when compared to Figure 4-13c, as a large fraction of particulate matter was observed after the leaching process. It is therefore likely that the leached pre-oxidized/reduced particles may require less energy to reduce the particle size to a d_{90} of 75 μm (pre-reduction)/ d_{80} of 74 μm (oxidative sintering) required for pelletization before being smelted. It is however proposed that this observation be further investigated as it may likely

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form an important aspect when approaches to incorporate hydrogen-based reduction of chromite are developed.

4.5. Conclusions

In this study, we investigate the effect of pre-oxidation on the hydrogen reducibility of chromite. It is shown that by implementing pre-oxidation, higher Fe metallization was achieved under milder conditions when compared to unoxidized chromite. Using un-oxidized chromite, an Fe metallization of 92% was achieved by hydrogen-based reduction at 1100 °C for 180 min, while 84% was achieved for oxidized chromite reduced at 1100 °C and 60 min

Hydrogen-reduced unoxidized chromite revealed the formation of three distractive layers, which were characterized by an unreacted center, a Fe-deprived phase, and a Fe-enriched outer layer. A dissimilar reduction mechanism was observed when chromite was oxidized before reduction. The chromite oxidation resulted in the formation of an exsolved Fe_2O_3 phase throughout the particles, which was the preferred nucleation point for Fe metallization. Subsequent hydrogen reduction resulted in the formation of a relatively prominent Fe layer, as well as numerous Fe-enriched phases through the particle.

The Fe leaching procedure used showed that Fe^0 present in the outer $34.1 \pm 4.9 \mu\text{m}$ of the chromite particles was removed, while intra-particle Fe^0 remained. This was considered an important observation as it can guide decision making during the development of a process that incorporates pre-oxidation and subsequent hydrogen reduction. Considering that the total Fe^0 content was not removed by the hot acid leaching procedure employed here, it is likely that this value is under-reported.

Lastly, pre-oxidation of chromite results in the formation of an $\alpha\text{-Al}_2\text{O}_3$ -stabilized eskolaite-type phase, which is more resistant to reduction when compared to naturally

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occurring chromite. The formation of the eskolaite-type phase is however jointly ascribed to the removal of Fe from the chromite spinel due to subjecting chromite to oxidation.

Funding: This study and APC were funded by the Research Council of Norway (RCN) as the Thanos project (INPART Project 309475) and is gratefully acknowledged. The Department of Science and Innovation (DSI), South Africa, and HySA Infrastructure Centre of Competence, South Africa, are also gratefully acknowledged for their financial support through the KP5 program.

Conflicts of Interest: The authors declare no conflicts of interest.

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The findings presented in Chapter 5 formed the core of the article submitted to *Metall. Mater. Trans. B*.

CHAPTER 5: PRE-REDUCTION OF UNITED MANGANESE OF KALAHARI ORE IN CO/CO₂, H₂, AND H₂/H₂O GAS ATMOSPHERES

At the time of submission, this manuscript presented in Chapter 5 was submitted to *Metallurgical and Materials Transactions B*. The proof of submission is shown in Appendix C.

5.1. Author list and contributions

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Contributions

The contributions of the various co-authors were as follows:

Author Contributions: The majority of work, i.e., experimental, data processing and interpretation, research, and writing of the scientific paper, was performed by the candidate, J.D. S.P.D.P. (supervisor) assisted by providing conceptual ideas and recommendations regarding experimental work and writing of the article. M.T., T.L. and S.P.D.P contributed to the reviewing and editing of the article. Financial support was provided by M.T.

The findings presented in Chapter 5 formed the core of the article submitted to *Metall. Mater. Trans. B*.

Abstract

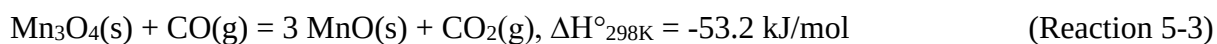
The influence of hydrogen on the pre-reduction of United Manganese of Kalahari (UMK) ore from South Africa was investigated. Isothermal experiments were performed in 70% CO 30% CO₂ (reference), 70% H₂ 30% H₂O, and 100% H₂ gas atmospheres at 700, 800, and 900 °C. Phase stability diagrams were thermodynamically determined and compared to experimental results. The pre-reduction process involved two reactions proceeding in parallel, i.e., the pre-reduction of higher oxides, and the decomposition of carbonates. A thermogravimetric (TG) furnace was employed for the pre-reduction of the ore in the various atmospheres. The calculated weight loss percentage was used to determine the degree and rate of pre-reduction. The chemical analysis showed that the higher Fe- and Mn- oxides in the samples reduced in 70% H₂ 30% H₂O and 70% CO 30% CO₂ completely reduced to FeO and MnO, respectively, while in 100% H₂ the FeO further reduced to metallic Fe. The majority of carbonates were decomposed in the CO/CO₂ atmosphere at 900 °C, and at ≥ 700 °C in the H₂/H₂O and H₂ atmospheres. The degree and rate of reduction were accelerated by increasing the pre-reduction temperature and by employing a hydrogen-containing gas atmosphere (70% H₂ 30% H₂O, and 100% H₂). Scanning electron microscopy and electron microprobe analysis showed that the pre-reduced ore consisted of three phases: i) Mn- and Fe-rich, ii) Mg- and Ca-rich, and iii) Mg-, Si-, K-, and Na-rich. The influence of hydrogen as a reductant on the decrepitation and porosity of pre-reduced ore was also investigated. No appreciable differences in porosity and decrepitation were found for ores reduced in CO/CO₂ and hydrogen-containing atmospheres.

Keywords: Hydrogen, pre-reduction, manganese ore, manganese oxides, carbonate decomposition, water vapor, iron.

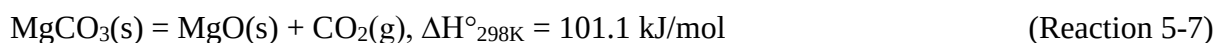
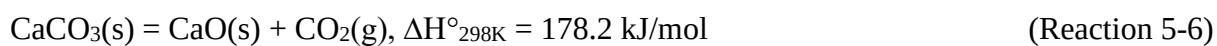
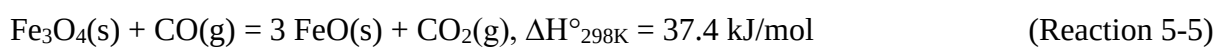
The findings presented in Chapter 5 formed the core of the article submitted to Metall. Mater. Trans. B.

5.2. Introduction

Manganese (Mn) is one of the most versatile additives in the steel industry where it is responsible for decreasing the brittleness while enhancing the strength and abrasion resistance of steel. Additionally, the inclusion of an Mn-alloy during steel production is to deoxidize the respective steel. Mn is also relatively inexpensive and readily available ^[1,2]. The industrial production of ferromanganese (FeMn) alloys is usually performed in a submerged arc furnace (SAF), with solid carbon (C) as the primary reductant. During the production process, carbon monoxide (CO) is generated from the reaction between Mn-oxide and C occurring in the smelting zone (hottest area) of the SAF. The CO permeates towards the upper parts of the SAF where it reacts with the raw ore in the furnace charge, initiating the pre-reduction of higher Mn- and iron (Fe)-oxides present in the ore, as indicated below.^[3,4]



The pre-reduction of the higher Mn-oxides to MnO and Fe₂O₃ to Fe₃O₄ (Reactions 5-1 to 5-4) is exothermic and will increase the overall temperature of the charge when contacted with CO as the charge descends in the SAF.^[3] There are also endothermic reactions taking place during the smelting process, such as the reduction of Fe₃O₄ to FeO (Reaction 5-5), the decomposition of carbonates (Reaction 5-6 and 5-7), and the Boudouard reaction (Reaction 5-8). These endothermic reactions have a significant influence on the C and energy consumption of FeMn production.

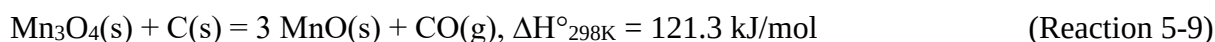


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A separate pre-treatment, i.e., pre-reduction, unit in FeMn production is relatively unexplored when compared to other metal-producing processes e.g., ferrochromium production. It is generally accepted by the FeMn industry, that due to the exothermic nature of Reactions 5-1 to 5-4, such reactions are advantageous to occur within the SAF during smelting procedures.

Including a separate pre-treatment step in the FeMn process can also be advantageous. At temperatures above 800 °C, Reaction 5-3 (reduction of Mn_3O_4 to MnO) and Reaction 5-8 (Boudouard reaction) proceed concurrently in the coke bed. Hence, the CO_2 produced by Reaction 5-3 is consumed by Reaction 5-8 to form CO . In addition, C is consumed during the direct reduction reaction, i.e., Mn_3O_4 is directly reduced to MnO in the presence of C following Reaction 5-9. Both Reactions 5-8 and 5-9 are endothermic, thereby increasing the overall energy consumption, as well as C consumption.^[3,5]



Furthermore, not all the ascending CO is utilized during the pre-reduction process and is ultimately expelled from the SAF as part of the off-gas. Typically, the off-gas contains approximately 60 vol.% CO .^[3] The excess consumption of C and energy, and loss of unused CO in the off-gas, can be avoided by implementing a pre-treatment unit where the ore is pre-reduced before entering the furnace.

If the hot CO -rich off-gas is redirected to a pre-reduction process, as a heat source and to partake in the pre-reduction reactions, the overall energy demand of the specific FeMn producing SAF can decrease by up to 25%.^[6,7] One example is given by the CDK Kashima Works in Japan where pre-treatment of different Mn-sources is performed in a rotary kiln in sequence with the SAF. In addition to a C -source being combusted, CO -rich off-gas from the SAF provides additional energy to the pre-reduction kiln. This additional pre-treatment step

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leads to a decrease in the overall energy consumption.^[7] Furthermore, Tangstad et al. (2015) showed that supplying hot Mn ore to a SAF reduced the specific SAF's energy consumption by approximately 20% (i.e., 400 – 500 kWh/ton FeMn).^[7]

To avoid the Boudouard reaction, and hence reduce the C and energy consumption, the CO₂-producing reactions (Reactions 5-1 to 5-7) should occur at a lower temperature than the Boudouard reaction (Reaction 5-8), which is estimated at around 800 °C. The solid-state pre-reduction of the higher oxides is controlled by the kinetics rather than the thermodynamics of the reaction. Studies have shown that parameters such as ore porosity and particle size, the furnace heating rate, and the gas atmosphere affects the rate of pre-reduction.^[4,8-10] The gas atmosphere used in industrial furnaces consists of CO/CO₂, hence many studies performed on the pre-reduction of Mn ore used a CO/CO₂ gas mixture. However, several studies have shown that the inclusion of hydrogen as a reductant in the gas atmosphere reduces the oxygen partial pressure (pO₂) and increases the degree and rate of pre-reduction.^[8,11]

Bhalla et al. (2015) studied the pre-reduction of Mamatwan ore originating from South Africa. The experiments were performed in a TG furnace in several CH₄-Ar gas mixtures at 1100 and 1200 °C. During the pre-reduction process, CH₄ underwent cracking which supplied hydrogen gas (H₂) and fine solid C to the surface of the ores, allowing intimate contact. The excess fine C caused the regeneration of the reductants CO and H₂ from CO₂ and H₂O provided by the reduction reactions, which resulted in a low pO₂ at the reduction sites.^[11]

Ngoy et al. (2020) performed non-isothermal experiments in a TG furnace on Nchwaning (also referred to as Assmang, the respective South African mine) and Comilog (Gabon) ores to investigate the effect of hydrogen on pre-reduction. Both ores were subjected to hydrogen-containing CO/CO₂ gas mixtures i.e., 41% CO 18% H₂ 41% CO₂ and 41% CO 41% H₂ 18% CO₂, up to 1000 °C. The author found that for the same pO₂, the reduction rate increased by 20 – 30% when hydrogen was included in the CO/CO₂ gas mixture. It was also

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seen that a higher reduction rate was achieved with a lower pO_2 of the gas mixture with or without hydrogen.^[8]

The influence of hydrogen on the rate and degree of pre-reduction of Nchwaning ores was investigated by Schanche et al. (2021). The ore was reduced at 600 – 800 °C in a CO/CO₂ and/or hydrogen atmosphere at various pO_2 . It was found that the degree and rate of reduction improved with an increase in temperature and a decrease in pO_2 . It was found that the degree and rate of reduction improved with an increase in temperature and a decrease in pO_2 . The inclusion of hydrogen caused the reduction rate to increase by a factor of 1.3. and 2.6 for low and high pO_2 , respectively. The authors assumed that the increase was due to the improved diffusivity characteristics of hydrogen (i.e., the ability to penetrate ore particles).^[4]

Larssen et al. (2022) investigated the potential influence of hydrogen (in the form of hydrogen and water vapor) and the occurrence of the water-gas shift reaction (WGSR) on the pre-reduction kinetics of Comilog and Nchwaning ore. The ores were subjected to CO/CO₂/H₂, CO/CO₂/H₂O(g), and CO/CO₂ gas atmospheres at different pO_2 in a TG furnace. The highest reduction rate was achieved in the CO/CO₂/H₂ gas atmosphere, while the lowest was obtained in the CO/CO₂ gas atmosphere. Furthermore, the highest degree of reduction was achieved at the lower pO_2 when hydrogen was present in the gas atmosphere. The authors also found that at low temperatures, the WGSR proceeded to some degree without reaching equilibrium, however, equilibrium was reached at higher temperatures.^[12]

Most of the later studies were performed on Mn ore with a low carbonate content, such as Comilog and Nchwaning ores. However, during the pre-reduction of Mn ores rich in carbonates (e.g., UMK, Mamatwan, and Gloria ores originating from the Mamatwan environment of the Kalahari basin in South Africa), CO₂ in the off-gas mainly originates from carbonate decomposition. Furthermore, due to the endothermic nature of carbonate decomposition, a fraction of the energy demand during pre-reduction is due to the

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decomposition reactions, i.e., Reactions 5-6 and 5-7.^[3] Nevertheless, it is beneficial that most of the CO₂ formation occurs during the pre-treatment step (i.e., pre-reduction) to mitigate the CO₂ supply for the Boudouard reaction during smelting procedures.

Calcite (CaCO₃), magnesium carbonate (MgCO₃), and dolomite (CaMg (CO₃)₂) are the most abundant carbonates in Mn ores. The decomposition of calcite (CaCO₃) initiates at approximately 900 °C; this temperature corresponds with the temperature required for the Boudouard reaction (Reaction 5-8) to initiate. Nevertheless, the magnesium carbonate (MgCO₃) and dolomite (CaMg(CO₃)₂) decompose at <800 °C.^[3] Using hydrogen as a reductant will yield H₂O, which will lower the pCO₂, compared to when CO is used as a reductant (Reactions 5-1 – 5-5). The lower pCO₂ atmosphere will accelerate the decomposition of carbonates. It is therefore important to quantify the effect of hydrogen as a reductant on the rate and degree of carbonate decomposition. Carbonate decomposition is also dependent on temperature and is accelerated at higher temperatures.^[13,14]

A fundamental study on the pre-reduction and decomposition of Mn ores with hydrogen was performed using 100% H₂ and 70% H₂ 30% H₂O atmospheres. UMK ore, a carbonate-rich ore from South Africa, was considered as the case study ore. As a reference, the ore was subjected to pre-reduction in a 70% CO 30% CO₂ gas atmosphere. The 70% CO 30% CO₂ and 70% H₂ 30% H₂O atmospheres had similar pO₂, which suggests that both atmospheres had comparable thermodynamic driving forces for the pre-reduction reactions (Reactions 5-1 – 5-5) and decomposition reactions (Reactions 5-6 and 5-7). The pre-reduction and carbonate decomposition reactions were investigated by isothermal experimentation using a TG furnace at various temperatures.

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5.3. Materials and methods

5.3.1. Experimental

UMK ore with a size fraction of 9.5-16.0 mm was selected for the experiments. UMK is a semi-oxidized (Mn_2O_3) ore from the Mamatwan environment. The ore mainly consists of braunite I ($3(\text{Mn,Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), and hausmannite (Mn_3O_4). Kutnahorite ($(\text{Ca,Mn,Mg,Fe})(\text{CO}_3)_2$), bixbyite ($(\text{Mn,Fe})_2\text{O}_3$), and hematite (Fe_2O_3) is also found but to a lesser degree.^[15]

The raw ore was dried at 105 °C to remove any surficial moisture. The dried ore was then divided into individual batches of approximately 156 g which were utilized in the experiments. A TG furnace was used to investigate the solid-gas pre-reduction and decomposition reactions of the ore. Experiments were performed in an Entech VTF 80/15 (Ängelholm, Sweden) vertical resistance tube furnace. The ore was placed in a high-temperature gas-tight stainless-steel (253 MA) double-wall crucible (Figure 5-1) which was suspended from a balance (Mettler Toledo PR2003DR, Greifensee, Switzerland) to record the weight changes during the experiments. Figure 5-1 presents a schematic illustration of the crucible used in the experiments. While the crucible was freely suspended, the furnace position could be altered vertically so that the crucible could be inside or outside the furnace hot zone during the heating and cooling periods, respectively. The heating of the furnace was controlled by a Eurotherm PID controller and measured with a calibrated S-type thermocouple. A K-type thermocouple placed in an alumina tube and positioned in the middle of the charge was used to measure the charge temperature. All temperature values reported here are based on the measurements made using the K-type thermocouple.

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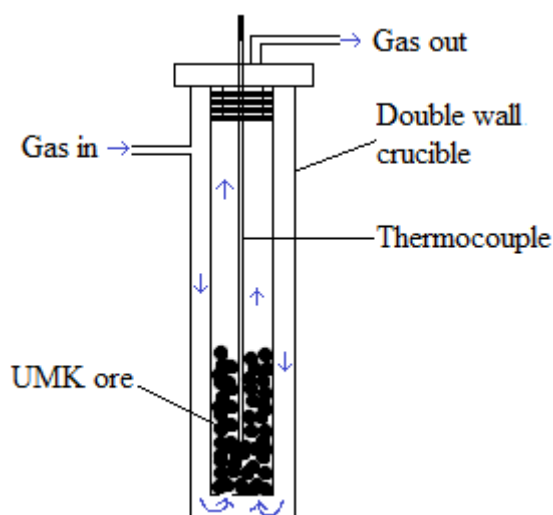


Figure 5-1 Schematic illustration of the double wall crucible used in the pre-reduction experiments. The illustration also indicates the direction of the gas flow (blue arrows) during the pre-reduction process.^[16,17]

Flexible gas inlet and outlet pipes were connected to the top of the crucible which allowed multiple gasses to mix before entering the crucible. In all the experiments the total gas flow rate was 4 L/min. The gas was preheated as it moved along the double wall of the crucible down to the sample (Figure 5-1). Each gas line had its mass flow controller (Bronkhorst F-201C, United Kingdom). In this investigation, Ar (99.999%), CO (99.97%), CO₂ (99.9992%), and H₂ (99.9%) were used.

In addition, the weight of the sample before and after the experiment was recorded on an external Ohaus Pioneer PA4202 scale (New York, USA) to confirm the net weight loss obtained from the TG data. The samples were pre-reduced at isothermal temperatures of 700, 800, and 900 °C. However, due to the heating time, pre-reduction of higher oxides (exothermic) and decomposition of carbonates (endothermic) partly occurred during heating to set temperatures, and thus the samples did not experience a true isothermal condition. After the experiment was complete the sample was allowed to cool to ambient temperature in Ar.

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A portion (25%) of the pre-reduced samples was crushed and a fraction thereof was used for chemical analysis. The remainder was pulverized in a Retsch Vibratory Disc Mill RS 200 (Haan, Germany) at 900 rpm for 90 sec. A sample from the unreduced material was prepared similarly. The grinding set consisted of tungsten carbide grinding rings and a plate. XRD analyses were performed on the pulverized samples by using a Bruker D8 A25 DaVinci X-ray Diffractometer (Billerica, USA) with $\text{CuK}\alpha$ radiation and LynxEye™ SuperSpeed Detector. The results were obtained in a total of 7200 sec at a scanning angle of 2θ and a range of 10 to 90° with 0.013° step sizes. The DIFFRAC.EVA V5.1 software together with the PDF-4+ database was used to index the phases present in the samples.

The chemical composition of the pulverized raw and pre-reduced ores was examined by X-ray fluorescence (Bruker AXS S4 Pioneer X-Ray fluorescence spectrometer) using the fused bead technique. Permanganometric titration (ASTM 465-11:2017) was employed to measure the excess oxygen above MnO which is expressed as MnO_2 . The C concentration was analyzed with a LECO (Combustion-IR) instrument and the CO_2 concentration was determined by assuming that all C in the ore is in the form of CO_2 . The loss on ignition (LOI) was thermogravimetrically measured to a stable weight at 950°C in air.

The microstructure and elemental composition of the raw material and pre-reduced samples were analyzed in secondary and backscattered electron mode by a scanning electron microscope (SEM) equipped with an energy-dispersive x-ray spectrometer (EDS). A Zeiss - Supra 55VP - FEG-SEM including an EDAX OCTANE PRO-A EDS detector (sensor area 10 mm^2) operating at 10 kV and a working distance of 10 mm was used. The samples were mounted in epoxy and polished (Struers, Tegramin-20, Ballerup, Denmark) with traditional wet metallographic methods. The samples were C-coated before SEM-EDS analysis. Element mapping of the samples was done by using Electron Probe Micro Analysis (EPMA). FE-EPMA

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with JEOL WDS system (JEOL JXA 8500, Sydney, Australia) was used for the EPMA analysis.

Porosity measurements were performed on raw ore and pre-reduced samples. The porosity was determined by the ratio between absolute and apparent density. The absolute density was measured by Accupyc 1330 helium pycnometer, while the apparent density was determined by a GeoPyc 1360 pycnometer.

The decrepitation of the reduced samples was measured after the pre-reduction experiments by sieving the charge through a sieving stack consisting of 9.50, 6.70, 4.75, 3.15, 1.60, and <0.50 mm sieves.

5.3.2. Calculations

A time series of five seconds was used to detect the mass loss of the solid charge during the TG performed in different gas atmospheres at various temperatures. The experimental weight loss data from the TG system was used to calculate the weight loss percentage. The corresponding O/Mn ratio as a function of time is calculated from the weight loss percentage through Equation 5-1.

$$O/Mn_{(t)} = O/Mn_{(i)} - \frac{wt.\% \text{ loss } (t)}{\text{Theoretical wt.\% loss}} \times (O/Mn_{(i)} - 1) \quad (\text{Equation 5-1})$$

Where wt.% loss (t) is the weight loss percentage at time t, theoretical wt.% loss is the theoretical weight loss percentage, O/Mn_(t) is the O/Mn mol ratio at time t and O/Mn_(i) indicates the initial O/Mn mol ratio before reduction. The O/Mn_(i) value is calculated from the chemical analysis of the raw ore (Table 5-2) i.e., the total Mn measured in XRF and the MnO₂ measured from the titrimetric method. The O/Mn_(i) value can be calculated through Equations 5-2 and 5-3 when assuming that all the Mn absent in MnO₂ is present in MnO, and in this case, the O/Mn_(i) is calculated to be 1.39. Previous studies have calculated the O/Mn_(i) ratio of UMK ore to be between 1.3^[18] and 1.45^[19,20]. The variation in the O/Mn_(i) ratio can be due to the heterogeneity

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of the ore and/or to some of the Mn being present as manganese carbonate (MnCO_3) which will affect the O/Mn ratio.^[20]

$$O/Mn_{(i)} = \frac{2 \cdot \text{mol MnO}_2 + \text{mol MnO}}{\text{mol Mn}} \quad (\text{Equation 5-2})$$

$$\text{mol MnO} = \text{mol Mn} - \text{mol MnO}_2 \quad (\text{Equation 5-3})$$

Furthermore, the theoretical weight loss is determined by the chemical analysis (Table 5-2) of the raw ore by determining the LOI, CO_2 , O/Mn, and Fe content of the ore. The calculation is based on three assumptions; i) all Fe is initially in the Fe_2O_3 form and reduces to FeO, ii) Mn reduces from $O/Mn_{(i)}$ to MnO, iii) and all the C present in the raw ore represents carbonates that will decompose to CO_2 .

Considering the measuring method of LOI, it is assumed that all carbonates decomposed, and all volatiles were evaporated. Furthermore, according to Figure 5-2, the most stable oxides of Mn and Fe at 950 °C are Mn_3O_4 and Fe_2O_3 , respectively.^[4] Hence the LOI contains water vapor, carbonates, and decomposed Mn (Mn_3O_4), and the amount of water vapor can be calculated by subtracting the wt.% CO_2 shown in the chemical analysis and the decomposed Mn.^[20] The calculated theoretical weight loss for UMK ore is shown in Table 5-1.

$$\text{wt. \% loss Fe} = \frac{\text{wt. \% Fe}}{\text{Molar mass Fe}} \times \text{Molar mass O} \times (\text{FeO}_{1.5} - \text{FeO}_1) \quad (\text{Equation 5-4})$$

$$\text{wt. \% loss Mn} = \frac{\text{wt. \% Mn}}{\text{Molar mass Mn}} \times \text{Molar mass O} \times (O/Mn_{(i)} - 1) \quad (\text{Equation 5-5})$$

$$\begin{aligned} \text{wt. \% loss H}_2 &= \text{wt. \% LOI}_{950} - \text{wt. \% loss CO}_2 - \frac{\text{wt. \% Mn}}{\text{Molar mass Mn}} \times \text{Molar mass O} \cdot (O/ \\ &\text{Mn}_{(i)} - 1.33) \end{aligned} \quad (\text{Equation 5-6})$$

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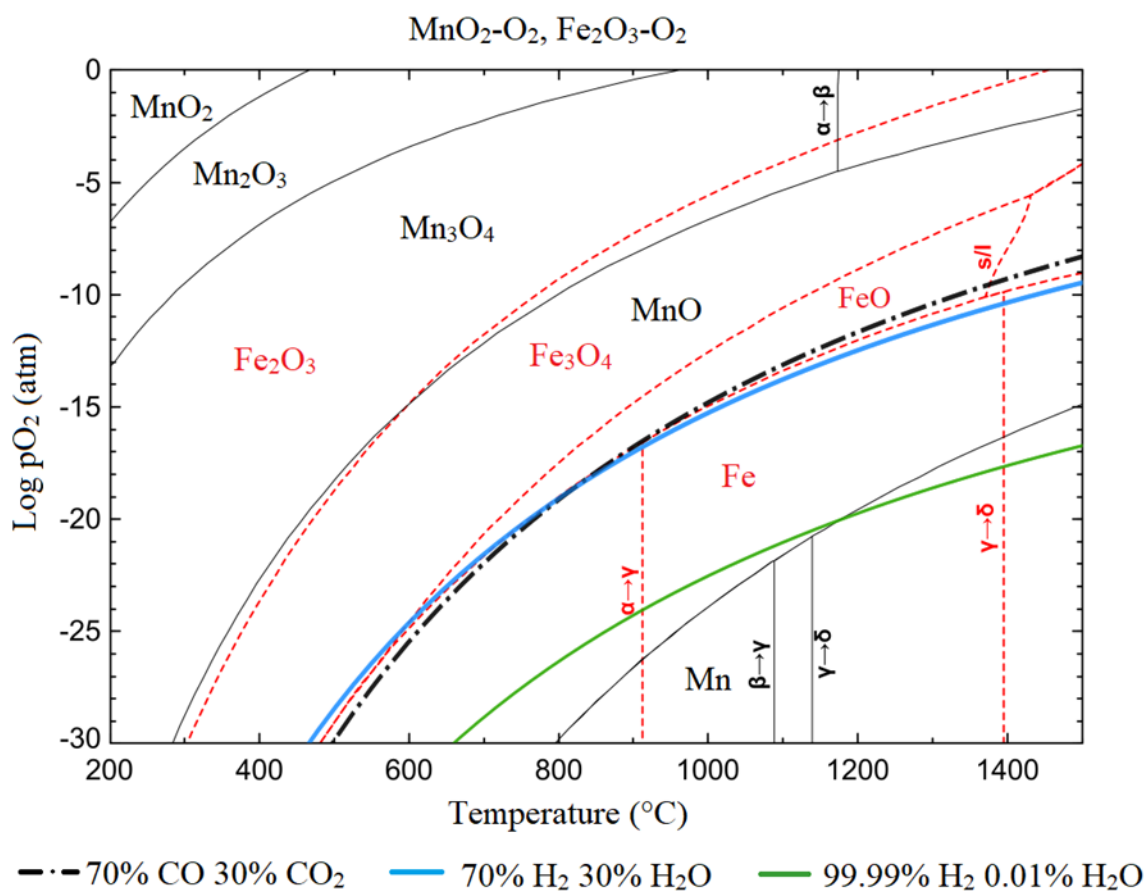


Figure 5-2 The Fe-O and Mn-O stability diagrams show oxygen partial pressure as a function of temperature.^[4] The pO₂ of (black stripe-dotted, blue, and green lines) are superimposed on the stability diagram. Factsage^[21] and HSC Chemistry 10^[22] were used for the calculation of the stability diagrams and the pO₂, respectively.

Table 5-1: Calculated theoretical weight loss of UMK ore (wt.%)

	Theoretical weight loss (wt.%)
Pre-reduction of O/Mn _(i) to MnO	3.47
Fe-pre-reduction of Fe ₂ O ₃ to FeO	0.89
Fe-pre-reduction of Fe ₂ O ₃ to Fe	2.56
Carbonate decomposition	17.0
Water evaporation	0

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5.4. Results and discussion

5.4.1. Characterization

Table 5-2 summarizes the chemical composition of the raw and pre-reduced ore and the O/Mn ratios obtained for the three different gas atmospheres i.e., 70% CO 30% CO₂, 70% H₂ 30% H₂O, and 100% H₂ at three different temperatures i.e., 700, 800, and 900 °C. The MnO₂ value (<0.05 wt.%) obtained through chemical analysis indicates that all the samples are completely reduced to MnO.

Very little CO₂ was detected in the samples subjected to the hydrogen-containing gas atmospheres i.e., 70% H₂ 30% H₂O, and 100% H₂ as well as the sample pre-reduced in 70% CO 30% CO₂ at 900 °C, meaning that almost all the carbonates decomposed in these samples. The percentage of decomposed carbonates was calculated from initial values and the results are shown in Figure 5-3.

Table 5-2: Chemical composition (wt.%) and the Mn/Fe and O/Mn ratio of raw material and pre-reduced samples as determined by various analytical techniques.

	Raw Ore (wt.%)	Gas atmospheres								
		70% CO 30% CO ₂			70% H ₂ 30% H ₂ O			100% H ₂		
		700 °C	800 °C	900 °C	700 °C	800 °C	900 °C	700 °C	800 °C	900 °C
C	4.65	3.19	2.4	0.19	0.20	0.17	0.08	0.15	0.22	0.17
CO ₂	17.0	12.0	8.80	0.70	0.73	0.37	0.29	0.55	0.29	0.62
Mn	33.71	39.51	42.00	45.06	45.75	45.92	46.11	46.32	48.44	47.17
Fe	5.86	5.86	5.66	6.08	6.84	6.34	6.75	5.98	7.10	6.10
SiO ₂	7.34	6.94	6.17	8.25	8.94	8.42	8.42	7.30	7.58	7.53
Al ₂ O ₃	0.37	0.38	0.37	0.60	0.54	0.48	0.55	0.44	0.90	0.49
CaO	17.01	18.3	19.3	20.62	17.91	18.73	18.10	21.97	15.56	20.57
MgO	2.61	3.2	3.07	3.76	3.54	3.66	3.94	3.49	3.28	3.55
P	0.015	0.018	0.015	0.021	0.023	0.023	0.023	0.020	0.024	0.020
S	0.010	0.024	0.028	0.032	0.021	0.024	0.021	0.035	0.029	0.032
TiO ₂	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
K ₂ O	0.06	0.12	0.21	0.06	0.14	0.28	0.23	0.11	0.39	0.15
BaO	0.06	0.04	0.06	0.04	0.05	0.08	0.04	0.04	0.77	0.06
MnO ₂	20.55	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
LOI 950	16.89	7.28	3.40	-4.82	-4.56	-5.00	-5.14	-6.30	-7.01	-6.92
Mn/Fe	5.75	6.74	7.42	7.41	6.69	7.24	6.83	7.75	6.82	7.73
O/Mn	1.39	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

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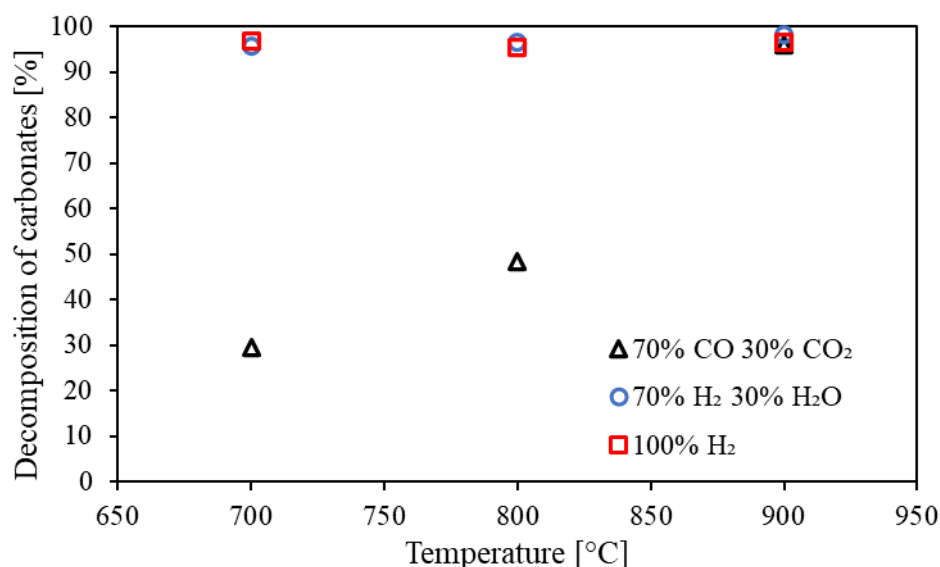


Figure 5-3 A fraction of the total wt.% of carbonates decomposed in UMK ore as a function of temperature.

As stated earlier, no CO₂ is generated during the pre-reduction reactions (Reaction 5-1 to 5-5) when hydrogen is used as the reductant; hence a lower pCO₂, and subsequently, a higher decomposition driving force is obtained during pre-reduction in a 70% H₂ 30% H₂O atmosphere when compared to a 70% CO 30% CO₂ atmosphere.^[13,23,24] Figure 5-3 shows that a lower percentage of carbonates decomposed at 700 °C (29.4%) and 800 °C (48.2%) for samples reduced in 70% CO 30% CO₂, whereas near 100% carbonate decomposition was achieved for the hydrogen-containing atmospheres.

Figure 5-4 was compiled to show the phase-stability diagram for selected carbonates, where the y-axis represents the partial pressure of CO₂ (pCO₂), and the x-axis represents temperature. It can be seen that in a 70% CO 30% CO₂ atmosphere (log pCO₂ = -0.3 that is, pCO₂ = 0.501 atm) the magnesium carbonates (MgCO₃), manganese carbonates (MnCO₃), dolomite (CaMg(CO₃)₂) and calcite (CaCO₃) all decompose at different temperatures i.e., 272, 308, 389, and 810 °C, respectively. Similar observations were made by Olsen et al. (2007)^[3] and Schanche et al. (2021)^[4]. Thermodynamic calculations suggest that calcite (CaCO₃)

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decomposition initiates at temperatures above 810 °C, while the other carbonates decompose at temperatures below 389 °C. Hence, the carbonates still present in samples pre-reduced in a 70% CO 30% CO₂ atmosphere at 700 and 800 °C are most likely calcite (CaCO₃).

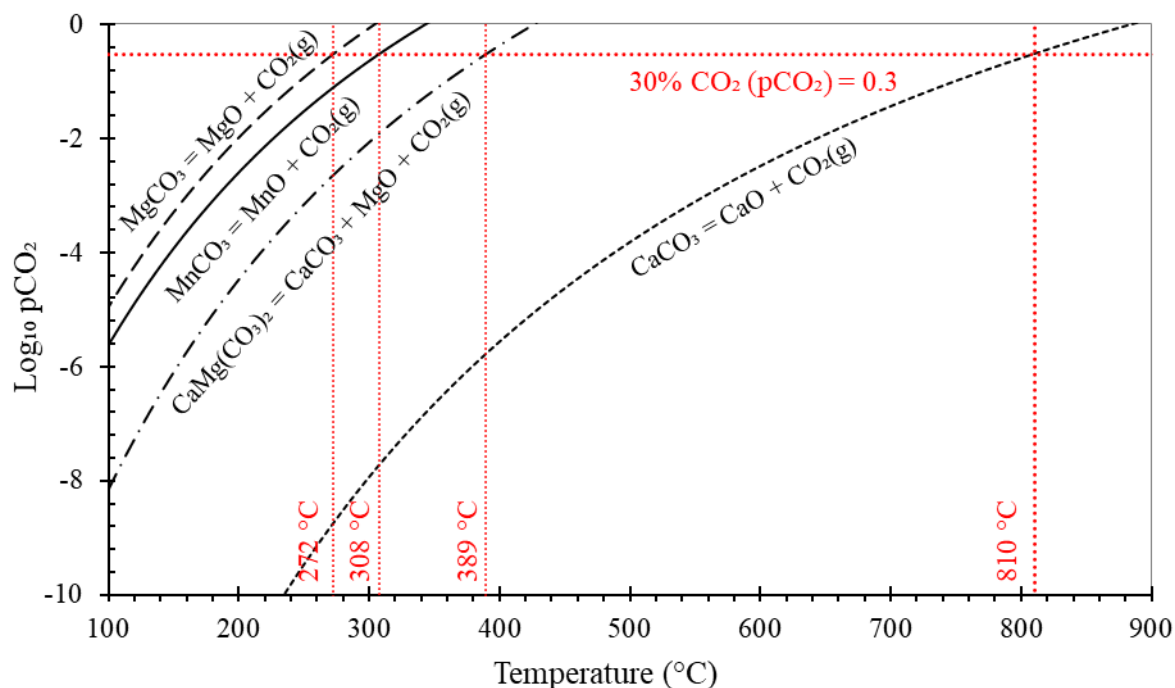


Figure 5-4 Phase-stability diagram for selected carbonates as a function of log pCO₂ and temperature. In the 70% CO 30% CO₂ gas atmosphere the log pCO₂ = -0.3 is indicated by the horizontal, red dotted line. The equilibrium temperature at log pCO₂ = -0.3 for each carbonate is shown by the vertical, red dotted lines. The stability diagram and pCO₂ were calculated using HSC Chemistry 10.^[22]

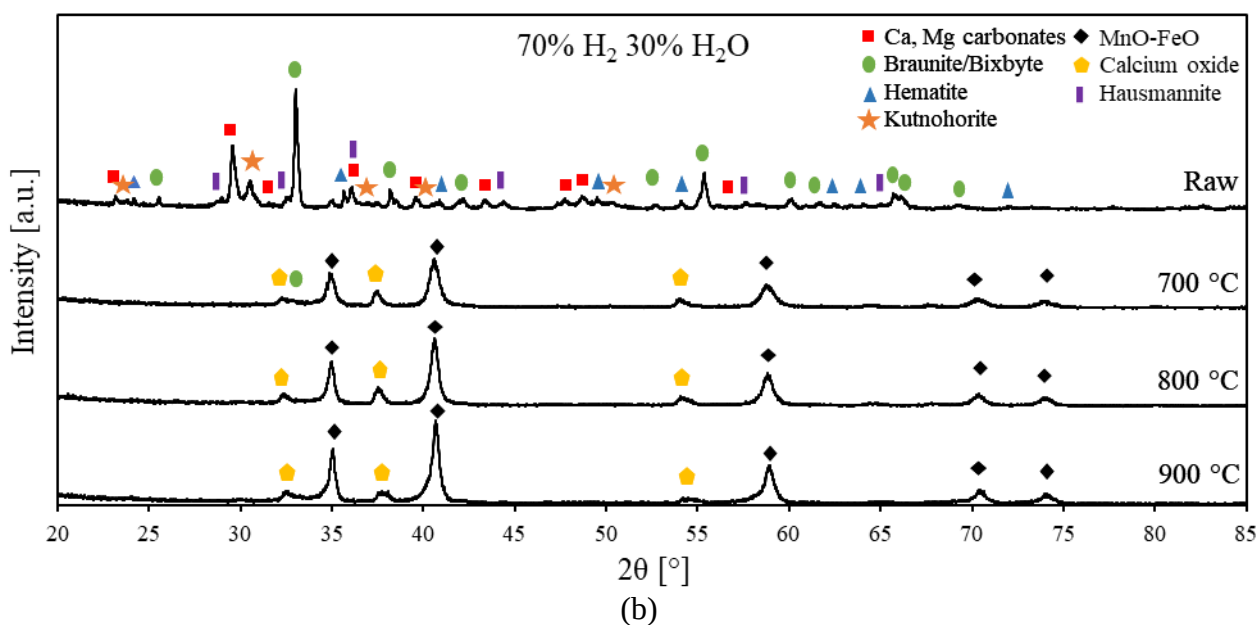
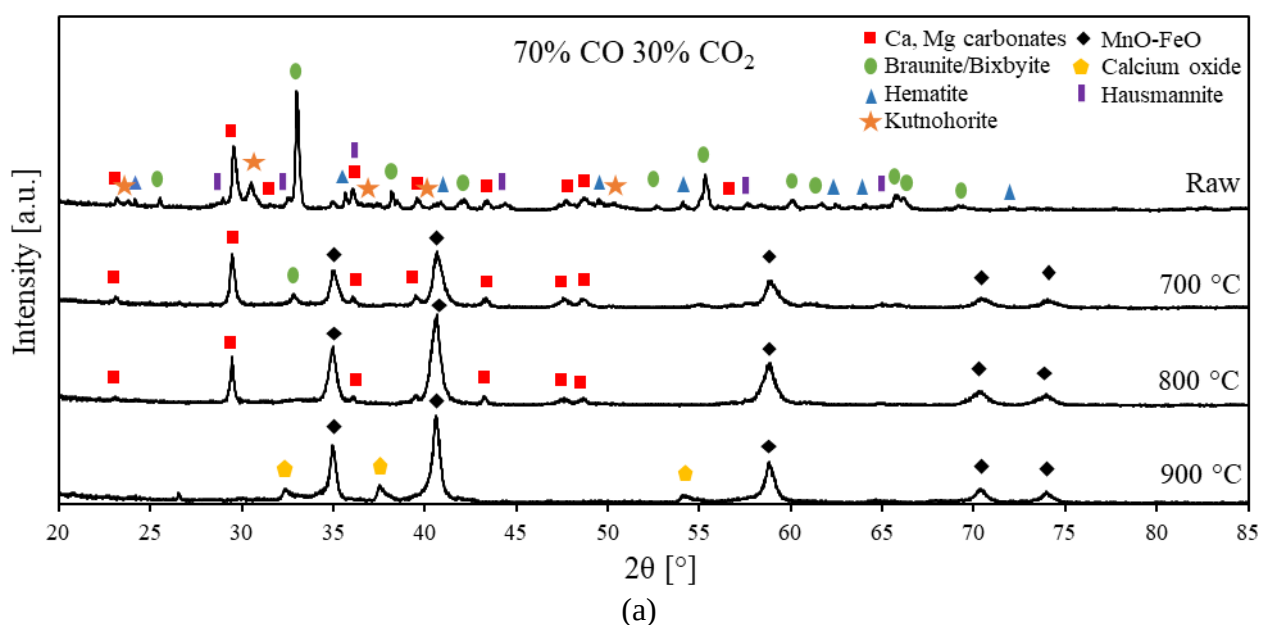
5.4.2. Mineralogical phase transformation during pre-reduction

XRD analysis of raw and pre-reduced ores is shown in Figure 5-5. The chemical formulas of detected phases are shown in the figure caption. The carbonates present in the raw ore were detected as Calcite (CaCO₃), Magnesium carbonate (MgCO₃), and Kutnahorite ((Ca,Mn,Mg,Fe)(CO₃)₂). For the samples pre-reduced in CO/CO₂, no kutnahorite was detected at 700 and 800 °C, while some Ca- and Mg-carbonates were still present. The main Ca- and

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Mg-carbonate peaks at approximately 29° contained more Ca (0.936) than Mg (0.064) which explains why only Calcium oxide (CaO) peaks are visible at 900°C . As determined using thermodynamical calculations (Figure 5-4), calcite (CaCO_3) is mainly present at 700 and 800°C . Furthermore, all the carbonates decomposed at 900°C .

The XRD patterns of the hydrogen-containing gas atmospheres indicate that all the carbonates decomposed in the 700 to 900°C temperature range. These results are in correlation with the chemical analysis shown in Table 5-2 and the thermodynamic results in Figure 5-4.



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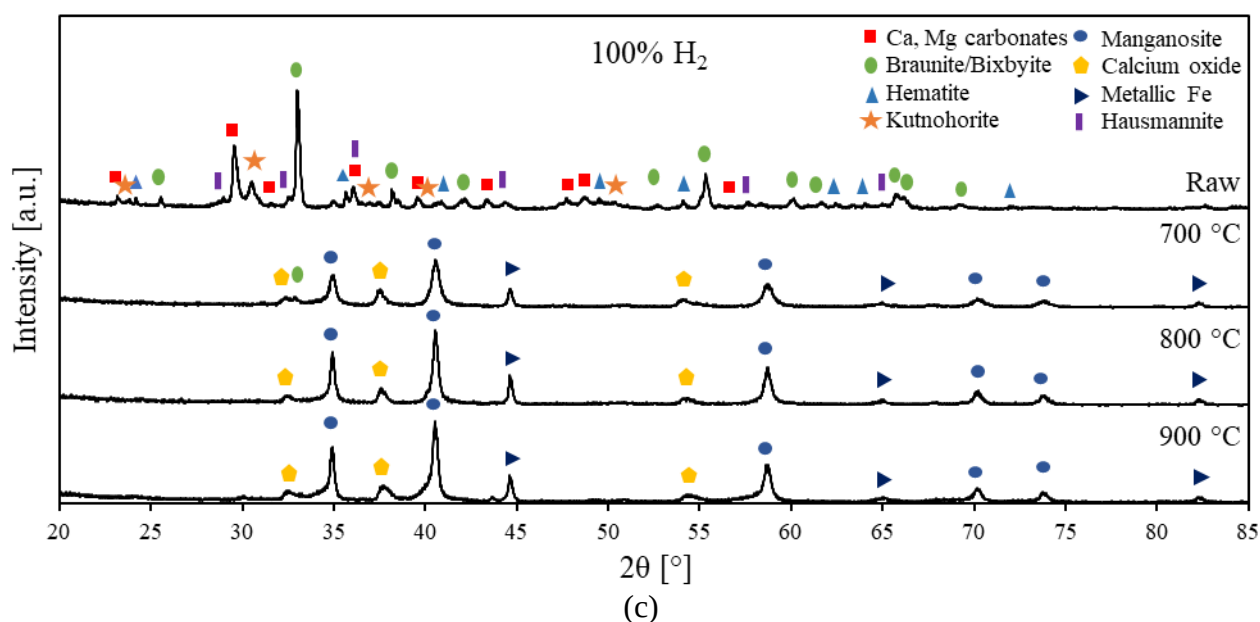


Figure 5-5 XRD patterns of the raw ore and samples pre-reduced in 70% CO 30% CO₂ (a), 70% H₂ 30% H₂O (b), and 100% H₂ (c) at 700, 800, and 900 °C. Chemical formula of compounds: calcite (CaCO₃); magnesium carbonate (MgCO₃); braunite (3(Mn,Fe)₂O₃·MnSiO₃); bixbyite ((Mn,Fe)₂O₃); hematite (Fe₂O₃); kutnohorite ((Ca,Mn,Mg,Fe)(CO₃)₂); manganosite (MnO); calcium oxide (CaO); hausmannite (Mn₃O₄).

The XRD of the raw ore showed that braunite (3(Mn,Fe)₂O₃·MnSiO₃) and bixbyite (Mn,Fe)₂O₃) were the two main Mn-containing phases, hence the original state of Mn before pre-reduction procedures was Mn³⁺ (Mn₂O₃).

The XRD patterns of all the pre-reduced samples showed that braunite (3(Mn,Fe)₂O₃·MnSiO₃) and bixbyite ((Mn,Fe)₂O₃) were pre-reduced to manganosite (MnO) without the formation of hausmannite (Mn₃O₄). The absence of hausmannite (Mn₃O₄) in the pre-reduced samples could be due to the initial content in the unreduced ore or that the intermediary hausmannite (Mn₃O₄) was reduced at a rapid rate.^[4]

A study by Zaki et al. (1997) showed that a stepwise reduction (more specifically, its decomposition) of synthetic Mn-oxides (MnO₂) was only seen in an oxidizing (O₂, air)

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atmosphere. In a reducing atmosphere, the MnO_2 reduced directly to MnO without the generation of stable intermediates, i.e., Mn_5O_8 , Mn_2O_3 , and Mn_3O_4 .^[25]

Small amounts of braunite ($3(\text{Mn,Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$)/bixbyite ($(\text{Mn,Fe})_2\text{O}_3$) were still present in the samples pre-reduced at 700 °C, even though the chemical analysis (Table 5-2) suggests that the Mn-oxides were completely reduced to MnO ($\text{O/Mn} = 1$, $\text{MnO}_2 = <0.05 \text{ wt.}\%$). It has previously been observed that the Fe content of the Mn source lowers the MnO_2 measurement from the chemical analysis which explains the discrepancy between the chemical analysis and the XRD analysis.^[4] However, the peak intensity was low, hence the discrepancy between the XRD and chemical analysis is not that significant.

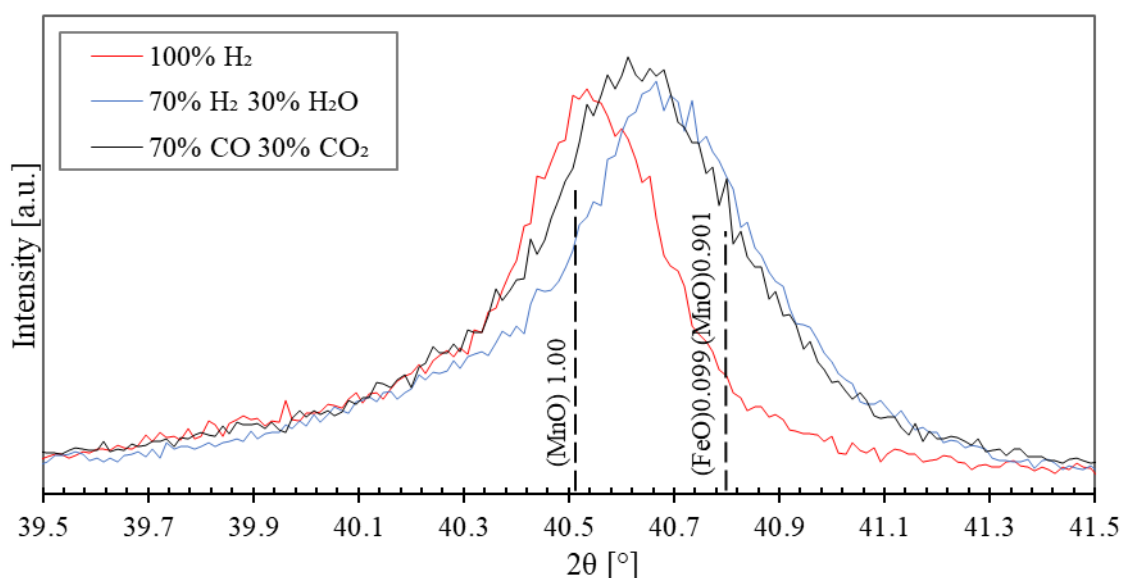


Figure 5-6 Main peak from the manganosite (MnO) phase of the sample pre-reduced in 70% CO 30% CO_2 , 70% H_2 30% H_2O , and 100% H_2 at 900 °C. The vertical dashed lines indicate the 2θ value (°) where manganosite (MnO) and Fe- and Mn- oxide (FeO-MnO) peaks form during XRD analysis.

Furthermore, the XRD analysis revealed that metallic Fe was present in samples pre-reduced in 100% H_2 at all temperatures, and low-intensity Fe-oxide peaks were detected in the manganosite (MnO) phase. In Figure 5-6 the main manganosite (MnO) peak of the sample pre-

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reduced in 100% H₂ shifted to the left compared to the sample pre-reduced in 70% CO 30% CO₂, which is indicative of a lower Fe-oxide content. This is in accordance with the observations made in Figure 5-5c regarding metallic Fe since the formation of Fe warrants its depletion from the oxide phase.^[4] In addition, the manganosite (MnO) peak of the sample pre-reduced in 70% H₂ 30% H₂O is shifted more to the right, indicating a higher Fe-oxide content than the sample pre-reduced in 70% CO 30% CO₂. As was seen in Figure 5-5a and b, no metallic Fe was detected in samples reduced in a 70% CO 30% CO₂, and 70% H₂ 30% H₂O atmospheres. The utilization of hydrogen as reductant, hence, improves the reduction of Fe-oxides. This improvement was also seen in previous studies based on the reduction of Fe ores.^[26-30]

The pO₂ of the gas atmospheres is included in the Fe-O and Mn-O stability diagram (Figure 5-2) to show that metallic Fe formation in 70% CO 30% CO₂ and 70% H₂ 30% H₂O gas atmospheres are not thermodynamically feasible at the given experimental conditions. However, Figure 5-2 showed that not only kinetically, but also thermodynamically, metallic Fe would form when UMK ore is reduced in 100% H₂ in the 700 – 900 °C temperature range.

5.4.3. SEM morphology and EPMA on raw and pre-reduced UMK ore

Based on the SEM observations presented in Figure 5-6, it is evident that two phases were present in the raw ore, i.e., referred to here as light and dark phases. From SEM characterization by Sukhomlinov et al. (2021)^[14] in a previous non-related study using the same ore-type, the lighter phases were rich in braunite (3(Mn,Fe)₂ O₃·MnSiO₃), bixbyite ((Mn,Fe)₂O₃) and hausmannite (Mn₃O₄), whereas the darker phases were enriched in Ca and Mg (the main carbonate-associated phases) which were detected at concentrations up to 28 wt.% and 4.5 wt.%, respectively. Therefore, the UMK ore consisted of a fine-grained structure (Figure 5-7a), which contained carbonate-rich ovoid and laminae (Figure 5-7b).^[14]

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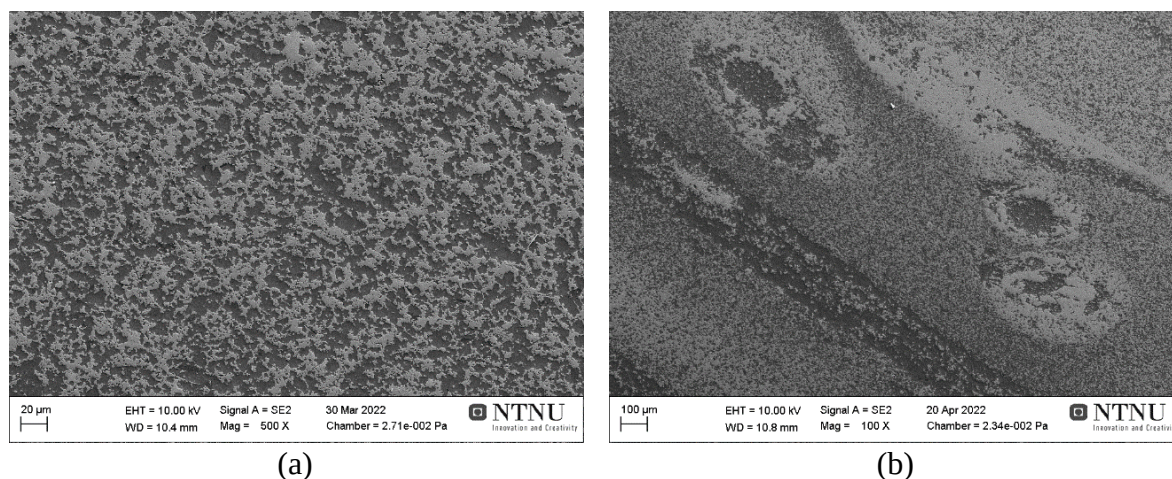
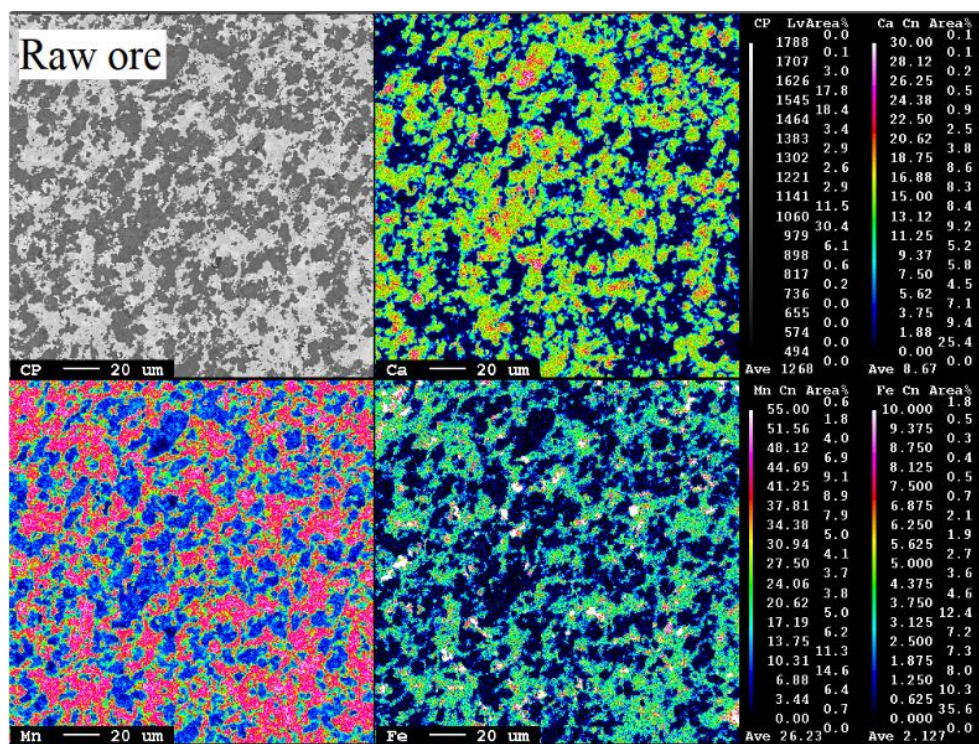


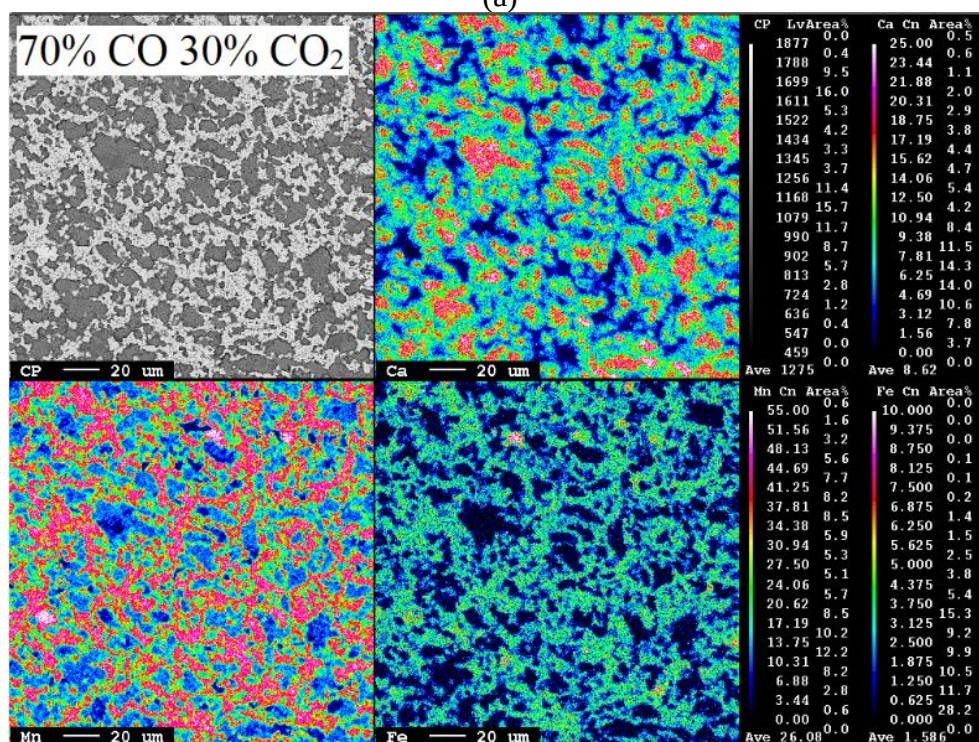
Figure 5-7 Secondary electron SEM micrographs showing the fine-grained structure (a) and carbonate-rich ovoid and laminae (b) of raw UMK ore.

EPMA was performed on cross-sectioned and polished raw ore and all samples pre-reduced at 800 °C to determine how the microstructure of the ore changes when hydrogen is used as reductant (Figure 5-8). EPMA of the raw ore was included as a reference (Figure 5-8a). According to Figure 5-8a-d three phases were observed: the Fe- and Mn-rich (Figure 5-8a to d, white areas), Ca- and Mg-rich (Figure 5-8a to d, dark grey areas) phases, and an Mg-, Si-, K- and Na-rich (light grey) phase (Figure 5-8e), mainly occurring as a segregated phase. The chemical composition of the detected phases is included in Table A1 (Supplementary information).

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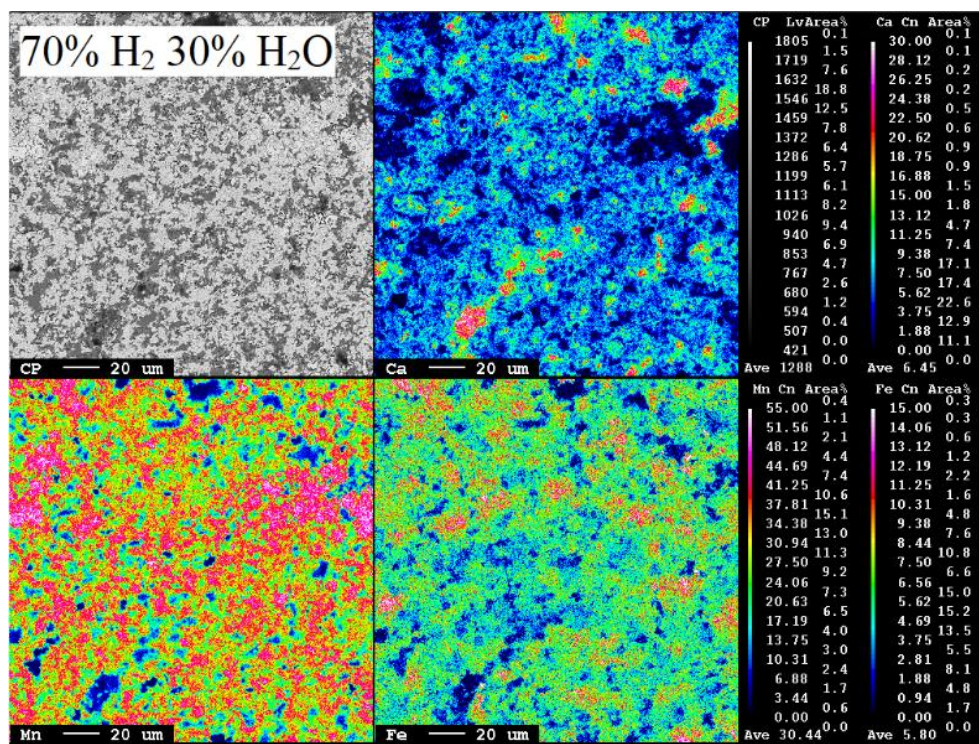


(a)

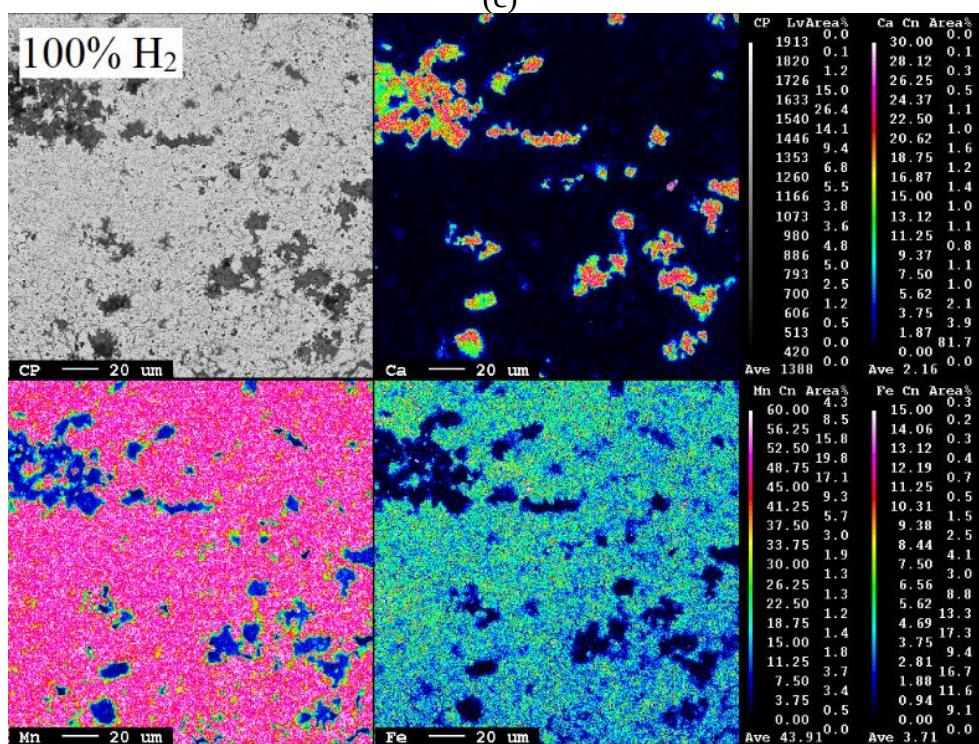


(b)

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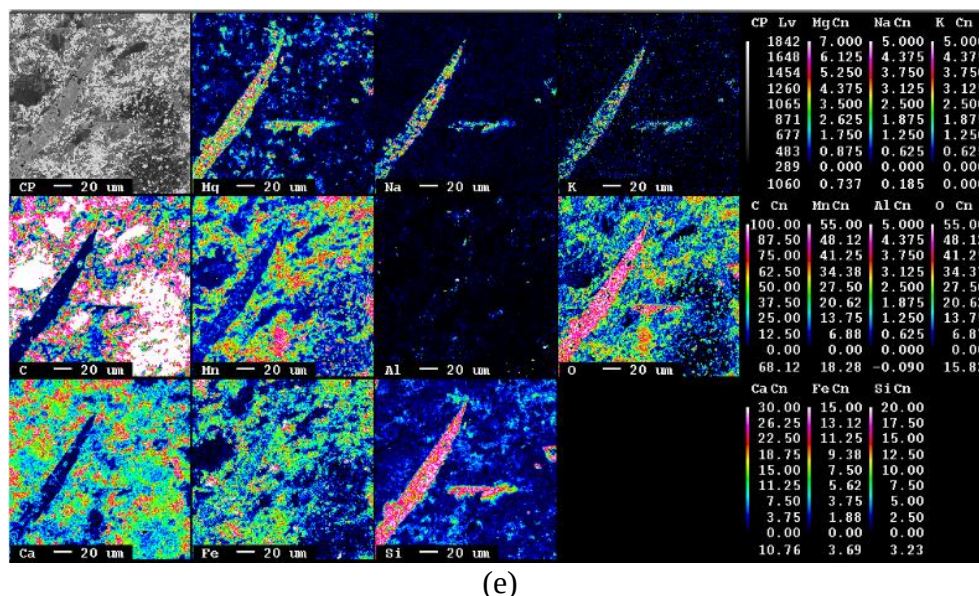


(c)



(d)

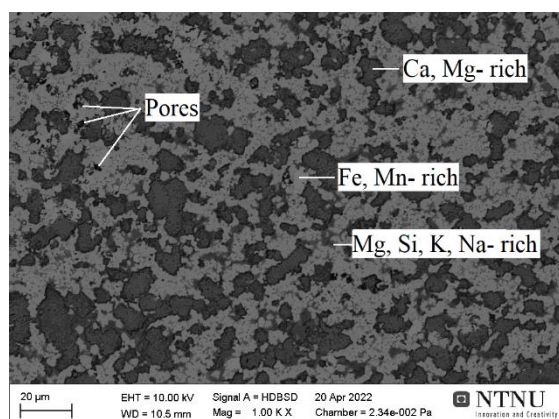
The findings presented in Chapter 5 formed the core of the article submitted to Metall. Mater. Trans. B.



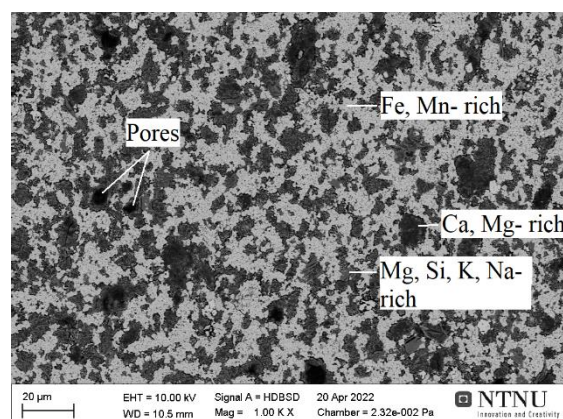
(e)

Figure 5-8 EPMA performed on cross-sectioned and polished raw ore (a), samples pre-reduced in 70% CO 30% CO₂ (b), 70% H₂ 30% H₂O (c), and 100% H₂ (d) atmospheres at 800 °C, and Mg-, Si-, K-, Na - rich phases embedded as a segregated phase in samples pre-reduced in a 70% H₂ 30% H₂O atmosphere (e).

SEM analysis was performed on cross-sectioned polished samples pre-reduced in the various gas atmospheres at 800 °C to determine the presence and extent of pore formation (i.e., open spaces present in the ore particles), as well as to elucidate the distribution of the phases presented in Figure 5-8.



(a)



(b)

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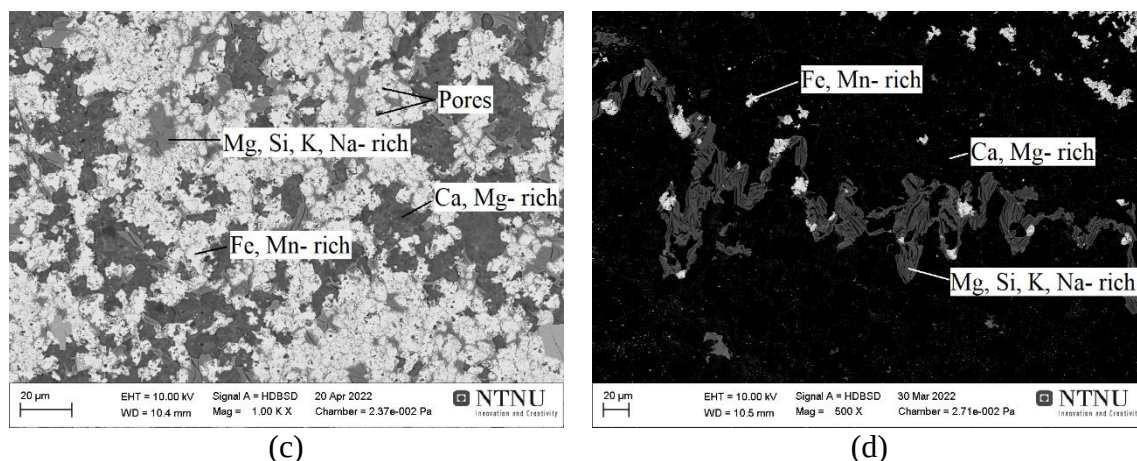


Figure 5-9 Backscattered electron SEM micrographs of cross-sectioned and polished samples pre-reduced in 70% CO 30% CO₂ (a), 70% H₂ 30% H₂O (b), 100% H₂ (c) gas atmospheres at 800 °C, and Mg-, Si-, K-, Na - rich phases embedded as a segregated phase in the sample pre-reduced in a 70% H₂ 30% H₂O gas atmosphere at 800 °C (d).

The black spots observed in Figure 5-9 are representative of pores (i.e., open spaces). The average diameter (measured between the two furthest ends) of the pores present in the pre-reduced samples shown in Figure 5-9a, b, and c were measured as 2.7, 5.9, and 1.5 µm, respectively. Hence, the largest pores formed during pre-reduction in a 70% H₂ 30% H₂O atmosphere (Figure 5-9b), whereas smaller pores formed during pre-reduction in the 70% CO 30% CO₂ (Figure 5-9a) and 100% H₂ (Figure 5-9c) atmospheres. The pores formed were relatively large when compared to the size of the pores that formed in the Mn-rich area inside reduced Nchwaning ore (average diameter of 0.1 µm).^[9] In a non-related study using UMK ore (heated to 400 °C in a synthetic air atmosphere), the pore size diameter ranged from 3.6 to 7.1 µm.^[19] Furthermore, Figure 5-9d and Figure 5-8e show how the Mg-, Si-, K-, and Na-rich phase formed in different shapes between the Fe/Mn-rich and Ca/Mg-rich phases. According to the EDS results, the light grey area in Figure 5-9d mainly consisted of Si (12.8 wt%) and Mg (14.9 wt%).

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Considering that Fe was detected by XRD (Figure 5-5c) for the ore pre-reduced in the 100% H₂ atmosphere, a high magnification (x 10 000) SEM micrograph of the white area (Fe- and Mn-rich phase) seen in Figure 5-9c was prepared (Figure 5-10).

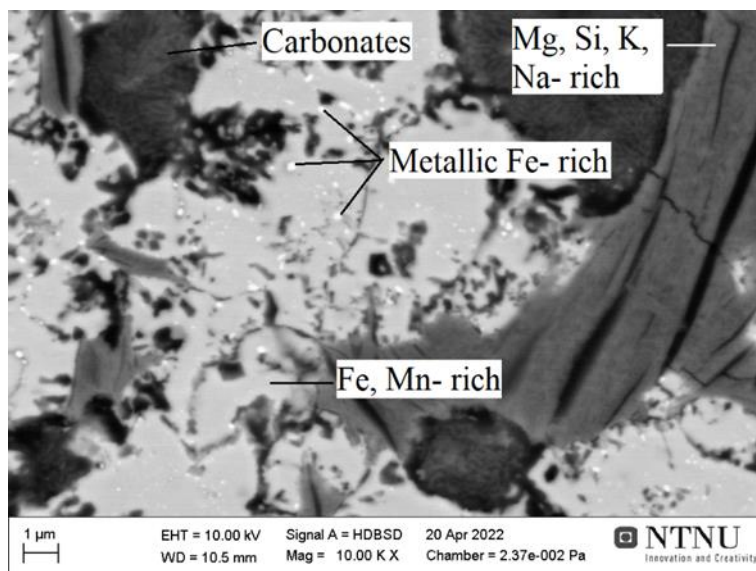


Figure 5-10 Secondary electron micrograph at 10 000 magnification of the Fe- and Mn-rich phase shown in Figure 5-9c. The sample was pre-reduced in a 100% H₂ atmosphere at 800 °C.

Figure 5-10 shows the presence of various phases. Of particular importance here were the relatively small and bright spots observed within the Fe- and Mn-rich phases. These spots were analyzed by EDS and contained 7.71 wt.% Fe and 50.7 wt.% Mn. The Fe- and Mn-contents of the Fe- and Mn-rich phases were determined to be 1.68 and 58.0 wt.%, respectively.

The Mn/Fe ratio of the bright spots and the Fe- and Mg-rich phases were calculated as 6.58 and 34.5, respectively. However, EDS analysis is a semi-quantitative technique, hence the true composition of the bright spots is difficult to determine from the EDS analysis as it is so small and embedded in the large Fe- and Mn-rich phase. Thus, based on the Mn/Fe ratio and the XRD patterns (Figure 5-5c) of the samples pre-reduced in 100% H₂ it is assumed that these bright spots are rich in metallic Fe.

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5.4.4. Porosity analysis of UMK ore

A higher porosity provides more surface area for gas-solid reactions to proceed which will increase the reduction of higher Fe- and Mn- oxides and improve the reactivity of the ore.^[2] However, an increase in porosity leads to a decrease in the ore's thermal strength.^[15,31] A higher porosity makes it more feasible for the ore to absorb moisture, hence when rapidly heated the ores may crack due to the high pressure caused by the water evaporation (elimination of structural water).^[32] In addition, adding fine ore material to the FeMn smelting process will limit the permeability of the gas flow in the furnace and may cause sintering of the furnace bed. This will have a retarding effect on the reduction rate during the FeMn smelting process^[33] and may lead to potentially catastrophic bed turn-overs.

Porosity analysis was performed on raw ore and samples pre-reduced in all three gas atmospheres at 800 °C. The results can be seen in Table 5-3. The apparent and absolute density of the raw UMK ore particles were the same, hence, the porosity of the raw UMK ore was calculated to be 0%. Low porosity of 2.6% and 0-10% was also seen by Biørnstad et al. (2020)^[19] and Reiersen et al. (2020)^[20], respectively. The apparent and absolute density of three raw ore particles was determined to be 3.74 g/cm³, 3.61 g/cm³, and 3.66 g/cm³, respectively.

During pre-reduction procedures, the reduction of higher oxides and carbonate decomposition results in the formation of intra-particle pores. The higher Mn-oxides in all the samples reduced to manganosite (MnO) at 800 °C (Table 5-2). However, the higher Fe-oxides in samples pre-reduced in 70% CO 30% CO₂, and 70% H₂ 30% H₂O reduced to FeO, while in 100% H₂ the FeO further reduced to Fe. Furthermore, most of the carbonates decomposed in the hydrogen-containing gas atmosphere at 800 °C while only half of the carbonates (8.8 wt.%, see Table 5-2) decomposed in 70% CO 30% CO₂ at 800 °C. Considering this one would expect the samples pre-reduced in 100% H₂ at 800 °C to have the highest porosity, while the samples

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pre-reduced in 70% CO 30% CO₂ at 800 °C to have the lowest. However, the porosity average in Table 5-3 shows that the gas atmosphere used for pre-reduction had an insignificant effect on pore formation. This could be attributed to the heterogeneity (high standard deviation of 7.77) of the ore.

Table 5-3: Porosity measurements (%) of raw and pre-reduced UMK ore at 800 °C. Three randomly selected particles per gas atmosphere were used for analysis.

Particle	Raw ore	Atmosphere		
		70% CO 30% CO ₂	70% H ₂ 30% H ₂ O	100% H ₂
1	0	42.0	32.8	35.3
2	0	28.7	46.9	30.0
3	0	42.3	37.8	43.5
Average	0	37.7	39.1	36.3
Standard deviation	0	7.77	7.15	6.80

5.4.5. Degree and rate of pre-reduction and carbonate decomposition

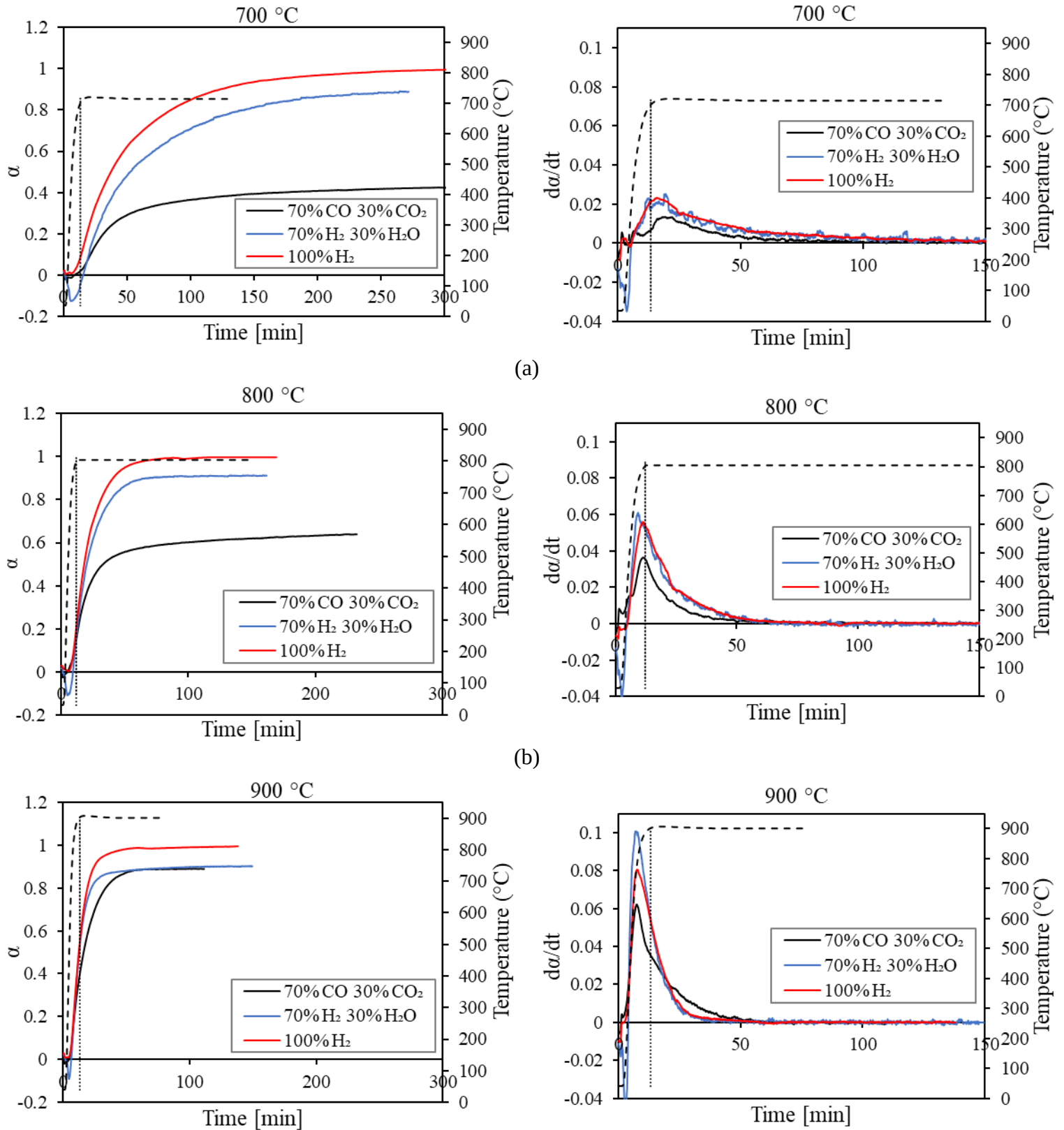
According to the chemical analysis, the majority of weight loss was caused by the decomposition of carbonates. The rest of the weight loss was due to the pre-reduction of Fe- and Mn-oxides (see Table 5-1). Hence the degree of pre-reduction and decomposition of carbonates are presented as the fractional conversion, α , which is defined in Equation 5-7.

$$\alpha = \frac{w_o - w(t)}{w_o - w_h} \quad (\text{Equation 5-7})$$

Where w_o is the initial weight (wt%), w_h is the highest weight loss (wt.%) obtained from the samples pre-reduced in 100% H₂ and $w(t)$ (wt.%) is the measured weight as a function of time. When $\alpha = 0$ no reduction or decomposition has taken place, while when $\alpha = 1$ the sample is fully reduced (the higher Mn-oxides completely reduced to manganosite MnO) and all the carbonates decomposed. The pre-reduction and decomposition rates are obtained by differentiating α with respect to time. Figure 5-11 presents the degree and rate of pre-reduction and decomposition from the experiments performed in 70% CO 30% CO₂, 70% H₂ 30% H₂O,

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and 100% H₂ atmospheres at 700 (Figure 5-11a), 800 (Figure 5-11b), and 900 °C (Figure 5-11c).



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(c)

Figure 5-11 Experimental data obtained from the TG furnace for samples pre-reduced in 70% CO 30% CO₂, 70% H₂ 30% H₂O, and 100% H₂ gas atmospheres at 700 (a), 800 (b), and 900 °C (c) are reported in the form of α and its first derivative, the reaction rate as a function of time. The crucible temperature of the reference experiments is presented on the secondary axis as a function of time. During the reference experiments, quartz was subjected to the same gas atmospheres and temperatures as the ore. The vertical dotted line indicates at what time (between 12 – 13 min) the target temperature (700, 800, and 900 °C) was reached.

It is evident from Figure 5-11a to c that within the 70% CO 30% CO₂ gas atmosphere, the degree and rate of pre-reduction and decomposition increased with an increase in temperature. The increase is consistent with other studies conducted at a similar temperature range.^[4,14,19] In the hydrogen-containing gas atmospheres, only the rate of pre-reduction and decomposition increased with an increase in temperature while the degree stayed more or less the same. The 100% H₂ and 70% H₂ 30% H₂O gas atmospheres had relatively the same reaction rate. However, one would expect the 100% H₂ gas atmosphere to have a higher reduction rate due to its lower pO₂^[4] and it provides 4 L/min instead of 2.8 L/min of hydrogen during the pre-reduction process. The abnormality can be explained by the following two reasons. Firstly, there is more noise present in the data obtained from the 70% H₂ 30% H₂O gas atmosphere which makes the results less accurate. Secondly, the weight increase at the beginning (first 12 – 13 min) of the pre-reduction in 70% H₂ 30% H₂O causes the reaction rate to increase.

During the first 5 – 7 min of pre-reduction in the 70% H₂ 30% H₂O gas atmosphere, an increase in weight was observed. The crucible gradually heated up from around 29 °C to the target temperature as it moved into the furnace. The target temperature was reached between 12 – 13 min as indicated by the dotted line in Figure 5-11. The 70% H₂ 30% H₂O gas enters

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the crucible at 29 °C causing the water vapor to condense which leads to an increase in weight. As the crucible temperature increase the condensed water starts to evaporate causing the weight percentage to decrease explaining the negative bump at the beginning of the experiment. The higher the temperature of the furnace the faster the crucible will heat up to reach the target temperature, causing the variation in bump broadness at each target temperature. Reference experiments were run with quartz and a similar bump appeared at the beginning of the pre-reduction process.

The rate of pre-reduction and decomposition was the highest in the hydrogen-containing gas atmospheres. The rate increase was expected when assuming that the diffusion characteristics of the gas atmosphere improve with the presence of hydrogen. Hydrogen has a kinetic diameter of 2.89 Å, which is smaller than that of CO (3.76 Å) and CO₂ (3.30 Å) gas.^[34] The 100% H₂ gas had a maximum reduction rate that was 88%, 45%, and 30% higher when compared to the 70% CO 30% CO₂ gas mixture at 700, 800, and 900 °C, respectively. Thus 100% H₂ gas had a more significant effect at lower temperatures than at higher temperatures. Similar results were obtained by Ngoy et al. (2020)^[8] and Schanche et al. (2021)^[4]. In Figure 5-11a to c, the alpha curves of samples pre-reduced in 70% CO 30% CO₂, 70% H₂ 30% H₂O, and 100% H₂ gas atmospheres at 700 (a), 800 (b), and 900 °C (c) flattened after a certain period indicating that all the Mn-oxides in the sample reduced to manganosite, this was also confirmed by the chemical analysis (Table 5-2). In addition, the flattening of the alpha curves shows that the discrepancy between the chemical analysis and the XRD (Figure 5-5) analysis (as discussed in Section 3.2) is negligible.

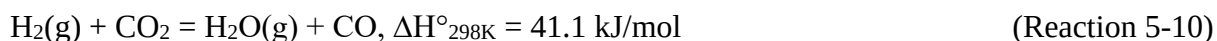
Furthermore, considering the chemical analysis it is expected that all the 70% H₂ 30% H₂O alpha curves (Figure 5-11a to c) and the 70% CO 30% CO₂ at 900 °C alpha curve in Figure 5-11c end at $\alpha = 1$ like the 100% H₂ curves at 700 (a), 800 (b) and 900 °C (c). However, this is not the case and can be explained by the calculated theoretical weight loss (Table 5-1)

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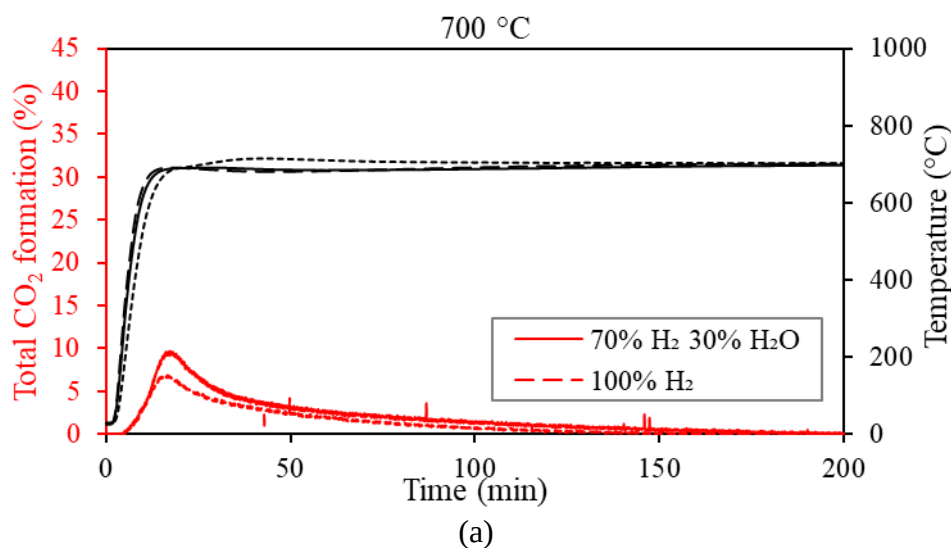
and XRD analysis (Figure 5-5). The highest weight loss percentage, i.e., 23 wt.%, was obtained in samples pre-reduced in 100% H₂. The calculated theoretical weight loss was 21 wt.%, which is 2 wt.% lower than the highest weight loss detected. This weight difference is due to the complete reduction of Fe-oxides (Fe₂O₃ to Fe) because when assuming that the Fe-oxides reduce to metallic Fe the calculated theoretical weight loss is 23 wt% (the same as the highest weight loss detected).

5.4.6. Total CO₂ formation from carbonate decomposition

The utilization of 100% H₂ and 70% H₂ 30% H₂O gas atmospheres as reductants during the pre-reduction process caused the WGSR to take place. The WGSR proceeds according to Reaction 5-10.



Hydrogen and water vapor were the input gas, and the CO₂ only formed due to the decomposition of carbonates. Hence, CO and water vapor formed endothermically. The sum of the %CO and %CO₂ detected by the gas analyzer was used to determine the relative percentage of CO₂ formation from the decomposition of carbonates during the pre-reduction process. These curves are shown in Figure 5-12.



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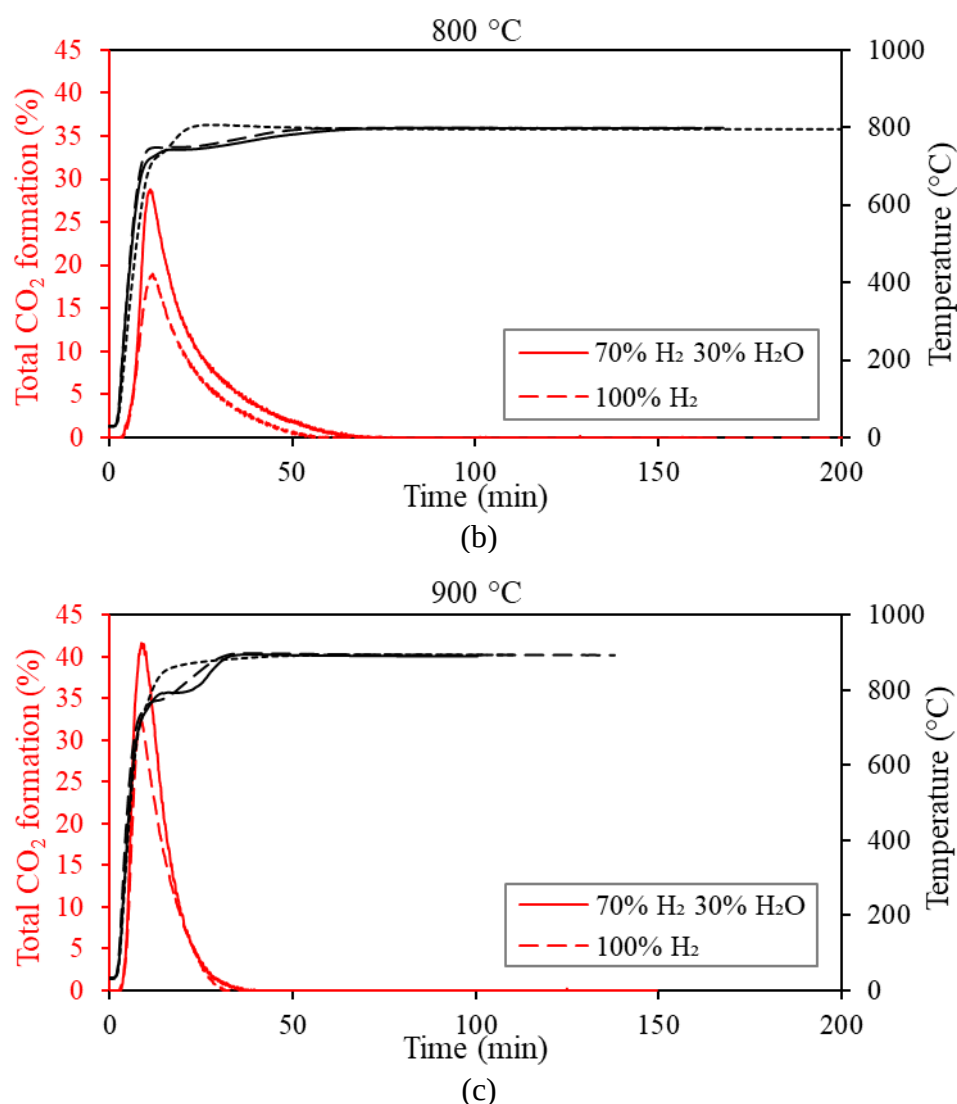


Figure 5-12 Total percentage CO₂ formation achieved through carbonate decomposition detected by the gas analyzer during the pre-reduction of UMK ore in 100% H₂ and 70% H₂ 30% H₂O gas atmospheres at 700 (a), 800 (b), and 900 °C (c). The crucible temperature of the gas mixtures as a function of time is presented on the secondary axis. The black lines represent the crucible temperature in the 70% CO 30% CO₂ (dotted), 70% H₂ 30% H₂O (solid), and 100% H₂ (dashed) gas atmospheres.

Figure 5-12 shows that an increase in temperature caused the peaks to intensify and become narrower, meaning that the rate of carbonate decomposition increased with an elevation in temperature while the percentage of carbonate decomposition stayed the same.

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The slightly lower total %CO₂ formation peak achieved in 100% H₂ gas atmosphere could be due to the %CO and %CO₂ in the off-gas being more diluted when reaching the gas analyzer comparing the 70% H₂ 30% H₂O gas atmosphere. During the pre-reduction in 70% H₂ 30% H₂O gas atmosphere 30% less H₂ enters the crucible meaning that 30% less H₂ will exit the crucible toward the gas analyzer. The added water vapor and the water vapor that forms during the pre-reduction process move out of the crucible into a glass bottle where the water vapor condenses, hence it does not affect the gas analyses. Therefore, the percentage of measured CO and CO₂ gas in the off-gas per minute will be higher in 70% H₂ (2.8 L/min) 30% H₂O gas atmosphere than in 100% H₂ (4.0 L/min).

Furthermore, Figure 5-11 shows that the rate of carbonate decomposition is faster at the beginning of the pre-reduction process when the pCO₂ is still low (and the driving force high) but after the maximum total %CO₂ formation is reached the decomposition rate starts to slow down. This could be due to kinetics where the CO₂ in the outer part of the particle experience a lower pCO₂ but in the middle of the particle it sees a pCO₂ of 1 atm. Thus, the H₂ has to diffuse in and out of the particle, hence it is natural that the decomposition rate slows down as the decomposition happens more and more to the center of the particle.

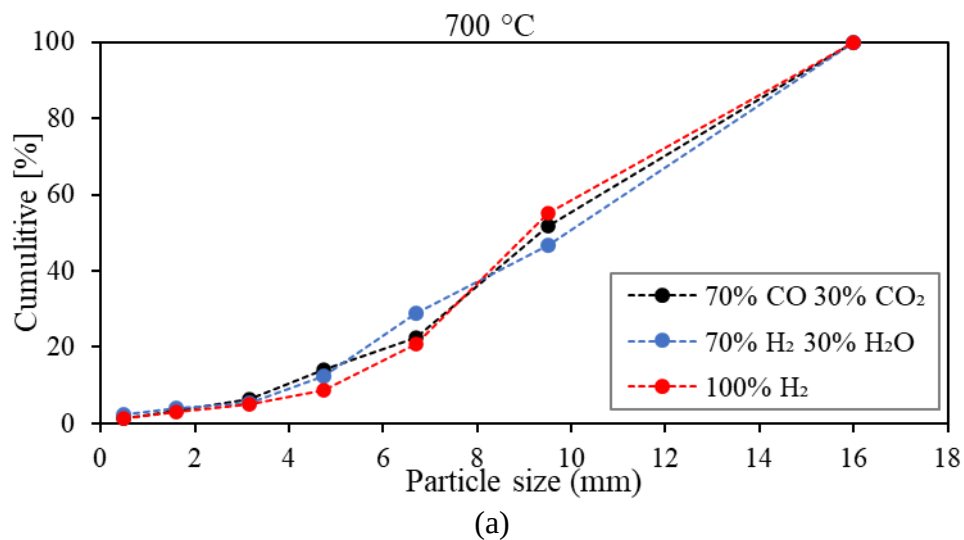
As previously mentioned, carbonates decompose faster in the hydrogen-containing gas atmospheres than in the 70% CO 30% CO₂ gas atmosphere (Figure 5-11), hence the hydrogen-containing gas atmospheres requires more energy. The higher degree and rate of carbonate decomposition caused the sample temperature in the hydrogen-containing gas atmospheres to be lower in comparison to the sample temperature measured for the 70% CO 30% CO₂ gas atmosphere. The decrease in sample temperature can be seen in Figure 5-12.

5.4.7. Decrepitation of UMK ore

In the industry, the presence of undersized Mn-ore material in the furnace will limit the permeability of the pre-reduction zone by stopping the uniform gas flow. The gas flow is

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responsible for the pre-reduction of the Mn ores higher up in the furnace. Hence, it is desired that the charge fed to the furnace does not decrepitate too much.^[19] Decrepitation is caused by several factors. When the ore heats up the outer layer heats up faster than the inside of the ore, causing the areas to expand differently which will increase the internal stress of the ore.^[19] Stress can also be caused by phase transformation due to generating an anisotropy which forms cracks that would eventually fracture.^[35] Elimination of structural water will cause an increase in vapor pressure inside the pores that can lead to crack formation.^[35] Furthermore, the decomposition of carbonates and the loss of oxygen through the pre-reduction of higher oxides of the ore will also contribute to the increase in decrepitation.^[32] Figure 5-13 shows the sample size fraction distribution after pre-reduction of UMK ore in 70% CO 30% CO₂, 70% H₂ 30% H₂O, and 100% H₂ at 700 (Figure 5-13a), 800 (Figure 5-13b), and 900 °C (Figure 5-13c).



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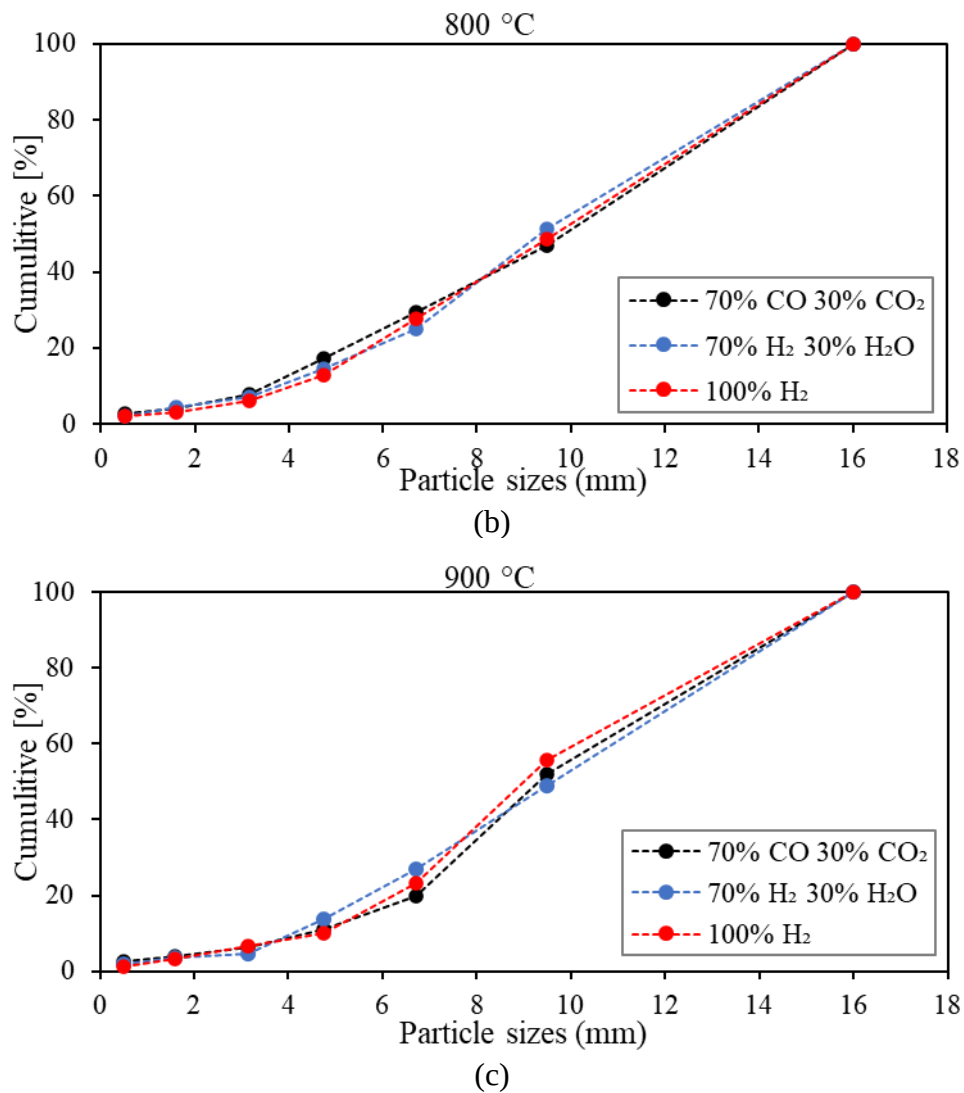


Figure 5-13 Size distribution after reduction experiments in 70% CO 30% CO₂, 70% H₂ 30% H₂O and 100% H₂ at 700 (a), 800 (b), and 900 °C (c).

According to Figure 5-13, the size distribution of the UMK ore after pre-reduction shows that 45-55% of particles are finer than 9.5 mm, indicating that about half of the ore remained in their original particle size (9.5 to 16 mm). Similar results were obtained in Reiersen et al. (2020)^[20] and Mukono et al. (2022)^[36]. This was observed for all the samples, thus can it be seen that the employment of 70% H₂ 30% H₂O, and 100% H₂ as reductants does not change the decrepitation of UMK ore in the 700 to 900 °C temperature range compared to 70% CO 30% CO₂.

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Furthermore, the slope beyond less than 9.5 mm is flatter at 800 °C than at 700 and 900 °C indicating that the samples pre-reduced at 800 °C decrepitated into finer particles. According to the chemical analysis, all the samples were completely reduced and most of the carbonates decomposed in the samples pre-reduced in 70% H₂ 30% H₂O, 100% H₂, and 70% CO 30% CO₂ at 900 °C. Even though, the lower temperature CO/CO₂ experiments still had some remaining carbonates (Figure. 5-3) it did not decrepitate differently. Hence, it seems like the release of CO₂ from the ore during the decomposition of carbonates has an insignificant effect on the degree of decrepitation. These results are also in agreement with the porosity analysis (Table 5-3).

5.5. Conclusions

Isothermal experiments were performed to investigate the pre-reduction of UMK ore in hydrogen-containing and CO/CO₂ gas atmospheres at temperatures of 700 to 900 °C. According to the chemical analysis, the majority of the weight loss was caused by the decomposition of carbonates (17 wt.%). The rest of the weight loss was due to the pre-reduction of Fe- and Mn- oxides, i.e., 0.89 wt.% (Fe₂O₃ to FeO) or 2.56 wt.% (Fe₂O₃ to Fe) and 3.47 wt.% (O/Mn_(i) to MnO), respectively. The pre-reduction of higher oxides and the decomposition of carbonates proceeded in parallel.

The higher Mn-oxides in all pre-reduced samples reduced to MnO. The higher Fe-oxides were reduced to FeO in the 70% CO 30% CO₂ and 70% H₂ 30% H₂O atmospheres, while complete reduction (Fe₂O₃ to Fe) was achieved in the 100% H₂ gas atmosphere. Most of the carbonates decomposed in samples pre-reduced in CO/CO₂ at 900 °C and in the hydrogen-containing atmospheres at all temperatures. The use of hydrogen as a reductant increased the rate of pre-reduction and carbonate decomposition, which was further accelerated at elevated temperatures.

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The XRD results showed that the braunite ($(\text{Mn,Fe})_2\text{O}_3 \cdot \text{MnSiO}_3$)/bixbyite ($(\text{Mn,Fe})_2\text{O}_3$) reduced to manganosite (MnO) without a stable intermediary phase (hausmannite (Mn_3O_4)). For the CO/CO_2 and $\text{H}_2/\text{H}_2\text{O}$ gas atmospheres, the FeO was contained in the monoxide phase. This was not the case in 100% H_2 atmosphere where the FeO had been reduced to metallic Fe. Therefore, the use of hydrogen as a reductant allowed the complete reduction, i.e., metallization, of Fe-oxides present in the ore.

Small Fe-rich dots embedded in the Mn- and Fe-rich phase of samples pre-reduced in 100% H_2 at 800 °C was observed in SEM analysis. The SEM and EPMA showed that the pre-reduced ore consisted of Mg- and Ca-rich, Mn-and Fe-rich, and Mg-, Si-, K- and Na-rich phases. The employment of hydrogen during the pre-reduction process did not have a significant effect on the porosity or decrepitation of UMK ore.

Acknowledgment

This study was funded by the Research Council of Norway (RCN) as the Thanos project (INPART Project 309475) and is gratefully acknowledged.

Appendix tables

Table A1: Chemical composition (wt.%) derived from the EPMA analysis of the detected phases shown in Figure 5-8

	Area	O	Mn	Fe	Ca	Mg	Si	K	Na
Raw ore	White	40–65	41-55	3.8-10	0.0-5.6	0.0	2.5-7.5	0.0	0.0-0.4
	Dark grey	24-32	0.0-6.9	0.0-1.9	17-30	1.9-3.8	0.0-1.3	0.0	0.0-0.4
70% CO 30% CO_2	White	25-37	31-55	3.8-10	0.0-3.1	0.0-0.9	1.3-3.8	0.0-0.6	0.0-0.4
	Dark grey	25-31	0.0-10	0.0-1.9	16-25	2.6-5.3	0.0-1.3	0.0-0.6	0.0-0.4
	Light grey	37-43	0.0	0.0	0.0	5.0-7.5	7.5-15	1.9-3.1	1.3-5.0
70% H_2 30% H_2O	White	28-39	31-55	4.7-15	0.0-3.8	0.0-0.9	3.0-4.5	0.0-0.6	0.0-0.4
	Dark grey	11-17	0.0-10	0.0-1.9	16-30	3.5-6.1	0.0-1.5	0.0-0.6	0.0-0.4
	Light grey	41-55	0.0	0.0-1.3	0.0	4.4-7.0	15-20	1.9-3.1	1.3-5.0
100% H_2	White	22-39	41-60	4.7-11	0.0-3.8	0.0-0.9	0.0-3.8	0.0-0.6	0.0-0.4
	Dark grey	11-28	0.0-11	0.0-1.9	15-24	3.8-7.5	0.0-3.8	0.0-0.6	0.0-0.4
	Light grey	28-48	0.0	0.0-1.3	0.0	5.0-10	10-18	1.9-3.1	1.3-5.0

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CHAPTER 6: PROJECT EVALUATION AND PROSPECTS

6.1. Project evaluation

For self-evaluation, the project was evaluated against the objectives set in Chapter 1. The points listed below correlate with the objectives set in Section 1.2. Regarding the overall aim of the dissertation and the specific objectives presented in Chapter 1, Section 1.2., the following conclusion can be drawn concerning the chromite- and Mn-ore-related objectives:

Chromite-ore-related objectives:

1) Perform fundamental thermodynamic calculations to better understand the aspects that govern the behavior of the chemical species partaking in the reaction.

In Chapter 3 predominant area phase-stability diagrams were used to graphically present the thermochemical equilibrium conditions of compounds in reaction. These diagrams were formulated utilizing the methodology presented by Ramos-Hernandez et al. (2013) together with updated thermochemical data from several old and new sources. A (Cr, Fe)-C-H-O diagram was used to determine the thermochemical conditions of the Cr and Fe reduction processes in chromite when C or hydrogen were used as reductants. The equilibrium constant ($\log K$) value, which is related to the standard Gibbs free energy as $\Delta G^\circ = -RT \log K$ was used to determine the thermochemical viability of each chemical reaction. Hence it was observed that the reduction of Cr and Fe from Cr_2FeO_4 (i.e., pure chromite) is more viable than the reduction of Cr from Cr_2O_3 , while the reduction of Fe from FeO being more viable than from Cr_2FeO_4 . A predominant area phase-stability diagram for the (Cr, Fe)- H_2 - H_2O system was also compiled and revealed that Fe and Cr will exclusively reduce if the partial pressure of H_2O ($p_{\text{H}_2\text{O}} \leq 0.0001 \text{ atm}$) and when the $p_{\text{H}_2\text{O}}$ is between 0.0001 and 0.3162 atm, the Fe and Cr_2O_3 species will predominate.

2) Determine the effect of reduction parameters on the extent of Fe and Cr metallization in chromite.

As-received chromite ore was size partitioned into four different size fractions in Chapters 3 (<106, 106 to 250, 250 to 500, and 500 to 1000 μm) and 4 (<106, 106 to 212, to 425, and 425 to 850 μm). Subsequently, the d_{90} , d_{50} , and d_{10} values of each size fractions were determined. The different size fractions were reduced in hydrogen to determine the effect of particle size on the reducibility of chromite. It was found that a decrease in particle size increased the degree of reduction. In Chapter 4, chromite was reduced in 150 mL/min and 750 mL/min hydrogen flowrate to determine the effect of hydrogen availability on the reducibility of chromite. The increase in flow rate increased the %Fe and Cr metallization from 1.77 to 49.3% and 0.01 to 0.17%, respectively, for the smallest size fraction ($d_{90} = 133 \mu\text{m}$). Furthermore, the chromite was reduced for different periods in Chapters 3 (15 to 30 min) and 4 (60 to 180 min) to determine the influence of reduction time on the degree of Fe and Cr reduction in chromite. The results revealed that an increase in reduction time was advantageous for the reducibility of the Fe-oxide constituency of chromite, while Cr-oxide remained unaffected.

3) Evaluate the effect of pre-oxidation of chromite on its reducibility by hydrogen

In Chapter 4 the effect of pre-oxidation on the %Fe and Cr metallization was investigated. The effect of pre-oxidation was determined by oxidizing size fractioned chromite at 1100 °C for 60 min and subsequently reducing the size fraction chromite at 1100 °C for 60 min at a hydrogen flow rate of 750 mL/min. The %Fe and Cr metallization of pre-oxidized/reduced and reduced chromite particles were then compared. The results showed that the %Fe and Cr metallization of all the pre-oxidized/reduced size fractioned chromite samples significantly increased. For instance, chromite pre-oxidized for 60 min achieved 77.5%, and 0.3% Fe and Cr metallization, respectively, was slightly lower than the Fe and Cr metallization

of 92.1% and 2.0%, respectively, for unoxidized chromite reduced for 180 min. It was also found that metalized Fe was present throughout the chromite particle – therefore, the method used to solubilize Fe did not remove the inter-particle Fe metal. It was thus concluded that the 77.5% Fe metallization was slightly under-reported. The Cr metallization remained insignificant and did not exceed 0.3%. The effect of pre-oxidation on the migration of Fe ions through the chromite particle was also investigated by looking at SEM-EDS analysis of pre-reduced and pre-oxidized/reduced particles. A Widmanstätten pattern was observed in the pre-oxidized particles. However, after reduction, the pattern was no longer visible but rather numerous randomly scattered white Fe-rich areas within the pre-oxidized/reduced particle. Hence, the occurrence of metallic Fe inside the particle caused incomplete removal of Fe during the leaching procedure as only Fe from the surface and near-surface of the pre-oxidized/reduced particles were removed.

Manganese-ore-related objectives:

4) Investigate the effect of temperature and hydrogen as a reductant on the degree and rate of pre-reduction in UMK ore.

In Chapter 5 the TG technique was used to investigate the solid-gas pre-reduction reactions of UMK ore in three different gas atmospheres, i.e., 100% H₂, 70% H₂ 30% H₂O, and 70% CO 30% CO₂ (reference) at the target temperatures 700, 800, and 900 °C. The weight change in the ore was recorded during the pre-reduction process. This experimental weight loss data from the TG furnace was used to calculate the weight loss percentage. The weight loss is caused by the reduction of higher oxides and by carbonate decomposition. The curves revealed the degree and rate of pre-reduction (higher Fe- and Mn-oxides to FeO and MnO, respectively) and carbonate (MgCO₃, CaCO₃, CaMg(CO₃)₂, and MnCO₃) decomposition improved with the utilization of hydrogen as reductant when compared to CO/CO₂. Furthermore, did the results show that the Fe-oxide in the UMK ore completely reduced to metallic Fe when subjected to

100% H₂ gas atmosphere.

5) Evaluate the total CO₂ formation from carbonate decomposition when 100% H₂ and 70% H₂ 30% H₂O gas atmospheres are used as reductants during the pre-reduction of UMK ore.

In Chapter 5 the total %CO₂ and CO formation were detected by the gas analyzer. The CO₂ and CO formation were due to carbonate decomposition and the water-gas shift reaction (WGSR), respectively. This analysis was only possible in the 100% H₂ and 70% H₂ 30% H₂O gas atmospheres, as the input gas did not contain CO₂ and CO. The sum of the detected %CO₂ and CO were used to calculate the relative %CO₂ formation from the decomposition of carbonates during the pre-reduction process of UMK ore.

6) Evaluate the decrepitation and porosity of UMK ore after pre-reduction at different temperatures in three different gas atmospheres.

All the pre-reduced samples were sieved through a sieving stack which consist of 9.5, 6.7, 4.75, 3.15, 1.6, and <0.5 mm sieves to determine the amount of sample that remained its original size (9.5 to 16 mm). The results revealed that 45-55% of the particle were smaller than 9.5 mm, showing that half of the ore did not decrepitate. Hence the increase in temperature and the utilization of hydrogen as reductant had no significant influence on the decrepitation of the ore. The porosity of the raw ore and pre-reduced samples in all three gas atmospheres at 800 °C were determined by the ratio between the absolute and apparent density. The porosity measurements showed that the employment of hydrogen as a reductant did not influence the porosity of the pre-reduced samples in comparison to the samples that were reduced in the CO/CO₂ gas atmosphere.

6.2. Recommendation for future research

The use of hydrogen in the metallurgical industries is nearly a given as global efforts move towards reducing C emissions. It is therefore a near certainty that hydrogen will be

incorporated as a reductant during smelting procedures.

Having demonstrated that hydrogen can be used as a reductant, or at least as a partial reductant, in chromite and Mn-ore smelting, further research should be directed towards finding optimal operational conditions. It is paramount that near-complete hydrogen utilization is considered as some primary operational criteria, as any unconsumed hydrogen will be discarded as part of the off-gas. This is not only a technical consideration but also an economical one.

It is also proposed that the real-world feasibility of using hydrogen as a reductant be determined. For instance, can hydrogen be safely employed in existing smelting infrastructure, or would new infrastructure be required?

Lastly, one must consider that green hydrogen is relatively expensive – though the cost thereof has been decreasing in recent years as renewable energy sources (e.g., solar and wind) have become cheaper. Within the South African landscape, solar energy is the most likely renewable energy candidate, which will likely require a stage where produced hydrogen must be stored for a certain period (likely as a pressurized gas or as ammonia). Considering this, the implications of including hydrogen storage will increase the initial capital input and operational complexity. Nevertheless, increases in the cost of traditional reductants and the relative scarcity of high C-content reductants should also be factored in. More so, C taxes and pressure on FeCr and FeMn producers to curb C emissions are also a factor.

Future work should determine the feasibility of a Fe-alloy producer (e.g., FeMn and FeCr) to have onsite hydrogen production facilities, which can directly supply hydrogen where needed.

APPENDIX A: FRONT PAGE OF ARTICLE 1 (CHAPTER 3)



Article

The Use of Hydrogen as a Potential Reductant in the Chromite Smelting Industry

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Citation: Davies, J.; Paktunc, D.; Ramos-Hernandez, J.J.; Tangstad, M.; Ringdalen, E.; Beukes, J.P.; Bessarabov, D.G.; Du Preez, S.P. The Use of Hydrogen as a Potential Reductant in the Chromite Smelting Industry. *Minerals* **2022**, *12*, 534. <https://doi.org/10.3390/min12050534>

Academic Editor: Hongyu Zhao

Received: 24 March 2022

Accepted: 14 April 2022

Published: 25 April 2022

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Abstract: The chromium (Cr) content of stainless steel originates from recycled scrap and/or ferrochrome (FeCr), which is mainly produced by the carbothermic reduction of chromite ore. Ever-increasing pressure on FeCr producers to curtail carbon emissions justifies migration from traditional FeCr production routes. The interaction between hydrogen and chromite only yields water, foregoing the generation of significant volumes of CO-rich off-gas during traditional smelting procedures. For this reason, the use of hydrogen as a chromite reductant is proposed. In addition to thermodynamic modelling, the influence of temperature, time, and particle size on the reduction of chromite by hydrogen was investigated. It was determined that, at the explored reduction parameters, the iron (Fe)-oxides presented in chromite could be metalized and subsequently removed by hot-acid leaching. The Cr-oxide constituency of chromite did not undergo appreciable metalization. However, the removal of Fe from the chromite spinel allowed the formation of eskolaite with the composition of $(\text{Cr}_{1.4}\text{Al}_{0.6})\text{O}_3$ in the form of an exsolved phase, which may adversely affect the reducibility of chromite. The study includes the limitations of incorporating hydrogen as a reductant into existing FeCr production infrastructure and proposes possible approaches and considerations.

Keywords: chromite; hydrogen; ferrochrome/ferrochromium; pre-reduction

1. Introduction

Chromite ore is characterized by the unit formula $(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Cr}, \text{Fe}^{3+})_2\text{O}_4$ and serves as the only economically viable source of virgin Cr units [1,2]. The energy-intensive carbothermic smelting of chromite ore yields ferrochrome (FeCr)—a crude alloy of Cr and Fe [3–5]. Approximately 80 to 90% of produced FeCr is consumed by the stainless steel industry and is, therefore, considered equally important [4,6,7]. The significance of FeCr production is highlighted by the Cr constituency thereof, as the inclusion of Cr in stainless steel is the reason for the corrosion resistance thereof under standard ambient conditions [4].

Chromite smelting is typically performed in semi-closed or closed submerged arc furnaces (SAFs) and, to a lesser extent, closed direct current (DC) arc furnaces [6,8,9]. The energy consumption of a specific furnace is affected by factors such as material screening, chromite pre-heating, and pre-reduction [6]. For instance, the energy consumption of a



Article

The Effect of Pre-Oxidation on the Reducibility of Chromite Using Hydrogen: A Preliminary Study

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Abstract: The majority of ferrochrome (FeCr) is produced through the carbothermic reduction of chromite ore. In recent years, FeCr producers have been pressured to curtail carbon emissions, necessitating the exploration of alternative smelting methods. The use of hydrogen as a chromite reductant only yields water as a by-product, preventing the formation of carbon monoxide (CO)-rich off-gas. It is however understood that only the Fe-oxide constituency of chromite can be metallized by hydrogen, whereas the chromium (Cr)-oxide constituency requires significantly higher temperatures to be metallized. Considering the alternation of chromite's spinel structure when oxidized before traditional smelting procedures, the effects on its reducibility using hydrogen were investigated. Firstly, the effect of hydrogen availability was considered and shown to have a significant effect on Fe metallization. Subsequently, spinel alternation induced by pre-oxidation promoted the hydrogen-based reducibility of the Fe-oxide constituency, and up to 88.4% of the Fe-oxide constituency was metallized. The Cr-oxide constituency showed little to no reduction. The increase in Fe-oxide reducibility was ascribed to the formation of an exsolved Fe₂O₃-enriched sesquioxide phase, which was more susceptible to reduction when compared to Fe-oxides present in the chromite spinel. The extent of Fe metallization of the pre-oxidized chromite was comparable to that of unoxidized chromite under significantly milder reduction conditions.

Keywords: pre-oxidation; metallization; hydrogen; reduction; chromite; ferrochrome/ferrochromium



Citation: Davies, J.; Tangstad, M.; Ringdalen, E.; Beukes, J.P.; Bessarabov, D.; du Preez, S.P. The Effect of Pre-Oxidation on the Reducibility of Chromite Using Hydrogen: A Preliminary Study. *Minerals* **2022**, *12*, 911. <https://doi.org/10.3390/min12070911>

Academic Editor: Brajendra Mishra

Received: 27 May 2022

Accepted: 13 July 2022

Published: 20 July 2022

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1. Introduction

Chromite ore, unit formula of (Mg, Fe²⁺)(Al, Cr, Fe³⁺)₂O₄, is the only commercially exploited source of new chromium (Cr) units [1–3]. Approximately 90 to 95% of chromite ore is utilized to produce several grades of ferrochrome (FeCr) [3–5]. FeCr, a crude alloy between Cr and iron (Fe), is produced through the energy-intensive carbothermic smelting of chromite ore [4,5]. Temperatures of 1600–1700 °C within the smelting zone are required to allow metallization and separation of the metal and slag phases [6]. Semi-closed and closed submerged arc furnaces (SAFs) are mainly used during the production of FeCr in South Africa. Direct current (DC) arc furnaces are also used but to a lesser extent [3]. During smelting, the specific energy consumption of a furnace is affected by a variety of factors, e.g., feed material pre-screening, if a fraction of the Cr- and Fe-oxide content has been pre-reduced, and if the chromite charge is pre-heated. For instance, the energy consumption of a semi-closed SAF operating on unscreened feed materials can be as high as 4500 kWh/t FeCr produced, whereas a closed SAF operating on hot-fed pre-reduced chromite can be

APPENDIX C: PROOF OF MANUSCRIPT SUBMISSION (CHAPTER 5)

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Manuscript #	E-ORIG-22-516-B
Current Revision #	0
Submission Date	2022-08-05
Current Stage	Submission
Title	Pre-reduction of United Manganese of Kalahari ore in CO/CO ₂ , H ₂ /H ₂ O, and H ₂ atmospheres
Manuscript Type	Original Research Article
Symposia	N/A
Classification	Pyrometallurgy
Manuscript Comment	No comments
Corresponding Author	Stephanus P. du Preez (North-West University)
Contributing Authors	Jamey Davies , Merete Tangstad , Trygve L. Schanche
Abstract	The influence of hydrogen on the pre-reduction of United Manganese of Kalahari (UMK) ore from South Africa was investigated. Isothermal experiments were performed in 70% CO 30% CO ₂ (reference), 70% H ₂ 30% H ₂ O, and 100% H ₂ gas atmospheres at 700, 800, and 900 (degree sign)C. Phase stability diagrams were thermodynamically determined and compared to experimental results. The pre-reduction process involved two reactions proceeding in parallel, i.e., the pre-reduction of higher oxides, and the decomposition of carbonates. A thermogravimetric (TG) furnace was employed for the pre-reduction of the ore in the various atmospheres. The calculated weight loss percentage was used to determine the degree and rate of pre-reduction. The chemical analysis showed that the higher Fe- and Mn- oxides in the samples reduced in 70% H ₂ 30% H ₂ O and 70% CO 30% CO ₂ completely reduced to FeO and MnO, respectively, while in 100% H ₂ the FeO further reduced to metallic Fe. The majority of carbonates were decomposed in the CO/CO ₂ atmosphere at 900 (degree sign)C, and at ≥700 (degree sign)C in the H ₂ /H ₂ O and H ₂ atmospheres. The degree and rate of reduction were accelerated by increasing the pre-reduction temperature and by employing a hydrogen-containing gas atmosphere (70% H ₂ 30% H ₂ O, and 100% H ₂). Scanning electron microscopy and electron microprobe analysis showed that the pre-reduced ore consisted of three phases: i) Mn- and Fe-rich, ii) Mg- and Ca-rich, and iii) Mg-, Si-, K-, and Na-rich. The influence of hydrogen as a reductant on the decrepitation and porosity of pre-reduced ore was also investigated. No appreciable differences in porosity and decrepitation were found for ores reduced in CO/CO ₂ and hydrogen-containing atmospheres.
Key Reader	Not Assigned
Key Words	Hydrogen, pre-reduction, manganese ore, manganese oxides, carbonate decomposition
Subject Areas	Environment, Ferrous alloys, High-temperature materials chemistry, High-temperature reaction kinetics, Hydrogen (also deuterium), Phase stability, Pyrometallurgy

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