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Performance of Mixed Oxides in Chemical Looping – The Case of Ilmenite/Ni- $19\gamma Al_2O_3$

ausgeführt zum Zwecke der Erlangung des akademischen Grades eines Diplom-Ingenieurs unter der Leitung von

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To My Readers

This work was in some way a continuation or a renewal of scientific research interests dating back about 20 years. After working more than 18 years in the industry in a different field of research I have now returned to my (chemical) roots. The reasons for this return are twofold: on one hand the company which I was working for gave up the field of telecommunication where I worked during the last 10 years almost completely and changed their orientation so there were no further projects in this field, on the other hand there was perhaps an inner impulse to change again after so many years, the focus and orientation. Looking back, it is not easy to say what was cause and effect, but I would rather say, both things conditioned each other. And in the end the consequences are important. As a consequence I decided to look at the practical side of chemistry and began with my master studies in chemical process engineering at the University of Technology.

The past two years were among the most interesting and diversified periods in my life. Not only was I again allowed to return to the university as a student with the insight of an experienced employee and family father of three children, but I was also entering the university at a time, when the conditions for studying and the social, political and economic frame have changed significantly compared to the years before and compared to the time of my former studies. Unfortunately in many respects the situation and perspectives have not improved, neither for the universities nor for the students themselves: in the shadow of the financial crisis the budgets for the universities in Austria are frozen or even cut and the political willingness to see investments in education and research as investment in the future of the country is lacking personalities who are propagating and putting this idea into actions. In the field of politics, economy and finance often also ethical principles are neglected for the sake of short term interests and this aggravates the symptoms of the crisis and causes uncertainty. So it is my feeling that the role of the universities (and other educational institutions) has become more important but also more endangered, namely to educate self standing and critical people who are aware of the necessities of time and act according to ethical principles. Despite these adverse circumstances I found many of them and I am confident that the self organizing system university still works.

In some respects this work did not proceed as planned. Precisely speaking, the experiments (investigating the efficiency of mixed oxides of ilmenite/Ni-carrier in chemical looping) did not yield the expected results. This, however, is sometimes the case in science: we ask a question and nature gives us an (unexpected) answer. I would rather say that these are the more interesting cases, since they enable us to learn and to understand more deeply about how the mechanisms underlying the macroscopic phenomena work or why they don't work in the way we expect them to. And this was in fact the case: Contrary to intuition the conversion efficiency of natural gas did not increase very much when more Ni was added to the oxygen carrier which catalyses the reaction. Yet this surprising (and also a bit disappointing) result leads us - after close investigation of the facts and exclusion of some possibly simpler explanations - to the formulation of some ideas in order to explain this behaviour. And despite of the fact that a verification of the ideas could not be done in the frame of this work - this would require considerably more effort and extended chemical analysis - we could gain some interesting results and valuable insights. A more detailed explanation had to be left for the future. However, also the results of the present work will have some influence on the selection of further mixed oxides as oxygen carriers.

At this point I have to thank, first my fate, which led me back to that point of restart and allowed me not only to study again, but also to gain a lot of personal insights. It is not often

that someone can live certain periods of life twice, but I think I had this opportunity. I want to thank my family, my wife Gertrud and my children Moritz, Simon and Vera for their support and for their tolerance during these years with a sometimes absent minded, nervous and not always sensitive husband and father. I want to thank all my friends, in particular Martin Wimmer and Beatrix Pfanzagl for their personal support and their assistance in the review of this master thesis, their encouragement and also for their criticism and scepticism with which they accompanied my way during the past 2 years. I want to thank Professor Hermann Hofbauer whose commendable lectures flavoured with personal wit and humour evoked my interest in the field of fluidized beds and their applications. I am grateful to him also for his support in all questions I brought to him as master student since the beginning of my studies. My thanks also go to Tobias Pröll for his readiness to accept me as master student in his working group, for his personal active support in the experiments done, for the openness with which he communicated his ideas and listened to mine and for his support in the discussion and finalisation of this work, where he also directed my thoughts into the right direction. In particular I want to thank all my team colleagues, especially Klemens Marx and Karl Mayer for their active engagement and contributions (during the whole master thesis and especially in the phase of the reviews of this work), their support in the experiments, their continuous advice and critical remarks and their patience with which they answered the questions of a somewhat unorthodox master student. Stefan Penthor and Gerhard Schöny, Diana Carolina Guio-Perez and Simon Hinterhuber I thank for many interesting conversations and discussions. I enjoyed working with you all and never had the impression to be the older one! Last, but not least I want to thank my piano teacher Vedrana Kovac who guided my alter (musical) ego and thus allowed me to find a balance to the scientific work and to proceed in my search of the perfect musical sound.

Looking forward, it is – taking into account the current unstable world-wide economic situation and the financial crisis in the European Union – not easy to say where my path goes. As it was so far not conventional or straight but always interesting, I hope this will also be true for the future. It allowed me to collect a lot of different experiences in various fields and to meet a lot of interesting people. And this in turn shaped my way of thinking and my personal view of the world. Thus I want to dedicate this work to my children my sons Moritz and Simon and to my daughter Vera with the wish that whatever they do or pursue they might do it with the curiosity of a child, with courage and with the true wish to understand and appreciate deeply the complexity and relations of our world.

Abstract

In the frame of this work chemical looping combustion (CLC), a carbon capture and storage (CCS) technology with inherent CO_2 separation, has been used to investigate the performance and suitability of a novel set of mixed oxides for this technology. The key idea of CLC is to split the combustion of a hydrocarbon or carbonaceous material, into two separate processes, namely an oxidation and a reduction reaction, which can be conducted closer to equilibrium. The two processes in CLC are typically realized in two fluidized bed reactors, an air reactor (AR) and a fuel reactor (FR). The oxygen and the energy transfer between these two reactors have to be realized by an oxygen carrier, which is circulating between the two reactors and thus transporting the oxygen from the AR to the FR, where it is needed for combustion of the fuel. Regeneration of the reduced oxygen carrier is done in the AR using oxygen contained in air.

By process separation two off-gas streams are produced and the mixing of gaseous reaction products from the reduction and oxidation is avoided (thus avoiding the mixing entropy production) and CO_2 is obtained undiluted by other gases such as N_2 , only mixed with H_2O , from which it can easily be separated. Moreover, it leads to a reduction of the energy demand of the whole process. Both facts make CLC an appealing technology for use in connection with CCS.

The choice of a suitable oxygen carrier is a key issue for the success of CLC. For the experimental campaigns in this work a mixture of the natural mineral ilmenite and artificial Ni $19\gamma Al_2O_3$ particles was chosen as oxygen carriers. Ilmenite was chosen because of its capability to react with CO and H₂ as well as its cheapness and availability. Ni- $19\gamma Al_2O_3$ has been verified in other experiments as a promising reforming catalyst. This inspired the idea of a synergy effect between the two mixture components which could lead to a complete conversion of CH₄. It was assumed that this could be achieved already at low Ni- $19\gamma Al_2O_3$ mass fractions thus obtaining a cost effective yet highly performing oxygen carrier which could make the CLC technology competitive.

In order to verify this, experiments were planned in order to investigate the influence of increasing Ni-19 γ Al₂O₃ concentration and other parameters on the overall CH₄ conversion. Three experimental campaigns were conducted. In the course of the first experimental campaign experiments with pure ilmenite as oxygen carrier were carried out, at two fuel reactor temperatures (910°C and 965°), using two fuels (CH₄ and CO/H₂ = 1:1), several fuel power values in the fuel reactor (from 60 to 120 kW) and various air to fuel ratios (0.8 to 1.4). The operation point at 80 kW, T_{FR}=965°C and λ_{eff} = 1.1 was used as a benchmark in the following campaigns. Two further experimental campaigns followed, whereby the mass fraction of Ni-19 γ Al₂O₃ was increased from 0 to about 16 wt% and the same parameters as mentioned above were varied. In total, 51 operation points corresponding to 9 mixtures were investigated. The total solids inventory mass was kept close to 85 kg. All experiments were performed in a 120 kW dual circulating fluidized bed (DCFB) pilot plant located at the Vienna University of Technology.

Solid samples were drawn during operation, cooled and the composition of each mixture was analysed using X-ray fluorescence (XRF) techniques. For this purpose a simple mixture model based on least squares fitting was developed, which allows based on the XRF spectrum of a mixture to derive the ratio of the mixture components. The mixture model had to be complemented by a linear attrition model which allows drawing conclusions to the attrition rate of the mixture components. Solid samples taken at different operation points were

oxidized in a muffle furnace at 950°C and the weight increase was measured. This allows determining the degree of oxidation and the corresponding X_s values. Using an IPSEpro simulation model of the DCFB, it was possible to verify the mass balances and derive CH₄ conversion degrees, CO₂ yields, exhaust gas compositions, etc.

As a result of the experimental campaigns it turned out that the CH₄ conversion was not as high as expected, but increased only linearly between 40% and 50%. Several explanations for the low conversion efficiency were given and a trade-off between the alternatives was made. The most probable explanation is that Ni-19 γ Al₂O₃ as NiAl₂O₄ (nickel spinel) is so stable even under the conditions in the fuel reactor, such that no metallic Ni is formed which would be necessary for a fast reforming reaction of CH₄. The presence of NiO as Ni-19 γ Al₂O₃ exhibits slow reduction kinetics compared to the low mean residence time in the reactor. Locally there are low CO/CO₂ and H2/H₂O ratios because of the presence of Fe₂O₃/Fe₃O₄ and Fe₂TiO₅/FeTiO₃, leading to a competition for the CO and H₂ respectively. The low reforming activity (of ilmenite alone) leads to a low conversion of CH₄. A verification of this explanation is beyond the scope of this master thesis, but should be preferably carried out. This could help to understand the (chemical) properties of mixed oxides and could yield hints for choosing other combinations.

Using an inventory of 85 kg and an average fuel power of more than 100 kW also a relatively high attrition rate of ilmenite of 3-4 kg/h was observed. This corresponds to an estimated inventory/fuel power relation of about 1t/1 MW (whereas the best Ni-based oxygen carriers have an inventory of 25-50 kg/MW). Using the same reactor dimensions (diameter/height etc) and fluid properties this would mean an attrition rate of 30-40 kg/MWh.

Specifically, it can be concluded that the mixed oxides consisting of ilmenite/Ni-19 γ Al₂O₃ did not fulfill the expectations and are not a suitable oxygen carrier system for practical application. A general conclusion is that catalysts which exhibit highest steam reforming reactivity at fully reduced conditions are not necessarily suitable as rate promoters in mixed oxide CLC.

Kurzfassung

Im Rahmen dieser Arbeit wurde Chemical Looping Combustion (CLC), eine Carbon Capture und Storage (CCS) Technologie, die eine inhärente CO₂ Abtrennung erlaubt, eingesetzt, um die Effizienz und Anwendbarkeit von neuartigen Mischoxiden für diese Technologie zu untersuchen. Die Schlüsselidee von CLC ist es, den Verbrennungsprozess von Kohlenwasserstoffen oder kohlenstoffhaltigem Material, in zwei separate Prozesse, nämlich eine Oxidations- und eine Reduktionsreaktion aufzuspalten. Die zwei Prozesse werden in zwei räumlich getrennten Wirbelschichtreaktoren realisiert, einem Luftreaktor (AR) und einem der Brennstoffreaktor (FR). Der Sauerstoff- und auch der Energietransfer zwischen den beiden Reaktoren wird durch einen Sauerstoffträger realisiert, welcher zwischen den beiden Reaktoren zirkuliert und so den Sauerstoff vom AR in den FR transportiert, wo er für die Verbrennung gebraucht wird. Im AR findet dann eine Regeneration des reduzierten Sauerstoffträgers unter Verwendung von Luftsauerstoff statt.

Durch die Trennung in zwei Teilprozesse werden zwei Abgasströme produziert und die Mischung der gasförmigen Reaktionsprodukte der Oxidations- und der Reduktionsreaktion verhindert (wobei die Produktion von zusätzlicher Mischungsentropie vermieden wird). Dadurch erhält man CO_2 in konzentrierter Form, unverdünnt durch andere Gase wie N_2 und nur vermischt mit Wasserdampf, von dem es leicht abgetrennt werden kann. Dies führt auch zu einer Erniedrigung des Energiebedarfes für den Gesamtprozess. Beide Fakten machen CLC zu einer ansprechenden Technologie was die Verwendung in Verbindung mit CCS betrifft.

Die Auswahl eines geeigneten oxydischen Trägers ist eine Schlüsselfrage für den Erfolg der CLC Technologie. Für die experimentellen Kampagnen in dieser Arbeit wurde ein Sauerstoffträger, bestehend aus einer Mischung des natürlichen Minerals Ilmenit und von künstlich hergestellten Ni-19 γ Al₂O₃ Partikeln, vorgesehen. Ilmenit wurde sowohl seiner Fähigkeit mit CO und H₂ zu reagieren als wegen seines niedrigen Preises und seiner leichten Verfügbarkeit eingesetzt. Die Ni-19 γ Al₂O₃ Partikel haben sich bereits in anderen Experimenten als vielversprechende Reformingkatalysatoren erwiesen. Das wiederum inspirierte die Idee von einem Synergieeffekt, der zu einem kompletten Umsatz von CH₄. Es wurde angenommen, dass dieser bereit bei niedrigen Massenanteilen an Ni-19 γ Al₂O₃ erreicht werden könne und man so einen kostengünstigen, aber doch hochperformanten Sauerstoffträger hätte, der die CLC Technologie kompetitiv machen könnte.

Um dies zu verifizieren, wurden Experimente geplant, um den Einfluss einer zunehmenden Ni- $19\gamma Al_2O_3$ Konzentration und anderer Parameter auf die Gesamtkonversion von CH₄ zu untersuchen. Drei experimentelle Kampagnen waren vorgesehen.

Im Zuge der ersten experimentelle Kampagne wurden Experimente an reinem Ilmenite als Sauerstoffträger durchgeführt, bei 2 Brennstoffreaktortemperaturen (910°C und 965°C), mit zwei verschiedenen Brennstoffen (CH₄ und einem 1:1 Gemisch aus CO/H₂), verschiedenen Werten der Brennstoffleistung (von 60 bis 120 kW) und verschiedenen Luft/Brennstoffverhältnissen (zwischen 0.8 und 1.4). Ein Arbeitspunkt bei 80kW, TFR=965°C und $\lambda_{eff} = 1.1$ wurde als Referenzpunkt für die folgenden Kampagnen gewählt. Zwei weitere experimentelle Kampagnen folgten, wobei der Masseanteil an Ni-19yAl₂O₃ von 0% auf 16% erhöht wurde und die oben erwähnten Parameter variiert wurden. Das Gesamtbettmaterial wurde bei ca. 85 kg konstant gehalten wurde. Alle Experimente wurden in einer DCFB Pilotanlage an der Technischen Universität Wien ausgeführt.

Aus dem Festbett wurden im laufenden Betrieb Proben gezogen, abgekühlt und die Zusammensetzung jeder Mischung wurde unter Zuhilfenahme von Röntgenfluoreszenz (XRF) analysiert. Zu diesem Zweck wurden einfache Mischungsmodelle basierend auf einem Least Squares Fit (Methode der kleinsten Fehlerquadrate) entwickelt, welche erlauben ausgehend vom XRF Spektrum eines Gemisches Rückschlüsse zu ziehen auf das Verhältnis der Mischungskomponenten. Dazu musste ein zum Mischungsmodell komplementäres lineares Abriebmodell entwickelt werden, welches es erlaubt, Rückschlüsse auf die Abriebrate der Komponenten zu ziehen. Proben der Festbettmischungen, die bei verschiedenen Arbeitspunkten entnommen worden waren, wurden im Muffelofen bei 950°C oxidiert und die Gewichtszunahme bestimmt. Dies erlaubt eine Bestimmung des Oxidationsgrades und zugehörigen Xs-Werte (Feststoffkonversionswerte, solids conversion values). Unter Zuhilfenahme eines IPSEpro Simulationsmodells der DCFB war es möglich, die Massenbilanzen verifizieren und zu CH_4 Umsätze, CO_2 Ausbeuten, Abgaszusammensetzungen, etc. zu bestimmen.

Als Ergebnis der experimentellen Kampagnen zeigte sich, dass der CH₄ Umsatzgrad nicht so hoch wie erwartet war, sondern nur linear im Bereich 40-50% anstieg. Einige Erklärungen für den niedrigen Konversionsgrad wurden gegeben und diese in einem Auswahlverfahren untersucht. Die wahrscheinlichste Erklärung ist, dass Ni-19 γ Al₂O₃ als NiAl₂O₄ (Nickelspinell) auch unter den reduzierenden Bedingungen im Brennstoffreaktor so stabil ist, dass kein metallisches Nickel gebildet wird, welches für die rasch ablaufende Reformierungsreaktion von CH₄ notwendig wäre, gebildet wird. Das als Ni-19 γ Al₂O₃ vorliegende NiO zeigt eine nur langsame Reduktionskinetik verglichen mit der niedrigen mittleren Aufenthaltsdauer im Reaktor. Wegen der Anwesenheit von Fe₂O₃/Fe₃O₄ und Fe₂TiO₅/FeTiO₃, die zu einer Konkurrenz um das vorhanden CO und H₂ führt, kommt es zu lokal niedrigen CO/CO₂ und H2/H₂O Verhältnissen. Die niedrige Reformingaktivität (von Ilmenit allein) führt zu einem niedrigen Umsatzgrad an CH₄. Eine Verifikation dieser Erklärung geht über den Rahmen dieser Masterarbeit hinaus, sollte aber bevorzugterweise unternommen werden. Dies könnte helfen, die (chemischen) Eigenschaften der Mischoxide besser zu verstehen und darüber hinaus Hinweise für die Auswahl neuer Kombinationen liefern.

Unter Zugrundelegung eines Inventars von 85 kg und einer durchschnittlichen Brennstoffleistung von mehr als 100 kW ergab sich auch eine relativ hohe Abriebrate von Ilmenit von 3-4 kg/h, was einem geschätzten Inventar/Brennstoffleistungsverhältnis von 1t/1 MW entspricht (die besten Ni-carrier erreichen 25-50 kg/MW). Würde man dieselben Reaktordimensionen (Durchmesser/Höhe etc.) und dieselben fluidmechanischen Eigenschaften zugrundelegen, so ergäbe dies eine Abriebrate von 30-40 kg/ MWh.

Im speziellen kann der Schluss gezogen werden, das Mischoxide, bestehend aus Ilmenit/Ni- $19\gamma Al_2O_3$ die Erwartungen nicht erfüllten und keinen passenden Sauerstoffträger darstellen. Als allgemeiner Schluss kann gesagt werden, dass Katalysatoren, die im reduzierten Zustand höchste Dampfreformierungsaktivitäten aufweisen, nicht notwendigerweise effektive Umsatzbeschleuniger für CLC mit Mischoxiden sind.

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1 Introduction

1.1 Greenhouse Gases and Climate Change

It is now common knowledge that the greenhouse effect, a natural phenomenon, is responsible for the regulation of the Earth's surface temperature. This effect is caused by so-called greenhouse gases, such as CO₂, CH₄, N₂O and others. While these GHGs let pass through high frequency (visible and UV) radiation from the sun , they absorb (IR) radiation with lower frequency reflected form the Earth's surface thus trapping solar energy that would otherwise escape into space. Without this natural greenhouse effect, temperatures at the Earth's surface would be about 33°C lower than at present and life as we know it today would not be possible. Figure 1 depicts the relative fractions of GHG emissions in 2004. It is evident that CO₂ (from fossil fuels, deforestation and other sources) makes up the largest contribution.



Figure 1: Global anthropogenic greenhouse gas emissions in 2004 [1]

It is also understood now that human activities, such as fossil fuel use for energy provision and clearing of forests, have enhanced the natural greenhouse effect, causing the Earth's average temperature to rise. The effect of a GHG and other human activities on the Earth's warming can be expressed by the radiative forcing in W/m^2 . Radiative forcing is a measure of how the energy balance of the Earth-atmosphere system is influenced when factors that affect climate are altered. A positive radiative forcing value for a factor or group of factors means that the energy of the Earth-atmosphere system will ultimately increase, leading to a warming of the system and vice versa for a negative radiative forcing. Figure 2 below provides a summary of the principal components of the radiative forcing on climate change. The values represent the forcings in 2005 relative to the start of the industrial era (about 1750). It can be seen that among the GHGs, CO₂ increases have caused the largest positive forcing over this period. Thus, technologies and measures that can prevent or minimise CO₂ emission by capturing CO₂, reusing it or alternatively, pumping it into underground geologic formations to securely store it away from the atmosphere will play a major role in the global efforts for the reduction of CO₂ and the mitigation of global warming. The latter strategies can be summarized under the term Carbon Capture and Storage (CCS).



Figure 2: Summary of the principal components of radiative forcing on climate change [2]

The global atmospheric CO_2 concentration has reached 379 ppm in 2005 which is significantly higher than the pre-industrial value of 280 ppm. At present the European Union has adopted a cap-and-trade system to set prices for the CO_2 – the so-called EU Emissions Trading system. The IEA has proposed two scenarios in order to keep the CO_2 emissions below 450 ppm or 550 ppm, respectively. Only the more rigorous 450 ppm Policy Scenario has the potential to keep global warming below 2 K global temperature rise in 2050 (compared to pre-industrialisation levels). In this scenario the cap-and-trade system is assumed to be extended to power and industry sectors of OECD+ countries (which includes OECD plus non-OECD EU countries) as of 2013 and to other major economies (which include China, Russia, Brazil, South Africa and Middle East) as of 2021. It is furthermore assumed that CO_2 is traded in two separate markets: the OECD+ and the other major economies [3].

1.2 Carbon Capture and Storage (CCS)

Carbon Capture and Storage (CCS) is seen as a mid-term mitigation option to keep the CO_2 levels below either 550 ppm or 450 ppm. Future emission can be simulated by assuming scenarios, which are alternatives, where to the future develops and allow analysing the driving forces for future emissions. IPCC has built a set of scenarios of what might happen to emissions up to the year 2100, whereby the scenarios were grouped into six groups and

termed as 'SRES scenarios' [4]. The six groups were organized into four 'families: 'Scenario families A1 and A2 emphasize economic development, whilst B1 and B2 emphasize global and local solutions for economic, social and environmental sustainability. In addition, two scenarios, A1F1 and A1T, illustrate alternative developments in energy technology in the A1 world [5]. The resulting ranges of CO_2 emissions are depicted in Figure 3 below.



Figure 3: Range of annual global CO2 emissions in the SRES scenario [4]

The SRES scenarios allow for deriving cumulative emissions. These are shown in Figure 4 for the period from 1990 to 2100 ranging from less than 2930 to 9170 $GtCO_2$ (800 to 2500 GtC). This range can be subdivided into four intervals, distinguishing between scenarios with high, medium-high, medium-low, and low emissions:

- high (\geq 6600 GtCO₂ or \geq 1800 GtC);
- medium-high (5320–6600 GtCO₂ or 1450–1800 GtC);
- medium-low (4030–5320 GtCO₂ or 1100–1450 GtC);
- low (≤4030 GtCO₂ or ≤1100 GtC).

Depending on the scenarios considered and the corresponding increase of CO_2 emission, this requires the reduction or even the complete prevention of cumulative emission of hundreds or even thousands of gigatonnes of CO_2 . It is evident that this cannot be achieved by use of a single technology, but will require a mixture of technologies accompanied by the implementation of socio-economic and institutional changes. In 2005 it was estimated that CCS could have contribute by 10% to the total CO_2 emission reduction already by 2013 with continued increase in share after 2030 [5]. The most promising strategy for reducing global CO_2 emission should therefore be a combination of:

- Enhanced energy efficiency
- Increased use of renewable energy
- Wide implementation of CCS

- Use of less carbon intensive fuels



Figure 4: Annual and cumulative global emissions from energy and industrial source in the SRES scenarios [4]

Figure 5 shows examples of relevant CO₂ sources, CO₂ transport systems and storage options.



Figure 5: Schematic diagram of possible CCS Systems [5]

While there is continuing rapid growth in the deployment of renewable energy technologies and in energy end-use efficiency gains, the IEA also expects a rapidly increasing role for CCS between 2025 and 2030. Once the lower cost options for energy efficiency and renewable

technologies have been pursued, CCS should become more competitive. The IEA estimates that by 2050 CCS is contributing by 19 % of least cost emission reductions. This contribution is more than that from renewables and more than three times the contribution from nuclear power [6].



Figure 6: Global CO₂ Emissions and GHG Reductions [6]

The total CO₂ emission from fossil-fuel in the year 2000 were approximately 24 GtCO₂ yr⁻¹, of which 60% can be attributed to large (>0.1 MtCO₂yr⁻¹) stationary emission sources such as power plants. Of these only the high-concentration sources which make up a small portion (about 2%) and which are within a 50 km range of suitable storage formations have the potential to generate revenues (via the use of CO₂ for enhanced hydrocarbon production through ECBM or EOR). These are potential primary candidates for early implementation of CCS technologies. Analysis shows that these high-concentration sources currently emit approximately 360 MtCO₂yr⁻¹ (which is 2.7% of the total CO₂ emission).

Table 1 shows that power plants contribute about $78.3 \ \%$ of the CO₂ emission from large stationary sources. Therefore it makes sense to look at possible carbon emission mitigation measures for such plants first.

Process	Cumulative number of sources	CO ₂ Emission (MtCO ₂ yr ⁻¹)	Percentage %
Fossil fuels			
Power	4942	10539	78.25%
Cement production	1175	932	6.92%
Refineries	638	798	5.93%
Iron and steel industry	269	646	4.80%
Petrochemical industry	470	379	2.81%
Oil and gas processing	N/A	50	0.37%
Other sources	90	33	0.25%
Biomass			
Bioethanol and bioenergy	303	91	0.68%
Total	7887	13468	100.00%

Table 1: Overview on large stationary CO₂ emission sources (according to [5])

Typically, when talking about CO_2 capture from fossil fuel usage, three first generation processes are discussed:

- Post-combustion capture
- Pre-combustion capture
- Oxyfuel combustion capture

Figure 7 provides an overview on such CCS processes. In all of these first generation CCS processes, an energy intensive gas-gas separation is needed for CO_2 separation or air separation, respectively. Currently there are also newer technologies underway. One example of such a second generation process is the Ca-looping, a technology which uses CaO as regenerable sorbent to capture CO_2 from the flue gases generated in power plants [7].



Figure 7: CO₂ Capture Systems [5]

Irrespectively whether CO_2 separation from exhaust gas or synthesis gas or air separation for subsequent oxyfuel combustion is required, this means additional energy consumption. As the energy required for gas separation cannot be recovered, this decreases the overall energy efficiency of such plants. Therefore concepts where the separation of CO_2 with other gases is inherently avoided are currently in the focus of research. One of the most promising concepts is Chemical Looping Combustion (CLC) which will be discussed in Subsection 1.3.

1.3 Chemical Looping Combustion (CLC)

The idea of CLC was originally proposed in a patent by Lewis and Gilliland in 1951 as method to produce pure CO_2 from "any oxidizable material" [8] and investigated in a laboratory installation [9]. Later, CLC was studied theoretically by Richter and Knoche in order to improve the reversibility of the combustion process [10], [11]. In 1987 the term "chemical looping combustion" was introduced by Isihida et al. [12]. Subsequently the concept was adapted in the 1990's and theoretically discussed as a promising technology for CO_2 capture in natural gas fired combined cycle power plants [13], [14].

The basic principle of CLC is to split the combustion reaction into (a) an oxidation and (b) a reduction reaction by use of a suitable metal (oxide) as an oxygen carrier. Separation of oxygen is achieved by fixing the air oxygen to the metal (oxide) in the so called air reactor (AR). In a second reactor, the fuel reactor (FR), subsequently the oxygen in the metal oxide is used in a reducing atmosphere to oxidize the fuel. Since the combustion air and the fuel are never mixed, the produced CO_2 is not diluted by air nitrogen and gas separation is inherently avoided. This leads to a reduction of the energy demand for the whole process compared to a normal combustion process. Moreover CO_2 becomes available in a more or less pure form after the process (see Figure 8 left part). If the oxygen is available in a sub-stoichiometric amount, the fuel cannot be fully oxidized and the process is called chemical looping reforming (CLR,see Figure 8 right part), where a synthesis gas is produced.



Figure 8: Principle of CLC (left) and CLR (right) (from [34])

Two overall reactions have to be taken into account. In the air reactor the oxygen carrier is oxidized by the supplied air stream:

$$Me_x O_{y-1} + \frac{1}{2} O_2 \rightarrow Me_x O_y \tag{R1}$$

In the FR the oxygen carrier is reduced and simultaneously the hydrocarbon or carbonaceous fuel is oxidized. If a hydrocarbon is used as a fuel the overall FR reaction can be written as:

$$C_nH_{2m} + (2n+m) Me_xO_v \rightarrow (2n+m) Me_xO_{v-1} + m H_2O + n CO_2$$
 (R2a)

If syngas, a mixture of CO and H_2 , is used, two reductive species are present as fuel and the reaction can be written as

$$nCO+mH_2 + (n+m) Me_xO_y \rightarrow (n+m) Me_xO_{y-1} + m H_2O + n CO_2$$
 (R2b)

In the case of CLC, the exhaust gas from the air reactor is O_2 depleted air, whereas the exit gas from the fuel reactor contains CO_2 and H_2O . In the case of CLR a syngas composed of CO, H_2 , CO_2 and H_2O is obtained. Depending on the oxygen carrier material and the fuel used, the overall reaction inside the fuel reactor is mostly slightly endothermic, while the reaction in the air reactor is always strongly exothermic; whereby the global heat release is equal to that of direct combustion of the fuel. In order to close the cycle the reduced oxygen carrier is then transported again to the air reactor.

1.4 Status of CLC

A number of reviews have been published in the past years, which provide overviews on the status and operational experience of CLC ([15], [16], [17] and [18]) or chemical looping in general [19]. Summarizing these reviews, it can be concluded that CLC is that it is ready for field demo using gaseous fuels and Ni based oxygen carriers.

1.5 Oxygen Carriers

A key issue in chemical looping is the selection of a suitable oxygen carrier. Oxygen carriers currently proposed can be made of synthetic materials consisting of a transition metal oxide (such as CuO, NiO, Fe₂O₃, Mn₃O₄) supported by an inert material such as Al₂O₃, SiO₂, TiO₂ and ZrO₂. Alternatively they can also be natural (oxidic) minerals. The most important requirements for an oxygen carrier are:

- 1. suitable reduction/oxidation potential (see also Subsection 2.1)
- 2. high reactivity and conversion rate with respect to fuel conversion to CO₂ and H₂O
- 3. high oxygen transport capability
- 4. high mechanical stability (i.e. resistance against fragmentation and attrition)
- 5. low agglomeration tendency even at increased temperature
- 6. high cyclic stability of the structure to maintain reactivity over repeated cycles of reduction and oxidation (i.e. long-term stability of structure)
- 7. resistance to contaminant and inhibition of solid carbon formation
- 8. stable pore structure
- 9. low production costs
- 10. preferably environmentally non-hazardous

Of these high reactivity and mechanical stability are the most critical requirements to fulfil. Comprehensive reviews of the current status of oxygen carrier development can be found e.g. in [15] and [16].

Natural oxygen carriers are usually minerals, iron ores or waste from steel production, which are cheap and available in big quantities. Synthetic oxygen carriers are metal oxides which are produced with specifically designed properties. The use of the inert support material increases porosity and reactivity of particles, helps to maintain structure and possibly increases the ionic

conductivity of the particles. The production methods for these are: wet impregnation, freeze granulation or spray drying followed by sintering under defined conditions.

Based on thermodynamic investigations of the ability to completely convert fuel to CO_2 and H_2O metal oxide systems such as NiO/Ni, Mn_3O_4/MnO , Fe_2O_3/Fe_3 , Cu_2O/Cu and CoO/Co have been identified as feasible oxygen carriers. The reactivity with respect to methane combustion falls significantly in the order Ni > Cu > Mn > Fe (see [15], [16]). However, there are some shortcomings with the monometallic oxides different from Ni:

- Cu-based oxygen carriers show relatively strong sintering tendencies above 800°C
- Fe-based oxygen carriers have weak redox capacity and are also very prone to sintering and agglomeration
- Mn-based carriers have very low conversion levels (of about 70%) and are chemically instable due to reactions between the metal and the alumina support (leading to the formation of aluminates, which are almost inert with respect to conversion)
- Co-based carriers show very limited conversion capabilities and progressively deteriorate throughout the cycles of CLC

Compared to other transition metal oxides, Ni-based carriers are still the most promising ones. They show high reactivity towards methane-based fuels like natural gas. They can be manufactured from materials which are commercially available in large quantities at prices as Ni itself ([15], [16]). Experiments indicated a high mechanical stability and a long lifetime, which could probably compensate for the high price in comparison to other materials, which are cheaper, but have a reduced lifetime (e.g. iron based oxygen carriers). The high reactivity also allows for a considerable reduction of the solids inventory which means a reduction of costs. Based on measured kinetics and assuming an ideal gas solids contact a very small solids inventory of 10-20 kg/MW would be sufficient to reach almost complete conversion, which again allows reducing costs. However, as the gas-solids contact in fluidized beds is not perfect – usually there is a bypass of gas induced by bubbles – and there is a tendency to underestimate the needed inventories within such TGA based reactor simulation models. Furthermore thermodynamics limit the CH₄ conversion to CO₂ using Ni to around 99%.

Therefore the approach to use materials which allow for CLOU (Chemical looping for oxygen uncoupling) might be useful. These are oxygen carrier materials which have the ability to release gaseous oxygen and, thus, are less depending on direct contact between fuel gas and oxygen carrier particles [16]. There are some indications that oxygen release by CLOU materials (such as CuO) could compensate for their lower reactivity with CH_4 and the lower fuel conversion rates.

1.5.1 The Role of Support Material

There is one aspect to mention in addition, which also influences the quality of an oxygen carrier, namely the influence of the oxygen carrier support material. It is well known that the support has an influence on several properties of the CLC system:

- the oxygen transport capacity,
- the thermodynamic properties of the carrier redox system,
- the reactivity
- the attrition rate and
- the agglomeration behavior

The oxygen transport capacity R_0 as defined in [17] is a measure of the relative amount of oxygen present in the oxidized form of the carrier in relation to the reduced form of the oxygen carrier:

$$R_{O} = \frac{m_{ox} - m_{red}}{m_{ox}} \tag{1}$$

The oxygen transport capacity R_0 is directly influenced by the support by diluting the mixture. The support material actually is a second redox system that can influence the carrier redox system by formation of intermetallic compounds. This can affect the thermodynamics or influence the oxygen carrier transport capacity. For example, for Fe-based oxygen-carriers supported on Al_2O_3 or TiO₂ the reduction of Fe(III) in Fe₂O₃ to Fe(II) in iron aluminate (FeAl₂O₄) or iron titanate (FeTiO₃) takes place [18]. In these cases, the oxygen transport capacity is increased because of the higher oxygen transport capacity in the iron oxide in relation to the smaller transport capacity for the redox system Fe₂O₃/Fe₃O₄ (see Figure 9 below, after [18]).



The influence of the support material on the thermodynamics of the redox system can be clearly observed e.g. in the CuO/Al₂O₃ system. In this case, where copper aluminate (CuAl₂O₄) is formed, the reduction of Cu(II) to Cu with CH₄ changes from an exothermic to an endothermic reaction. The opposite trend is observed for the Fe₂O₃/Al₂O₃ system [18].

Ni-based oxygen carriers prepared on γ -Al₂O₃ showed low reactivity and low CH₄ combustion selectivity towards CO₂ and H₂O, caused by the formation of NiAl₂O₄ thereby reducing the amount of free NiO. To avoid or to minimize the interaction of NiO with alumina a phase transformation of the γ -Al₂O₃ support to α -Al₂O₃ by thermal treatment at 1150 °C can be induced or the active centers at the support can be chemically deactivated with Mg and Ca oxides. Indeed, Ni-based oxygen carriers prepared on α -Al₂O₃, MgAl₂O₄, or CaAl₂O₄ as support show very high reactivity and high methane combustion selectivity to

 CO_2 and H_2O because the interaction between the NiO and the support is decreased. As an additional advantage these oxygen carriers have very low attrition rates and do not show any agglomeration problems during operation in fluidized beds [20]. However, by provoking the formation of NiAl₂O₄, the Ni can be distributed in the crystal matrix on an atomar level. When such materials are reduced to Ni and Al₂O₃ an extremely active catalyst with highest accessibility of Ni is generated. Such materials are used in CH₄ steam reforming.

In general, a porous support provides a larger surface for reaction, a binder for increasing the mechanical strength and attrition resistance, and also increases the ionic conductivity of solids. A larger surface of the oxygen carrier is indeed essential for CLC, as it increases the potential gas/solid contact area.

1.6 Mixed Oxides as Oxygen Carriers

Another approach to circumvent the shortcomings of monometallic oxygen carriers is to prepare oxygen carriers consisting of a mixture of two transition metal oxides. The underlying idea is to make use of the best properties of both materials. Such oxygen carriers consisting of a mixture of metal oxides may allow overcoming the limitations of mono-metallic oxides and create a positive synergy effect. These mixtures may be either physical mixtures (so-called mixed oxides) or chemically combined oxides (so-called combined oxides).

It is well known that the conversion of CH_4 to CO_2 and H_2O can be achieved with very small quantities of NiO, whereby the reaction proceeds with CO and H_2 as intermediates, which are not favourable for CLC. In addition, as already mentioned above, the high reactivity of NiO is partly outweighed by the high price and the health impact as well as the thermodynamic conversion limit, which is slightly above 99%. Fe₂O₃ is a cheap, abundant and not toxic oxygen carrier. Its reactivity towards CH_4 is low in comparison to NiO, because Fe_2O_3 is reduced to Fe_3O_4 rather than to metallic Fe, which could help to catalyse the decomposition of hydrocarbons. However, the reactivity of Fe_2O_3 with CO and H_2 has been found high [21]. The expected positive synergy effect of mixtures of Fe_2O_3 and NiO could be demonstrated and has been described in [22].

In a number of previous studies ilmenite (FeTiO₃ = FeO.TiO₂) has been identified as a promising candidate for the use as oxygen carrier in CLC for both, solid and gaseous fuels, because of its cheapness and availability in large quantities. These studies concentrated on the use of pure ilmenite as oxygen carrier [23], [24], its phase chemical description [25], the description of phase transitions and reaction mechanisms during oxidation [26], the characterization of redox behaviour and kinetics [27] or the investigation of the activation behaviour during consecutive redox cycles [28]. Experiments with pure ilmenite as oxygen carrier in CLC were carried out in a laboratory scale fluidized-bed reactor system [23].

Experiments with mixed oxides containing ilmenite with traces of NiO were carried out on a small scale as batch experiments in fluidized-bed reactor by alternating between oxidizing and reducing fluidized gas in a 300 W laboratory scale circulating fluidized bed reactor [30] and with varying percentage of NiO on γ -Al₂O₃ support [20]. Experiments with ilmenite based mixed oxides in a pilot scale dual circulating fluidized bed (DCFB) plant at Vienna University of Technology: Ilmenite/Olivine mixtures ([24] as well as ilmenite/VITO A/B mixtures [29] were investigated, whereby VITO A/B showed a considerable effect. Therefore it was decided to work with a highly active catalyst in order to overcome the weakness of ilmenite in CH₄ conversion.

1.7 Scope of Work

Therefore, in order to be able to draw authoritative conclusions about the behaviour and usability of mixed oxides of ilmenite/Ni-19 γ Al₂O₃ in CLC, it is necessary to do experiments on a pilot scale basis.

Within the current study using mixtures of ilmenite and Ni- $19\gamma Al_2O_3$ the following research questions shall be addressed:

- 1. Using natural gas, what is the effect of increasing Ni-carrier concentration on CH₄ conversion performance?
- 2. What is the effect of the temperature on CH_4 conversion performance?
- 3. What is the effect of increasing fuel power on the CH₄ conversion performance?
- 4. What is the effect of variation of air/fuel ratio on CH₄ conversion performance?
- 5. How effective is the syngas conversion performance?
- 6. Is the mechanical stability of the mixed oxides against attrition under variable conditions high enough?
- 7. Are there differences between the attrition rates of the mixture components?

Some physical properties of Ni-19γAl₂O₃ are listed in Table 2.

Table 2: Physical properties of Ni-197-Al₂O₃ (according to [31])

Property	Unit	Value
Particle size	[µm]	100-300
NiO content	[%]	19.5
Crushing strength	[N]	2.6
BET area	[m ²]	82.7
Carrier porosity	[%]	46.50
Solid density	[gcm ⁻³]	1.7

2 Theoretical Background

2.1 Thermodynamics of CLC

Direct combustion of fuels is a highly irreversible process due to the fact that the process is taking place far from equilibrium. This results in additional entropy production (or synonymously speaking exergy destruction). Mainly, three sub-processes are contributing to the global entropy production [32]:

- Reactant diffusion and oxidation
- Heat transfer between the reactants in the reactor
- Product mixing

It could be shown that the major contribution to the destruction of useful energy occurring in gaseous hydrocarbon fuel combustion is due to heat transfer between particles in the system. However, since kinetic and momentum transfers are inevitable, the only ways to reduce entropy production is to inhibit the conversion of "chemical energy" into "thermal energy" which causes the undesirable thermal energy exchange. In addition product mixing should be avoided. Both requirements are satisfied by the technique of chemical looping combustion.

It is a fact that reversible single-staged combustion of hydrocarbons requires impractically high working temperatures. Consequently the solution for this problem is to replace the single combustion event by two redox reactions that can be conducted reversibly at lower reaction temperatures and below present materials limits. Therefore a "practical" CLC process can be constructed using two Rankine cycles to generate shaft work. However, the maximum working fluid temperature is still far too high [33].

In addition losses in exergy can be diminished, if the immediate contact between fuel and oxygen is avoided and the combustion reaction is split into two redox reactions, one exothermic oxygen carrier oxidation occurring in the air and one (typical) endothermic fuel oxidation in fuel reactor. If thus one or both processes occur closer to equilibrium conditions, a cyclic Carnot like process between the heat source and the heat sink can be constructed and the mixing of gaseous reaction products is avoided (thus avoiding the mixing entropy production). For this reason the exergy delivered of the fuel as mechanical work can be maximized [10].

The oxidation potential of different oxygen carriers can be estimated from Figure 10 below. The horizontal broken lines in Figure 10 indicate the O₂ partial pressure in air (21 v %) and for a reasonable air reactor exhaust gas O₂ concentration of 4 v %. The other three broken lines indicate certain equilibrium concentrations of CO in a typical fuel reactor exhaust gas from CH₄ combustion containing 33 v % of CO₂. Suitable oxygen carriers should show good CO conversion in the fuel reactor but also have the potential for regeneration in the air reactor at reasonably low O₂ concentrations. The vertical distance between the curved lines and the 4 v % O₂ line is a rough measure of the driving force for oxidation. Farther distances indicate a higher driving force (compare also Figure 9). Interestingly, two of the most promising oxygen carrier systems are quite at the opposite limits of this picture: the NiO/Ni system will leave some unconverted fuel in the fuel reactor (about 0.15 v % CO and 0.25 v % H₂ at 850°C) and the CuO/Cu₂O system is already on the limit of oxidation in the air reactor.



Figure 10: Oxidation potential of different oxygen carrier redox systems in CLC. ([34])

2.2 Nickel based Oxygen Carriers

Both bulk nickel and supported Ni/NiO have been widely used as oxygen carriers in CLC. However, unsupported NiO displays poor performance in repeated oxidation and reduction cycles due to nickel agglomeration [35]. Therefore Al_2O_3 has been used as support material preferably due to its favorable fluidization properties and thermal stability. Ni is present as a dispersed NiO phase on this support. Although Ni agglomeration could be suppressed there is always the likelihood of formation of Ni Al_2O_4 (nickel aluminate) as a result of the interaction of Ni and alumina support at high temperatures. With the formation of Ni Al_2O_4 a certain fraction of Ni becomes unavailable for the oxidation/reduction cycle which results in a reduced reactivity [36]. In order to mitigate or prevent the loss of active Ni two approaches were chosen:

- (a) excess Ni was introduced in order to obtain a stable Al₂O₃ carrier whereby some of the excess Ni reacts with Al₂O₃ forming NiAl₂O₄ and the carrier becomes stable after some initial (reduction/oxidation) cycles [37], [38],
- (b) other support materials were used instead of Al₂O₃ with Ni: e.g. NiAl₂O₄, MgAl₂O₄
 [22], [39], [40], YSZ [22], [40]-[47], TiO₂ [40], [43], [48]-[55], SiO₂ or ZrO₂ [40], [50], [56]-[63].

However some of the proposed support materials showed other disadvantages: The Ni/NiO supported on NiAl₂O₄ is very stable under the high CLC oxidation and reduction temperatures; however, the oxygen carrier requires even more Ni than Ni/Al₂O₃ and thus is more expensive than the latter. In Ni supported on TiO₂ the NiO reacts with TiO₂ to form NiTiO₃ and a decrease in reactivity was observed (due to loss of active Ni) [51], [52], [53] and [54]. This carrier also displays some coke formation tendency which leads to the occurrence of CO₂ in the air reactor exhaust and to a decrease of the overall CO₂ capture

efficiency. With ZrO_2 and SiO_2 as the support the carrier shows a decreasing reactivity due to the formation of nickel complexes. Ni/YSZ showed excellent reactivity and regenerability, All these exotic support materials like ZrO_2 , YSZ have in common that they are very expensive.

In addition, since NiO is also harmful for health as a consequence of long-term exposition (causing lesions and in some cases cancer) there is a continuous search for less toxic and cheaper oxygen carriers. Natural abundant and harmless minerals such as ilmenite are in the focus of this search.

2.3 Ilmenite as Oxygen Carrier

Ilmenite (FeTiO₃) is the most abundant titanium mineral. The term is also commonly used for various ores with the approximate composition. As ilmenite most often contains appreciable quantities of magnesium and manganese, the full chemical formula can be expressed as (Fe,Mg,Mn,Ti)O₃. Ilmenite forms a solid solution with geikielite (MgTiO₃) and pyrophanite (MnTiO₃) which are magnesian and manganiferous end-members of the solid solution series. Ilmenite crystallizes in the trigonal system, and has the same crystal structure as corundum (Al₂O₃) and hematite (Fe₂O₃) (for crystal structure see Figure 11 below).



Figure 11: Crystal structure of ilmenite ([58])

Ilmenite is mostly used for producing TiO_2 and Ti metal. It is mined in substantial quantities in many countries. Australia was the world's largest producer and exporter of ilmenite ore in 2005–2006, with 1.1 million tones, followed by South Africa (952kt), Canada (809kt), China (~400kt) and Norway (380kt). Most ilmenite is mined for TiO_2 production, which is finely ground and used as a base pigment in paint, paper and plastics production. Conversion of ilmenite to TiO_2 production can be done via the sulfate process or via hydrochloric acid process [59]. Raw ilmenite is refined by decreasing the iron content. This can be done e.g. using the *Becher process* [60].

As already mentioned ilmenite is being investigated as an attractive oxygen carrier for the combustion of solid fuels [61] as well as CH_4 and syngas [23], [62], whereby the iron oxide is the active oxygen carrier phase. Also mixed oxides of ilmenite with up to 5% NiO based particles have been studied on a small scale basis in a batch fluidized reactor [30].

2.4 Particle Reaction Mechanism

When talking about reduction and oxidation of metal oxides in a CLC plant, it is assumed that the gas – solid reactions are carried out in the following steps¹:

- 1. Diffusion and/or convection of gaseous reactant across the gas film to the surface of the particle.
- 2. Diffusion of gaseous reactant through the pores of the particle.
- 3. Adsorption of the gaseous reactant onto the reactive pore surface.
- 4. Chemical reaction on the pore surface.
- 5. Desorption of gaseous product from the pore surface.
- 6. Diffusion of gaseous product out of the particle.
- 7. Diffusion and/or convection of gaseous product across the gas film to the bulk gas phase.

Based on these steps, the pore structure and pore volume in the particle significantly affects the reactivity of the particle. This can indeed be observed in the case of activated ilmenite, where an increased porosity compared to fresh ilmenite is observed [28]. Activation is obtained by performing several oxidation and reduction cycles with fresh ilmenite (see Subsection 2.5.3). In this case the particle reaction mechanisms involve also the formation of cation vacancies (see Subsection 2.5.2).

2.5 Air Reactor Reactions

In the air reactor re-oxidation of the bed material which has been reduced in the fuel reactor takes place. The generalized form of all air reactor reactions is (see (R1) in Subsection 1.3).

In case of ilmenite different end products for the oxidation process are possible depending on reaction time and temperature. Due to the existence of various valence states of Fe, phase transitions occur during the oxidation.

2.5.1 Ilmenite Oxidation

From thermodynamic calculations it follows that the end-product of the oxidation of ilmenite at temperatures higher than 853K are pseudobrookite (Fe_2TiO_5) and rutile (TiO_2) [64].

However, experiments showed that the end product of the oxidation by air depends on the reaction time and temperature. Depending on the temperatures three different oxidation products can be found [65]:

 $^{^{1}}$ The reaction mechanism described above is not valid for oxygen carrier particles which are able to release O_{2} in the CLOU process.

- In the temperature range between 773-1023 K the oxidation leads to hematite (Fe_2O_3) and rutile (TiO_2) as final products;
- Between 1043K and 1163K hematite (Fe₂O₃) and pseudorutile (Fe₂Ti₃O₉) are the final products.
- Above 1173 K pseudobrookite (Fe₂TiO₅) and rutile (TiO₂) are the oxidation products.

Summarizing, at temperatures below 1123 K a mixture of hematite, pseudobrookite (Fe₂TiO₅) and rutile (TiO₂) exists. Pseudobrookite (Fe₂TiO₅) is found as the only end-product, if temperatures above 1123 K are applied for a long time (> 24h).

From this it follows that the oxidation of ilmenite (FeTiO₃) proceeds as follows [27]:

$$2 \operatorname{FeTiO}_3 + 1/2O_2 \rightarrow \operatorname{Fe_2O_3} \cdot \operatorname{TiO}_2_{(s)} + \operatorname{TiO}_2_{(s)} \rightarrow \operatorname{Fe_2O_3}_{(s)} + 2 \operatorname{TiO}_2_{(s)}$$
(R3)

$$3 \text{ FeTiO}_3 + 3/4\text{O}_2 \rightarrow \text{Fe}_2\text{Ti}_3\text{O}_{9 (s)} + 1/2 \text{ Fe}_2\text{O}_3 \rightarrow 3/2\text{Fe}_2\text{TiO}_{5(s)} + 3/2\text{TiO}_{2 (s)}$$
(R4)

Thus the end-product of the oxidation of ilmenite is a mixture of Fe_2TiO_5 , Fe_2O_3 , and TiO_2 with a ratio depending on the reaction time and temperature.

2.5.2 Ilmenite Segregation Process

Even if ilmenite oxidation is carried out at relatively low temperatures (below 800°C) an iron oxide layer forms at the hull of ilmenite particles. Segregation of the Fe₂O₃ layer from the Ti rich phase occurs as a consequence of a different oxidation reaction through which cation vacancies are introduced in the ilmenite structure. Oxidation occurs by adding O²⁻ anions to the ilmenite lattice. The electrons needed to form these anions from O₂ are obtained from the oxidation of Fe²⁺ to Fe³⁺ and by the simultaneous creation of cation vacancies (denoted as \Box in (R5)).

$$Fe^{2+} + z/2 O \rightarrow z Fe^{3+} + (1-z) Fe^{2+} + z/3 \Box + z/2 O^{2-}$$
 (R5)

As bulk diffusion of O^{2-} is slower than diffusion of cations, this necessitates a flux of electrons from the interior of the grains to the surface. In order to achieve charge balance Fe²⁺ and Fe³⁺ ions migrate through the solid lattice towards the grain boundary forming the iron rich Fe₂O₃ layer [66]. At high temperatures the migration of Fe ions can be suppressed. This can probably be explained by the formation of rutile, as boundaries between rutile and ilmenite allow for a faster diffusion of oxygen. Therefore high temperature treatment of ilmenite in an oxidative atmosphere can help avoiding the formation of an iron hull at the particle surface which could lead to agglomeration during CLC operation.

2.5.3 Ilmenite Activation

When performing several reduction-oxidation (redox) cycles on ilmenite two phenomena can be observed:

1. There is a gain of reactivity in reduction as well as in oxidation with the number of cycles. The maximum reactivity is achieved after an activation period of several cycles and also depends on the type of fuel gas (as the reduction degree varies for different gases).

2. The oxygen transport capacity decreases with increasing number of oxidation/reduction cycles.

Both phenomena can be explained via the segregation process: With each redox cycle performed, the iron rich layer at the grain boundary grows while the core is depleted in iron; simultaneously the formation of pseudobrookite (Fe₂TiO₅) is prevented, because the oxygen cannot reach the lower layer. Thus with increasing number of cycles the fraction of free Fe₂O₃ rises at the expense of Fe₂TiO₅. As the reduction of free Fe₂O₃ to Fe₃O₄ allows transporting less oxygen (3.3 %) than reduction of Fe₂TiO₅ to FeTiO₃ + Fe₂TiO₄ (6.7 %), the oxygen transport capacity decreases from e.g. initially 4% to 2.1 % for H₂ as reducing gas [28].

2.5.4 Ni Oxidation

In the air reactor Ni is oxidized in a strongly exothermic reaction to NiO:

$$Ni + \frac{1}{2}O_2 \rightarrow NiO$$
 $\Delta H_f = -244,3 \text{ kJ/mol}$ (R6)

It is well known that NiO like many other transition metal oxides form a non-stoichiometric compound, meaning that the Ni:O ratio deviates from 1:1. Therefore the sum formula of the oxide should be better written as Ni_{1-y} O whereby the ratio between oxygen and metal differs from 1 (with 0,999 < 1-y < 1,000).

2.6 Fuel Reactor Reactions

Reactions in the fuel reactor are taking place under reducing conditions due to the absence of air and the presence of fuel. The fuel reactor reactions, among others, are the oxidation of the fuel to CO_2 and H_2O and the reduction of the metal oxide (see (R2a) and (R2b)).

2.6.1 Ilmenite Reactions

During reduction of oxidized ilmenite the oxygen is transferred from the carrier to the fuel gas. As already discussed above, oxidized ilmenite can be described as a mixture of Fe_2TiO_5 , Fe_2O_3 and TiO_2 . It shall be noted that magnetite (Fe_3O_4) can be considered as a mixture of Fe_2O_3 and FeO. Therefore the reduction of hematite to magnetite is assumed to be due to the reduction of 1/3 of the iron contained in hematite to FeO while the remaining 2/3 of iron are not reduced. In principle the reduction process consists of two stages on from Fe^{3+} to Fe^{2+} and the second one from Fe^{2+} to Fe^{0} . Whereas the first one is desired in the fuel reactor, the second one is not, because it leads to the formation of metallic iron particles which have a tendency to agglomerate.

Reactions with CH4

For the reduction using methane CH₄, the overall reactions can be formulated as [27]:

$$4 \operatorname{Fe_2TiO_5} + 4 \operatorname{TiO_2} + \operatorname{CH_4} \rightarrow 8 \operatorname{FeTiO_3} + \operatorname{CO_2} + 2 \operatorname{H_2O}$$
(R7)

 $12 \text{ Fe}_2\text{O}_3 + \text{CH}_4 \rightarrow 8 \text{ Fe}_3\text{O}_4 + \text{CO}_2 + 2 \text{ H}_2\text{O}$ (R8)

Thus a mixture of Fe₃O₄ (magnetite) and FeTiO₃ is formed.

Reactions with Syngas

Using syngas (a 1:1 mixture of CO and H_2) as reducing agent the overall reaction oxidized ilmenite (Pseudobrookite) can be formulated according to

$$Fe_2TiO_5 + TiO_2 + CO \rightarrow 2 FeTiO_3 + CO_2$$
 (R9)

$$Fe_2TiO_5 + TiO_2 + H_2 \rightarrow 2 FeTiO_3 + H_2O$$
(R10)

Similarly hematite can react with syngas

$$3 \operatorname{Fe}_2 \operatorname{O}_3 + \operatorname{CO} \to 2 \operatorname{Fe}_3 \operatorname{O}_4 + \operatorname{CO}_2 \tag{R11}$$

$$3 \operatorname{Fe}_2 \operatorname{O}_3 + \operatorname{H}_2 \to 2 \operatorname{Fe}_3 \operatorname{O}_4 + \operatorname{H}_2 \operatorname{O}$$
(R12)

The final products of all those reactions are FeTiO₃, Fe₃O₄, CO₂ and H₂O.

In an alternative reaction path Fe^{3+} is reduced to metallic Fe^{0} and CO_{2} and $H_{2}O$ are formed [22]:

$$Fe_2O_3 + 3 CO \rightarrow 2 Fe + 3 CO_2$$
 (R13)

$$Fe_2O_3 + 3 H_2 \rightarrow 2 Fe + 3 H_2O \tag{R14}$$

Reduction mechanisms for ilmenite can be formulated according to Sun et al. as [67]:

$$\begin{array}{ll} \text{FeTiO}_3 + \text{ CO} \rightarrow \text{Fe} + \text{ CO}_2 + \text{TiO}_2 & (\text{R15}) \\ \text{FeTiO}_3 + \text{ H}_2 \rightarrow \text{Fe} + \text{ H}_2 \text{O} + \text{TiO}_2 & (\text{R16}) \end{array}$$

The reduction to metallic iron will most probably not take place at the prevailing CO/CO_2 ratios (H₂/H₂O ratios respectively) in the fuel reactor, otherwise aggregation would be observed. A more detailed investigation from thermodynamic point of view is presented in Subsection 4.3.8

Reactions with H₂

Oxidized ilmenite (Pseudobrookite) reacts with H₂ according to

$$Fe_2TiO_5 + 3H_2 \rightarrow 2 Fe + TiO_2 + 3H_2O$$
(R17)

The formation of metallic iron according to the above mechanism was indeed observed. Sun et al. [67] who investigated the reduction of ilmenite pellets with hydrogen, found - after pre-oxidation at 1073 K and 1273 K - an enhanced reaction rate for following reduction step which goes as far as to Fe^0 in pure H₂ which is equivalent to a H₂/H₂O ratio of infinity.

Reactions with CO

Similarly the reduction of pseudobrookite with CO can be formulated as

$$Fe_2TiO_5 + TiO_2 + CO \rightarrow 2 FeTiO_3 + CO_2$$
 (R18)

Evidence for the occurrence of this reaction was found by Itoh and Kikuchi [68], who investigated the reduction kinetics of natural ilmenite ores with CO.

2.6.2 Fuel Decomposition Reactions

In addition to the reduction reactions of the oxidized ilmenite components the oxidation reactions of the fuel (e.g. CH_4) are taking place. The fuel oxidation is not a classical combustion reaction because it is a heterogeneous gas/solid reaction. The oxygen is being released by the oxygen carrier and exists in atomic or ionic form at the solid surface. In contrast to a classical combustion, atomic oxygen is present on the solids surface. When methane is used as a fuel, the CH_4 molecule can be activated thermally to produce a CH_3 radical which then reacts via several steps to CO and CO_2 :

$$CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow CO \rightarrow CO_2$$
 (R19)

A lot of other reactions are most probably taking place in the gas phase of the fuel reactor, influencing the number of species available for reaction. One very likely to occur is the endothermic *steam reforming reaction* which leads to the production of CO and H₂ and is favored by high temperatures (R20). The H₂O necessary for this reaction is introduced into the system via the loop seals fluidized with steam as well as from reactions (R7), (R10), R(12), (R14), (R16) and is also formed via the combustion reaction of CH_4/H_2 (R2a):

$$CH_4 + H_2O \leftrightarrow CO + 3 H_2$$
 $\Delta H_R = +206, 2 \text{ kJ/mol}$ (R20)

A second reaction is the *watergas-shift reaction* which leads to the production of CO_2 and H_2 (R21). As this reaction is slightly exothermic, high temperatures (900-950°C in the fuel reactor) will shift the equilibrium towards CO and H_2O . It is catalyzed by transition metal oxides such as Fe₂O₃:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 $\Delta H_R = -41,2 \text{ kJ/mol}$ (R21)

Depending on the fraction of H₂O present and the temperature two further reactions in principle are likely to occur. One is the endothermic *methane pyrolysis* through which carbon is formed (for $T > 600^{\circ}$ C), which is deposited at the (ilmenite) particles.

$$CH_4 \leftrightarrow 2 H_2 + C_{(S)}$$
 $\Delta H_R = 74.8 \text{ kJ/mol}$ (R22)

The other is the exothermic *Boudouard reaction* by which solid carbon could be formed and deposited for temperatures below 600°C:

$$2 \text{ CO} \leftrightarrow \text{CO}_2 + \text{C}_{(S)}$$
 $\Delta H_R = -173,3 \text{ kJ/mol}$ (R23)

The deposited carbon can react with the H₂O steam present in the fuel reactor according to

$$C_{(s)} + H_2O \leftrightarrow CO + H_2 \tag{R24}$$

Thus, at the (high) temperatures in the fuel reactor all deposited carbon is expected to be transferred to CO and H_2 . However, these two gases can react with ilmenite finally forming CO₂ and H_2O (see (R9)-(R18)).

2.6.3 Ni Reduction

Reduction with CH4

Under the conditions in the fuel reactor NiO should be reduced to metallic Ni⁰:

 $4 \operatorname{NiO} + \operatorname{CH}_4 \rightarrow 4 \operatorname{Ni} + 2 \operatorname{H}_2 \operatorname{O} + \operatorname{CO}_2$ (R25)

Inspection of the oxidation potential in Figure 10 leads to the conclusion that the reduction of Fe^{3+} to Fe^{2+} should in principle be favoured in comparison to the reduction of NiO. This means that the reduction of hematite and ilmenite to magnetite and of pseudobrookite to ilmenite (according to (R10), (R11) and (R18)-(R21)) should have precedence over the reduction of NiO. Only if most of the Fe^{3+} is reduced the reduction of NiO should start.

Also the partial oxidation of methane may occur, resulting in CO and H₂ generation:

$$NiO + CH_4 \rightarrow Ni + 2 H_2 + CO \tag{R26}$$

It shall also be mentioned that the steam reforming (R20) and the CO shift reaction (R21) are strongly catalysed by metallic Ni.

Reduction with CO, H₂

 $NiO + H_2 \rightarrow Ni + H_2O$

NiO can undergo reduction reactions also with CO and H₂ forming metallic Ni:

$NiO + CO \rightarrow Ni + CO_2$	(R27)

(R28)

2.7 Fluidized Beds

2.7.1 Fluidization Regimes

If a fluid is streaming through a bed of particles, different states of fluidization can be observed depending on the fluid velocity and particle properties as depicted in Figure 12 below.



Figure 12: Various fluidization states (Source: [69])

At low gas velocity the gas merely percolates through the void spaces of the stationary particles and we have a fixed bed. With increasing velocity the particles move apart and the bed is expanded. Velocities which characterise different fluidization regimes can be depicted in a diagram depicting pressure drop versus gas velocity (See Figure 13 below). Until the *minimum fluidization velocity* U_{mf} is reached the pressure drop increases proportional to the gas velocity. From this point on the bed does not expand much beyond its volume at minimum fluidization, but at a certain point agitation becomes more violent and bubbles form at the *minimum bubbling velocity* U_{mb} . At larger velocities slugging and entrainment of particles occurs.



Figure 13: Pressure drop diagram (Source: [69])

2.7.2 Fluid Mechanics

The flow of the fluid occurs through long and thin tortuous passages of varying cross section, so called capillary tubes or channels, each with a certain diameter D, where it experiences a pressure drop. The problem how to calculate the drop as a function of the layer thickness was tackled first by Kozeny and later by Karman, who derived an equation which is valid for the case of laminar flow through the channels (Re < 1):

$$\frac{\Delta p}{H} = 180 \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} \cdot \frac{\mu_G \cdot U}{(\varphi_P \cdot d_P)^2} \tag{1}$$

This equation which only takes into account the pressure drop (energy loss) due to viscosity of the fluid was expanded by Ergun [70] for Re > 1 by adding a term that takes into account also the energy losses due to turbulences:

$$\frac{\Delta p}{H} = 150 \cdot \frac{(1-\varepsilon)^2}{\varepsilon^3} \cdot \frac{\mu_G \cdot U}{(\varphi_P \cdot d_P)^2} + 1.75 \cdot \frac{1-\varepsilon}{\varepsilon^3} \cdot \frac{\rho_G \cdot U^2}{\varphi_P \cdot d_P}$$
(2)

With increasing fluid flow rate the particles will be loosened and thus the capillary tubes for the fluid become larger in order to keep the pressure drop. This results in a bed expansion whereby simultaneously the static friction forces between the particles fade. The force which is acting against bed expansion and leads to a pressure drop is the area specific weight of the solids which can be described by:

$$\frac{\Delta p}{H} = (\rho_P - \rho_G) \cdot (1 - \varepsilon) \cdot g \tag{3}$$

At a certain point, the onset of fluidization (where $U = U_{mf}$), the pressure drop due to bed expansion matches the pressure drop due to the area-specific weight of the solids:

$$\frac{\rho_G \cdot (\rho_P - \rho_G) \cdot (\varphi_P \cdot d_P)^3 \cdot g}{\mu_G^2} = 150 \cdot \frac{1 - \varepsilon}{\varepsilon^3} \cdot \frac{U_{mf} \cdot \varphi_P \cdot d_P \cdot \rho_G}{\mu_G} + \frac{1.75}{\varepsilon^3} \cdot \frac{U_{mf}^2 \cdot (\varphi_P \cdot d_P)^2 \cdot \rho_G^2}{\mu_G^2}$$
(4)

By introducing the Archimedes number and the particle specific Reynolds number

$$\operatorname{Ar} = \frac{\rho_G \cdot (\rho_P - \rho_G) \cdot d_P^3 \cdot g}{\mu_G^2}$$
(5)

$$\operatorname{Re}_{\mathrm{P}} = \frac{U_{mf} \cdot d_{P} \cdot \rho_{G}}{\mu_{G}}$$
(6)

Equation (4) can be simplified to

$$\frac{1.75}{\varepsilon^3 \cdot \varphi_P} \cdot \operatorname{Re}_P^2 + 150 \cdot \frac{1 - \varepsilon}{\varepsilon^3 \cdot \varphi_P^2} \cdot \operatorname{Re}_P - \operatorname{Ar} = 0$$
(7)

By defining

$$K_1 = \frac{1.75}{\varepsilon^3 \cdot \varphi_P}$$
 and $K_2 = 150 \cdot \frac{1 - \varepsilon}{\varepsilon^3 \cdot \varphi_P^2}$ (8)

Equation (4) can be written as

$$K_1 \cdot \operatorname{Re}_{P}^2 + K_2 \cdot \operatorname{Re}_{P} - \operatorname{Ar} = 0 \tag{9}$$

Wen and Yu [71] were the first to notice that K₁ and K₂ had the same values for different kinds of particles over a wide range of conditions (0,001 < Re < 4000). Since then several investigators have proposed values for the two constants K₁ and K₂ based on experimental data for φ_P and ε at the onset of fluidization i.e. minimum fluidizing conditions (see e.g. [69]). Taking these values for the constants the quadratic equation (7) can be solved to yield a relationship between the Reynolds number and the Archimedes number. From this relation it follows that Re_{p, mf} (and therefore the *minimum fluidization velocity U_{mf}*) is a function of Ar, which is only dependent on particle and fluid properties:

Grace:
$$\operatorname{Re}_{P,mf} = \sqrt{27,2^2 + 0,0408 \cdot \operatorname{Ar} - 27,2}$$
 (10a)

Wen/Yu:
$$\operatorname{Re}_{P,mf} = \sqrt{33,7^2 + 0,0408 \cdot \operatorname{Ar} - 33,7}$$
 (10b)

Besides the *minimum fluidization velocity* U_{mf} the so-called *terminal velocity* u_t plays an important role in the description of fluidized beds. It can be estimated from the model of a (spherical) particle of size d_p falling through fluid. In this case gravitation, friction, uplift and acceleration have to be in balance:

$$\frac{\pi}{6} \cdot (\rho_P - \rho_G) \cdot d_P^{-3} \cdot g - C_w \cdot A_p \frac{u_t^2 \cdot \rho_G}{2} = \frac{\pi}{6} \cdot d_p^3 \cdot \rho_p \cdot \frac{du_t}{dt}$$
(11)

In the case of a floating particle the acceleration term can be set to zero and with the projection area of the particle normal to the direction of the flow assumed as

$$A_p = \frac{d_p^2 \pi}{4} \tag{12}$$

the terminal velocity U_t can be expressed as

$$U_t = \sqrt{\frac{4}{3} \cdot \frac{\rho_P - \rho_G}{\rho_G} \cdot \frac{d_P \cdot g}{C_W}}$$
(13)

where C_w is (an experimentally determined) drag coefficient. In dimensionless form this equation can be written as

$$\operatorname{Re}_{P,t}^{2} = \frac{4}{3} \cdot \operatorname{Ar} \cdot \frac{1}{C_{W}}$$
(14)
Using equations (5), (6) and (14) a dimensionless particle size d_p^* and a dimensionless velocity U^{*} can be defined as

$$\operatorname{Ar}^{\frac{1}{3}} = d_{p} \cdot \left(\frac{\rho_{G} \cdot (\rho_{P} - \rho_{G}) \cdot g}{\mu_{G}^{2}}\right)^{\frac{1}{3}} = \left(\frac{3}{4}\operatorname{Re}_{p}^{2} C_{w}\right)^{\frac{1}{3}} = d_{p}^{*}$$
(15)

$$\frac{\operatorname{Re}_{p}}{Ar^{\frac{1}{3}}} = U \cdot \left(\frac{\rho_{G}^{2}}{\mu_{G}^{2}(\rho_{p} - \rho_{G}) \cdot g}\right)^{\frac{1}{3}} = \left(\frac{4}{3} \frac{\operatorname{Re}_{p}}{C_{w}}\right)^{\frac{1}{3}} = U^{*}$$
(16)

Looking at these equations it can be expected that a diagram where one axis which is independent of the particle size is plotted against the other axis which is independent of the particle velocity might be most useful for mapping the different fluidization regimes and for practical applications.

2.7.3 Particle Properties

In gas/solid fluidized beds different flow conditions occur depending on the properties of the particles, the gas and the gas velocity. In order to categorize bulk materials with respect to their fluidization, Geldart has introduced a classification system, which allows to group bulk materials into four groups [72]:

Group A: consists of materials having a small mean size and/or a low particle density (less than about 1.4 g/cm3). Particle diameters are between 30 to 100 μ m. Beds of powders in this group expand considerably before bubbling commences. The reason is that they are slightly cohesive. Gross circulation even occurs if only few bubbles are present, resulting in heavy mixing. Materials of this group are of high practical importance and well suited for strongly expanded circulating beds. Typical examples are cracking catalysts.

Group B: Particles in this group are of intermediate size (100-800 μ m) and a density between 1.4 and 4 g/cm3). The cohesive forces between particles are negligible. A homogeneous phase does not exist and bubbling starts at or only slightly above minimum fluidization velocity. The bed expansion is small and the bed collapses very rapidly, when the gas supply is cut off. There is little or no powder circulation in the absence of bubbles. Sands are typical examples of this group.

Group C: Powders in this group are very fine (particle size $\leq 20 \ \mu$ m) and very cohesive. Fluidization of powders of this group is extremely difficult, because the inter-particle forces are greater than the forces which the fluid can exert. The material tends to build channels or plugs and the gas passes up voids extending from the distributor to the bed surface. Particle mixing and consequently heat transfer between surface and bed are much poorer than for particles of Group A or B. Fluidization is possible by using mechanical stirrers or vibrators.

Group D: Coarse particles ($d_p \ge 1$ mm) and particles with high density fit into this group. The regime is spouting and solids' mixing is rather poor. Typical examples are corn and coffee beans.

The boundaries between the different groups can be depicted in a plot $\Delta p=p_s-p_g$ vs. d_p as in Figure 14.



Figure 14: Geldart classification of particles (Source: [69])

One of the limitations of Geldart's classification is that it is not applicable for elevated pressure and temperature and for beds fluidized by media other than air. There are ample evidences reported in the literature indicating that normally Geldart Group B powders at ambient conditions, such as polymer particles, can behave like a Group A powder under polymerization conditions at elevated pressure and moderate temperature with substantial emulsion-phase expansion, relatively small bubbles, smooth fluidization, and reduced gas bypassing. When plotting the dimensionless density, $(\rho_p - \rho_f)/\rho_f$, against the Archimedes number Ar, a modified Geldart chart emerges. This chart allows to successfully demarcate the boundary between the Group A and to successfully transform the normally Geldart Group B particles at ambient conditions to Group A classification when fluidized at elevated pressure and temperature [73]. However, for the present mixed oxides carrier these modifications do not make any changes, as operation takes place at normal pressure and the dimensionless densities are $(\rho_p - \rho_f)/\rho_f \ge 2000$. Calculating the modified A-B boundary by use of Yang's equation [73] yields values of Ar < 40.

2.7.4 Mapping of fluidized Bed Regimes

Different regime maps exist for classifying the different fluidization regimes. The most important are the regime maps by Reh [74] (Figure 15 left) and by Bi and Grace [75] (Figure 15 right).



Figure 15: Regime maps (Sources: left: [74]; right [69])

Whereas Grace uses the plot of the dimensionless velocity vs. the dimensionless particle size, Reh uses a plot of the particle specific Froude number vs. the particle specific Reynolds number.

$$Fr_{P} = Fr \cdot \frac{D}{d_{P}} = \frac{U^{2}}{g \cdot d_{P}}$$
(17)

It can however be shown that both approaches are equivalent. As d_p^* is proportional to the actual particle diameter d_p the boundaries between the Geldart groups C-A, A-B and B-D appear as vertical lines in the Grace diagram.

3 Experimental and Data Collection

3.1 Description of CLC Pilot Plant at Vienna University of Technology

3.1.1 Design of the Pilot Plant

The pilot plant was designed as a dual circulating fluidized bed (DCFB): It consists of two reactors, an air reactor and a fuel reactor, which are interconnected by two loop seals, the upper and the lower loop seal. In order to enable solids circulation, fluidization of the reactors is necessary. The air reactor is fluidized with air, while the fuel reactor is fluidized by the gaseous fuel (in our experimental campaign natural gas or syngas). The loop seals are fluidized by steam to avoid dilution of the fuel reactor exhaust. The fuel reactor incorporates his own inner solids circulation loop with a steam fluidized loop seal, the internal loop seal. Therefore we can distinguish between two solids circulation loops; the global solids circulation loop and the internal solids circulation loop. One important feature of the DCFB system is that direct hydraulic communication of the two circulation and results in a stable solids distribution in the system. Further details and benefits of the DCFB system have been described in [76]. A sketch of the DCFB pilot plant is given in Figure 16.



Figure 16: DCFB Scheme (from [24])

The fluidizing air stream to the air reactor is provided by a compressor. Also gas fuels (such as methane or propane) can be added as additional heat input to the air reactor via a support fluidization port in the inclined part of the LLS. Additional heat input to the air reactor can also be provided via an air pre-heater, which allows for air temperatures of up to 400°C. This is necessary for start-up and can be used to influence the reactor temperature at the operating

points. If during start-up the heat provided by the pre-heater is insufficient, a burner with a fuel power of up to 40 kW attached to the fuel reactor can be used for additional heating.

Both exhaust gas streams are cooled in heat exchangers separately, thereafter gas samples are taken and sent to gas analysers. The exhaust gases are then mixed in the fire tube boiler, where remaining fuel components are combusted by use of a natural gas support flame. After filtration in a bag filter this gas is sent to a chimney.

In order to allow comfortable and secure operation a programmable logic controller (PLC) is installed which collects all measured parameters from the plant and allows visualization of the operating states.

3.1.2 Operating Range

Table 3 provides an overview on the design and operating data of the pilot plant. The air reactor is designed as riser and is operated in fast fluidization regime, while the fuel reactors is running as high velocity bubbling fluidized bed or also in turbulent mode.

Parameter	Unit	Air reactor	Fuel reactor
Reactor inner diameter	[m]	0.15	0.159
Reactor height	[m]	4.1	3.0
Height of primary gas inlet	[m]	0.025	0.06
Height of secondary gas inlet	[m]	1.325	N/A
Inlet gas flow	[Nm ³ /h]	138	12
Outlet gas flow	[Nm ³ /h]	113.9	35.9
Temperature in reactor	[K]	1213	1123
Design fluid for calculation	[-]	depleted air	$H_2O/CO_2 = 2/1$
Mean particle size	[mm]	0.12	0.12
Particle apparent density	[kg/m3]	3200	3200
Particle sphericity	[-]	0.99	0.99
Archimedes number	[-]	7.55	9.13
Superficial velocity	[m/s]	7.32	2.08
Ratio U/U _{mf}	[-]	1280.4	315.4
Ratio U/u _t	[-]	15.5	3.8
Fuel power (natural gas)	[kW]	-	120
Lower heating value of fuel	[MJ/kg]	-	48.8
Design air/fuel ratio	[-]		1.2

Table 3: DCFB geometry and design data (from [76])

3.1.3 Solid Sampling, Insertion and Treatment

To obtain *solid samples* from the DCFB plant a device is used, which allows online sampling during the test runs under hot conditions. This device and its operation has been described in detail in [24]. Solid samples are taken as soon as the (fuel reactor) temperature is sufficiently constant (\pm 5°C) over a certain period of time. The solid samples taken via separate devices from the upper loop seal (ULS) and the lower loop seal (LLS) respectively are cooled in an

inert atmosphere of argon, by dipping the solids container into cold water. After cooling to room temperature the device is opened and the solids are transferred quickly to plastic containers, which are kept sealed until further analysis.

For solids insertion an existing large pneumatic handling device is used and (especially for insertion of small amounts of Ni-carrier) a separate smaller device has been constructed, allowing insertion of masses of Ni-carrier mixtures up to approximately 0.9 kg at once (see Figure 17). This has been necessary to be able to insert also small amounts of oxygen carrier in a safe way.



Figure 17: Device for (small) mass insertion

The device shown in Figure 17 works in the following way: At the three connections of the device there are three valves, denoted as V-1, V-2 and V-3. Attached to V-3 is a filter F-1, in order to avoid loss of solids (Ni-carrier and/or ilmenite) during hot injection. When material is to be introduced, the device is put upright, such that V-1 is on top. Then V-1 is opened, V-2 and V-3 are closed and the material is filled in through the upright end. After the device has been filled, V-1 is closed and the device is turned over. Before inserting the material to the reactor the air contained in the device must be substituted by N₂. For this purpose the valves V-2 and V-3 are opened, V-2 is connected via flexible pressure tubing to a pressure cylinder filled with N₂ and the device is put under slightly over-pressurized. While still connected the whole device is then mounted with the connection close to V-1 to a "solids injection port" which ends in the fuel reactor. For insertion V-1 is opened and the material still contained in the device is carried (by gravity and the excess pressure) to the reactor. Traces of material still contained in the device can be also flushed to the reactor by opening V-2 flushing with N₂.

3.2 Experimental Campaigns

Three experimental campaigns have been performed, whereby the important operational parameters (i.e. fuel, temperatures T, fuel power P and air/fuel ratio λ) have been varied. By

combining these parameters with the different mixtures a set of 51 operation points are obtained. An operation point can be characterized by a fuel reactor temperature value, which is kept constant over a certain period of time with the purpose to enable measurements. In order to achieve temperature variations below $\mp 5^{\circ}$ C additional energy supply to the air reactor via the air-preheater or via fuel addition may be necessary. A description of operation points, parameters and results can be found in Subsection 4.2.

- Ilmenite benchmark (MOEXC1) is performed using ilmenite as oxygen carrier in order to get specific performance reference values.
- Mixed oxides experimental campaign 2 (MOEXC2) was performed using ilmenite and Ni-carrier, whereby the mass fraction of Ni-carrier was increased from operation point to operation point up to 1.8 % w/w.
- Mixed oxides experimental campaign 3 (MOEXC3) was performed using ilmenite and Ni-carrier, whereby the mass fraction of Ni-carrier was planned to be increased from 1.8 % up to 22.3 % w/w.

Table 4 below provides an overview on the bed material mixtures as planned for the experimental campaigns. The second column provides the (planned) mixture compositions and the third and fourth column provide the corresponding masses of ilmenite and Ni-carrier, whereby for simplicity a constant total inventory of 85 kg has always been assumed.

Bed material mixture	Composition	Ilmenite [kg]	Ni19yAl ₂ O ₃ [kg]
M0	Ilmenite	85.00	0.00
M1	Ilmenite+0.1 wt% Ni19γAl ₂ O ₃	84.92	0.09
M2	Ilmenite+0.3 wt% Ni19 γ Al ₂ O ₃	84.75	0.26
M3	Ilmenite+0.7 wt% Ni19γAl ₂ O ₃	84.41	0.60
M4	Ilmenite+1.8 wt% Ni19γAl ₂ O ₃	83.47	1.53
M5	Ilmenite+4.3 wt% Ni19γAl ₂ O ₃	81.35	3.66
M6	Ilmenite+8.7 wt% Ni19γAl ₂ O ₃	77.61	7.40
M7	Ilmenite+12.0 wt% Ni19γAl ₂ O ₃	74.80	10.20
M8	Ilmenite+20.0 wt% Ni19γAl ₂ O ₃	68.00	17.00

Table 4: Planned bed material mixtures for the experimental campaigns

Table 5 below contains further operation parameters such as air/fuel ratio, fuel reactor temperatures, fuel composition and fuel reactor power values selected.

Operation Parameter	Unit	Value(s)
Air/fuel ratio λ	[.]	0.5, 0.7, 1.0, 1,1 and 1.2
Fuel reactor temperature $T_{\rm FR}$	[°C]	910; 960
Fuels	[-]	Syngas (CO: $H_2 = 1:1$)
		Natural gas
Fuel reactor power P	[kW]	60-120
Total active inventory	[kg]	25-40

3.3 Data Collection and Evaluation

As already mentioned above, data for analysis can be obtained from the pilot plant directly or are obtained indirectly after evaluation via IPSEpro simulation program. A scheme of measurement data collection and evaluation, indicating the most important steps and data is shown in Figure 18 below. More details about the data collection performed will be presented in the Subsections below. The data analysis will be presented in the following section.



Figure 18: Scheme of Data Collection and Evaluation

3.3.1 Gas Analysis

Gas samples obtained from the exhaust gas streams leaving the pilot plant are continuously analysed using a Rosemount NGA2000 multicomponent online gas analysator (ref to [77]). The analysis comprises three gas streams, the air reactor flue gas (AR_{fg}), the fuel reactor product gas (FR_{pg}) and the fire tube boiler off gas (FTB_{og}). Gas samples of all streams are taken after the heat exchangers, which allow transporting them in PTFE tubes instead of stainless steel tubes. The sample gases are heated to 200°C and are transported via the heated PTFE tubes to a gas preparation station in order to avoid condensation. Within the unit the gas samples are cooled to 4°C in order to ensure proper gas analysis, while the condensates are collected in three separate vessels. The gas streams are transported to the online gas analysers, where the AR_{fg} and FR_{pg} are analysed. In the AR_{fg} CO, CO₂ and O₂ are analysed (CO: 0100%, CO₂: 0-100% and O₂: 0-25%) while in the FR_{pg} the following gases are analysed: CO: 0-100%, CO₂: 0-100%, O₂: 0-25%, H₂: 0-100%, CH₄: 0-100%. These values are sent to the PLS system, integrated for visualisation and logged into a data file for further reference.

The fraction of gases like CO, CO_2 is measured via NDIR (non dispersive infrared radiation) whereby the IR radiation is generated by a heating coil in the light source (1). Then the radiation passes through the chopper wheel [light chopper wheel (3)] and through a filter cell (5). By chopping the thermal background can be offset from the desired signal. The radiation alternatively reaches the measuring side (8) and reference side (9) of the analysis cell [(7) separated in the middle into two halves by an internal separating wall] with equal intensity. The filter cell (5) screens interfering radiation areas out of the radiation spectrum. Behind this analysis cell the radiation passes a second filter cell (10) towards the gas detector (12), which compares the IR radiation intensities from measuring side and reference side and converts them into an AC voltage signal. The gas - specific wavelengths of the absorption bands characterize the type of gas while the strength of the absorption gives a measure of the concentration of the component measured. Due to a rotation chopper wheel, the radiation intensities coming from measuring and reference side of the analysis cell produce periodically changing signals within the detector. The absorption measurement in the UV spectral range uses the same principle as the IR measurement. A glow-discharge lamp [2] is used as radiation source. The UV radiation passes through the chopper [3] and a filter cell [6] into the dual-section analysis cell [7]. A second filter cell [6] is installed after the analysis cell. The photodetector [13], which follows, converts the pulsating radiation intensities from measuring [8] and reference side [9] of the analysis cell into electrical voltages. A scheme of the measurement principle is depicted in Figure 19 below (ref to [77]).

 O_2 is measured utilizing its paramagnetic properties. Inside a cell two nitrogen filled quartz spheres (N₂ is not paramagnetic) are arranged in a dumbbell configuration and placed, hinged to a platinum wire. A small mirror fixed to the wire reflects a light beam to a photo detector. The measuring cell is placed inside an inhomogeneous magnetic field generated by a strong permanent magnet. Due to their paramagnetic characteristics oxygen molecules within the sample gas are deflected into the area of highest field strength. This generates different forces on both spheres and the resulting torque turns dumbbell and mirror out of the rest position. Thus a photodetector signal is generated, because the beam is deflected, too. The measurement principle is depicted in Figure 20.



Figure 19: Measurement Principle for NDIR/UV measurement (from [77])



To measure gases like *Hydrogen* (H_2), *Argon* (*Ar*) or *Helium* (*He*), typically thermal conductivity (TC) sensors are used. The measurement principle through use of a Wheatstone bridge and the sensor cell are displayed in Figure 21 below.





Figure 21: Measurement principle and sensor cell of a thermal conductivity sensor from [77]

Four sensors are organized in a Wheatstone bridge. Their temperatures and their electrical resistances are dependent upon heat losses, which, in turn, result from heat transport in the surrounding gas to colder chamber walls. This heat transport is proportional to the thermal conductivity of the gas present between the sensor and the chamber wall. Initially the whole measurement cell with all sensors is thermostated to 75°C to minimize the influence of external temperature changes. If the temperatures and thus the resistances change, a signal is generated proportional to component concentration.

3.3.2 Particle Analysis

Particle Probe Preparation and Determination of Solids Conversion

A small amount of substance from each ULS or LLS are taken and transferred to a drying chamber, where it is dried at 100°C for 10 hours. The weight change (water loss by drying and slight oxidation in case of e.g. Ni containing substances) is determined. Afterwards the substance is transferred to a muffle furnace, where it is treated (oxidized) at 950°C for 12 hours. Then the probes are cooled to room temperature and the weight change is determined again. The complete weight increase by oxidation allows the determination of the corresponding *Xs* values which are input for the mass and energy balances.

The Xs value (18) identifies the conversion level of solids e.g. for oxidation processes. It is defined based on extensive quantities and is the ratio between the mass of oxygen on the oxygen carrier relative to the maximum possible mass of oxygen to be carried by the oxygen carrier:

$$X_{s,ox} = \frac{m - m_{red}}{m_{ox} - m_{red}}$$
(18)

Here m is the instantaneous mass, m_{red} and m_{ox} are the masses of the fully reduced and fully oxidized oxygen carrier, respectively.



Figure 22: Mass distribution of an oxygen carrier

The mass of the fully oxidized carrier can be determined by taking probes from the samples, oxidizing them in the muffle oven at 950°C for 10 h and determining the weight increase. For the case of the redox system Fe_2O_3/FeO , the fully reduced mass can be determined by:

$$m_{oxides} = m_{ox} \cdot w_{ox} \tag{19}$$

$$m_{oxides_red} = m_{oxides} \cdot \frac{2 \cdot M_{FeO}}{M_{FeO_3}}$$
(20)

And thus it follows that

$$m_{red} = m_{ox} - (m_{oxides} - m_{oxides_red}) = m_{ox} \cdot \left\{ 1 + w_{ox} \cdot \left(\frac{2 \cdot M_{FeO}}{M_{Fe_2O_3}} - 1 \right) \right\}$$
(21)

After the X_s values for the operation point sample probes taken near ULS and LLS have been calculated, the ΔX_s values can be calculated as an input for the IPSEpro model (see Table 6).

It shall be noted that for calculating the *Xs* values the whole weight increase of a sample probe (due to drying and due to treatment in the muffle furnace) is taken, whereby it is assumed that the increase is exclusively due to oxidation of (reduced) Ni and formation of hematite (Fe₂O₃) from Fe and FeO (in FeTiO₃) The formation of Fe₃O₄ and/or or the respective high temperature modifications of ilmenite such as pseudobrookite Fe₂TiO₅ from FeTiO₃ are not explicitly taken into account, but implicitly via the formation of hematite (Fe₂O₃). All mass fractions of the oxides contained in the oxygen carrier mixtures are determined from the values of the element composition gained from the XRF spectra analysis.

Typical values of the oxide contents and the *Xs* values for the different operating points can be seen in Table 6. The following important facts shall be noted:

- The X_s values for all operating points are high close to 1 indicating a high conversion level, while the ΔX_s values are low indicating low oxygen carrier utilization.
- Since the IPSEpro Model in the current version allows only a single redox system for solving the balances, the NiO mass fraction was taken into account as an increased Fe₂O₃ (hematite) content in the redox system. This is justified by the fact that although ilmenite contains traces of other oxides they do not contribute to the oxygen carrier capacity. Moreover with increasing Ni-carrier mass fraction only the concentration of Al and Ni rises, while it remains constant for other elements or even slightly decreases due to "dilution" by the Ni-carrier as in the case Fe or Ti (see Figure 31 and Figure 32). Al₂O₃ or TiO₂ however do not contribute to the oxygen carrier capacity, since they cannot be reduced under the conditions in the fuel reactor. The other oxides have a low mass fraction (see Table 6 below). Therefore all oxides except Fe₂O₃ and NiO are regarded as inert masses with respect to oxygen carrier transport capacity in the IPSEpro Model. Equation (21) above is therefore modified to

$$m_{red} = m_{ox} \cdot \left\{ 1 + w_{ox,Ni} \cdot \left(\frac{M_{Ni}}{M_{NiO}} - 1 \right) + w_{ox,Fe} \cdot \left(\frac{2 \cdot M_{FeO}}{M_{Fe_2O_3}} - 1 \right) \right\}$$
(22)

• In general further oxides could be taken into account by using the general form of equation (23) below. Anyhow, this is not always meaningful, because the share of oxidation of the reactants is usually not known.

$$m_{red} = m_{ox} - (m_{oxides} - m_{oxides_red}) = m_{ox} \cdot \left\{ 1 + \sum_{i} w_{ox,i} \cdot \left(\frac{v_i \cdot M_{red,i}}{M_{ox,i}} - 1 \right) \right\}$$
(23)

 Table 6: Typical input file for IPSEpro Model (from MOEXC1)

	Ilm	opPt2.1	opPt2.2	opPt2.3	opPt2.4	opPt2.5	opPt2.6	opPt2.7	opPt2.8	opPt2.9	opPt2.10	opPt2.11	opPt2.12	opPt2.13	opPt2.14	opPt2.15
Al ₂ O ₃ ¹⁾	1.016	1.016	1.628	1.628	1.628	1.264	1.264	2.096	2.096	2.096	1.862	1.862	1.862	1.862	1.862	2.636
CaO	0.698	0.698	0.815	0.815	0.815	0.468	0.468	0.561	0.561	0.561	0.594	0.594	0.594	0.594	0.594	0.614
CuO	0.036	0.036	0.033	0.033	0.033	0.022	0.022	0.027	0.027	0.027	0.028	0.028	0.028	0.028	0.028	0.027
Fe ₂ O ₃	46.640	46.640	47.029	47.029	47.029	45.929	45.929	45.708	45.708	45.708	48.777	48.777	48.777	48.777	48.777	46.143
K ₂ O	0.211	0.211	0.109	0.109	0.109	0.096	0.096	0.184	0.184	0.184	0.109	0.109	0.109	0.109	0.109	0.112
MgO	3.611	3.611	3.390	3.390	3.390	3.321	3.321	3.589	3.589	3.589	3.470	3.470	3.470	3.470	3.470	3.851
NiO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
P ₂ O ₅	0.033	0.033	0.015	0.015	0.015	0.017	0.017	0.019	0.019	0.019	0.017	0.017	0.017	0.017	0.017	0.022
SO_2	0.050	0.050	0.021	0.021	0.021	0.022	0.022	0.021	0.021	0.021	0.000	0.000	0.000	0.000	0.000	0.003
SiO ₂	4.497	4.497	3.684	3.684	3.684	3.386	3.386	4.193	4.193	4.193	3.539	3.539	3.539	3.539	3.539	5.053
SrO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.005	0.005	0.005	0.005	0.005	0.004
TiO ₂	43.144	43.144	43.118	43.118	43.118	45.331	45.331	43.465	43.465	43.465	41.448	41.448	41.448	41.448	41.448	41.405
ZnO	0.024	0.024	0.025	0.025	0.025	0.019	0.019	0.024	0.024	0.024	0.026	0.026	0.026	0.026	0.026	0.025
ZrO ₂	0.027	0.027	0.046	0.046	0.046	0.041	0.041	0.035	0.035	0.035	0.033	0.033	0.033	0.033	0.033	0.029
Xs-ULS	0.9697	0.9630	0.9606	0.9781	0.9663	0.9619	0.9639	0.9489	0.9556	0.9552	0.9310	0.9409	0.9462	0.9570	0.9597	0.9478
(w Ni)																
Xs-LLS	0.9450	0.9347	0.9361	0.9408	0.9388	0.9397	0.9391	0.9223	0.9103	0.8813	0.9082	0.9224	0.9254	0.9335	0.9316	0.9160
	0.0247	0.0292	0.0245	0.0272	0.0275	0.0222	0.0249	000266	0.0452	0.0720	0.0228	0.0195	0.0200	0.0225	0.0291	0.0219
(w Ni)	0.0247	0.0285	0.0245	0.05/5	0.0275	0.0223	0.0248	000200	0.0433	0.0739	0.0228	0.0185	0.0209	0.0255	0.0281	0.0518

¹⁾ All composition values for the oxides are in wt%.

Particle X-Ray Fluorescence Spectroscopic Analysis

Analysis of the solid raw materials (ilmenite and Ni-Carrier) as well as of the solid samples drawn from the pilot plant during operation was also done using X-ray fluorescence spectroscopy (XRF). This method is based on the principle that materials exposed to short-wavelengths (high energetic) X-rays or gamma rays experience ionization of inner (core) electrons, if the energy of the radiation is greater than the ionization potential of these electrons. When a core electron is removed, a hole is generated in an inner (electronic) orbital. The generated ion usually has an unstable electronic structure (meaning that it's total electronic energy is not minimal). Therefore an electron from an outer orbital "falls" into the inner orbital and energy is released in form of photons. The released energy (or radiation) is characteristic for the atom and proportional to the energy difference of the levels of the two orbitals. The process is shown in Figure 23 below.



Figure 23: XRF Principle ([78])

According to Figure 24 below only a limited number of transitions can take place, whereby the main transitions are given names: L, M \rightarrow K is denoted as K α , K β ; N, M \rightarrow L is denoted as L α , L β ; and so on.



The radiation emitted from the material has the energy characteristics of the atoms (elements) present within the sample. The energy of the peaks allows identification of the elements, while the peak intensity allows identification of the relevant concentration. Usually, since the re-emitted radiation has a lower energy than the radiation absorbed, the term "fluorescence" is used.

The wavelength of this fluorescent radiation can be calculated from Planck's Law (where λ is the wavelength, c is the velocity of light and v is the frequency of light, h is Planck's constant and E is the energy):

$$\lambda = \frac{c}{v} = \frac{hc}{E}$$
(24)

Usually X-ray generators in the 20–60 kV range are used, which allow excitation of a broad range of atoms. The continuous spectrum consists of "bremsstrahlung" radiation: radiation produced when high-energy electrons passing through the tube are progressively decelerated by the material of the tube anode (the "target"). Thus a typical spectrum consists of two parts: the relatively sharp peaks of the fluorescent radiation residing on the broad peak of the "bremsstrahlung" (see Figure 25 below).



The fluorescent radiation can be analysed either by sorting the energies of the photons (energy-dispersive analysis) or by separating the wavelengths of the radiation (wavelengthdispersive analysis). When using *energy dispersive analysis*, the fluorescent X-rays emitted by the material sample are collected by a solid-state detector which produces a "continuous" distribution of pulses, whereby the voltages are proportional to the incoming photon energies. Processing takes place in a multichannel analyser (MCA) which produces an accumulated digital spectrum. A typical XRF analysis reveals a spectrum similar to that in Figure 26.



Figure 26: XRF Energy Disperse Spectrum (taken from [78])

In *wavelength dispersive analysis*, the fluorescent X-rays emitted by the material sample are directed into a diffraction grating monochromator. The diffraction grating used is usually a single crystal (for the spectrum refer to Figure 27).



Figure 27: XRF Wavelength Disperse Spectrum (taken from [81])

A single X-ray wavelength can be selected by varying the angle of incidence on the single crystal. The Bragg condition (equation (25) below) states that incident X-rays produce a constructive interference (peaks of reflected radiation) only if their phase shift is a multiple of 2π . With d being the distance between the atomic layers in the crystal and θ being the angle between the incident ray and the atomic layer this can be formulated as:

$$n \cdot \lambda = 2d \cdot \sin(\theta) \tag{25}$$

The positions of lines (peaks with appropriate energies) provide information about the qualitative composition of the sample. The number of the X-ray quanta is a measure for the concentration of the elements (peak-height or peak-area).

In order to calculate the concentration the net count rates or measured variables derived from it are needed. Several steps are necessary for evaluation of energy dispersive spectra, before the computation of the element concentrations is possible (see also Figure 28):

- 1. Spectrum correction
- 2. Identification of the lines (qualitative analysis)
- 3. Bremsstrahlung computation (background approximation)
- 4. Deconvolution (determination of the net counts without line overlays)
- 5. Computation of the concentrations from the net count numbers (or derived values)



Figure 28: XRF Spectrum Correction (taken from [80])

Systematic and statistic errors are contained in the spectrum correction, bremsstrahlung computation and deconvolution. All three contribute to the total error of the determined measured concentrations. The choice of the correction model, i.e. whether net impulse numbers of or the ratio from characteristic and bremsstrahlung count numbers are used for quantification, affects the requirements to the bremsstrahlung computation (background determination). After the elements contained in a sample have been identified, a bremsstrahlung calculation is performed by assuming a concentration using the necessary geometrical and absorption parameters. A correction calculation checks the result and starts

(if necessary) a renewed background computation (background subtraction). Moreover, spectrum lines are broadened due to interaction effects in the detector and due to the electronic noise of the signal amplifiers. This often leads to a superposition of lines of different elements. A deconvolution has to be done to extract the portions of the individual elements from the "spectrum mountains" and to get the net pulse counts of the individual channels.

Sample Preparation for X-Ray Fluorescence Spectroscopic Analysis

For economic reasons sample preparation from probes must be easy, rapid and reproducible. Several methods are in use: In case of metals, solid polished disks are prepared, for powders, which are not affected by particle size limitations, preparation of solid pressed pellets is the most common method. Pelletizing can be achieved by applying pressures of up to 30-40 tons. The pelletizing method however has some pitfalls: e.g. in some cases a binder must be used, if the self-binding properties of the powder are not strong enough. This binder has to be free of contaminating elements, must have low absorption and must be stable under vacuum conditions. Another disadvantage may be that despite of the grinding and the pressure applied during pelletizing, the harder compounds in a matrix may still not be broken and thus may cause in-homogeneities on a macroscopic scale, which lead to systematic measurement errors. The same applies to the inter-element interferences and the particle sizes.

Some the above mentioned disadvantages of the XRF spectrum can be mitigated by dissolution or decomposition of the sample in a pulping agent or fusion into a homogeneous glass bead (see Figure 29). This was the technique applied in the case of ilmenite/Ni-carrier mixtures. This technique has several additional advantages:

- High or low specimen dilution for elimination of matrix effects
- Possibility of adding compounds such as heavy absorbers or standards in order to eliminate matrix effects
- Possibility of preparing standards of desired composition

The preparation of the glass bead proceeds in the following way: The sample is heated (usually in a Pt crucible) together with a flux (in our case Li-perborate) and heated to 800-1000°C so that the sample dissolves in the melting flux. When the mixture is transparent, a cooling procedure is applied in such a way that a clear and transparent glass bead is gained. It shall be mentioned that the probe preparation and the complete dissolution of all components is important in order to avoid systematic measurement errors.



Figure 29: XRF fused bead (taken from [82])

Further methods for sample preparation are liquid samples and filter samples, which are concentrated in order to bring the concentration into a range, where it can be detected by the spectrometer.

The XRF method is ideally suited for the purpose of CLC solid sample analysis, since it is a rapid, quantitative multi-element analysis technique with high precision. The accuracy of the determined concentration values varies depending on the elements and the contents. Detection limits are usually 10-100 ppm for heavier elements (like Fe, Ni etc.), lighter elements may be impossible to detect. The Axios Advanced XRF spectrometer used for determination of the XRF spectra allows detecting all elements down to boron [83].

XRF spectra were measured for the pure mixture compounds (ilmenite, Ni-Carrier) and for solid samples taken at selected operation points. Analysis of the XRF spectra yields the element contents of each sample in mass percent. Traces of Pt (from the crucible) and other not relevant trace elements are set to zero and the renormalization of the mass percentage values to 100% was done. This leads to the so-called XRF-derived (element) composition (XRFC).

3.4 Data Evaluation

For CLC data evaluation a number of important parameters can be defined. When methane is used as fuel:

1) The **methane conversion** X_{CH4} , which is an indicator of the reactivity of the oxygen carrier towards methane:

$$X_{CH_4} = 1 - \frac{x_{CH_4}}{x_{CH_4} + x_{CO_2} + x_{CO}} \Big|_{\text{FR exit}}$$
(26)

2) The **carbon dioxide yield Y_{CO2}**, which is an indicator of the full conversion of the hydrocarbons towards CO_2 , whereas the methane conversion only represents the

reactivity of the oxygen carriers towards carbon oxidation including also partial oxidation leading to CO:

$$Y_{CO_2} = \frac{x_{CO_2}}{x_{CH_4} + x_{CO_2} + x_{CO}}$$
(27)

Two important parameters can be defined, when syngas (a mixture of $CO/H_2 = 1:1$) is used as fuel:

1) The hydrogen conversion X_{H2} is an important measure of the reactivity and capability of the bed material to convert hydrogen:

$$X_{H_2} = \frac{\left(\dot{n}_{H_{2,in}} - \dot{n}_{H_{2,out}}\right)}{\dot{n}_{H_{2,in}}}$$
(28)

Whereby the **hydrogen flow** has to be calculated according to the following equation:

$$\dot{n}_{_{H_{2,out}}} = \frac{x_{H_2}}{x_{CO_2} + x_{CO}} \cdot \dot{n}_{_{H_{2,in}}}$$
(29)

2) The second parameter when using syngas fuelling is the **carbon monoxide** conversion X_{CO} , which is a measure for the overall CO conversion:

$$X_{CO} = \frac{x_{CO}}{x_{CO_2} + x_{CO}}$$
(30)

3) The **carbon dioxide yield for syngas** $Y_{CO2, syngas}$ is defined in analogy to the **carbon dioxide yield** Y_{CO2} . It can be expressed by X_{CO2} .

$$Y_{CO_2, syngas} = \frac{x_{CO_2}}{x_{CO_2} + x_{CO}} = 1 - X_{CO}$$
(31)

If additional heating is necessary in the air reactor (e.g. by supplying additional fuel), an effective air/fuel ratio λ_{eff} can be defined and calculated in the following way:

$$\lambda_{\rm eff} = \frac{L_{tot} - AD_{AR}}{AD_{FR}} \tag{32}$$

where L_{tot} is the total volume stream of air supplied to the air reactor, AD_{AR} is the stoichiometric air demand in the air reactor and AD_{FR} is the air demand of the fuel fed to the fuel reactor.

3.4.1 IPSEpro Model and Evaluation

IPSEpro is a model based stationary equation solver. Typically these models include at least the mass and energy balance. When validating experimental measurements the equation system to be solved is over-determined. IPSEpro is capable to handle such equation systems. This allows minimizing the errors for all the measured values. The structure of the modelling tool is depicted in Figure 30 below.

IPSEpro has a modular structure. It consists of a user interface (process simulation environment, PSE) which is the main component of IPSEpro. A model of the DCFB process exists where data can be entered/read. During calculation, data from the PSE (settings, parameters) are sent to the equation solver (Kernel). The solver has access to data from a model library that contains all information about the inner structure of the apparatuses used in the process. This model library can be changed or created by the user via a separate module of the package, the model development kit (MDK). The thermodynamic property data, i.e., functions of temperature, pressure, etc., are imported from external property libraries in the format of a dynamic link library (DLL). New substances can be introduced by the user since the creation of additional property-DLLs is possible.

Each result of a simulation run represents a steady-state operating point of a plant. There is no time dependency modelled which would allow description of dynamic system changes. More details can be found in [84].



Figure 30: Structure of IPSEpro Modelling Software (from [84])

To describe the thermodynamic properties of the involved substances the previously developed advanced energy and technology (AET) library is used. A number of redox systems are specified in the AET library, an extended version of a comprehensive model library previously built for gasification-based processes [85]. Using the IPSEpro modelling tools a simulation flow sheet which is actually a representation of the DCFB pilot plant has been developed. This flow sheet also contains representations of the AR and FR. For each reactor only one redox system can be specified for simplicity. In our case the redox system chosen was Fe_2O_3/FeO which best represents the assumed oxidation and reduction reactions of the oxygen carrier ongoing in the reactors. Other redox systems (such as NiO/Ni) which might also contribute to the oxygen carrier capacity are taken into account as an increased mass fraction of the Fe₂O₃/FeO oxygen carrier.

IPSEpro Model Input

The IPSEpro Model input consists of 52 measurement values (temperature, pressure, volume flows, the oxidation state of the oxygen carrier as X_s values, the mass fractions of the oxides contained in the oxygen carrier. the gas composition of the exhaust gases, etc.) which are imported into the simulation flow sheet. Those values, the flow sheet and the equations from each unit build an over-determined system which has a redundancy of 10. The over-determined system is solved using a solver based on the method of Lagrange multipliers. The difference between the reconciled and the measured values is then minimized by applying a least square fit.

IPSEpro Model Output

The simulation software IPSEpro is applied for measurement validation by mass- and energy balance checking. The result of the simulation represents a steady state operating point of a plant. The following information can be gained:

- Air/fuel ratios for the air reactor, air demands for the air and fuel reactor
- Solids mass flows (to air reactor), mean residence times in the AR and the FR, oxygen transport streams
- Conversions for CH₄, O₂, CO, H₂ and yields for CO₂
- Parameters for the CO shift equilibrium
- Measured FR and AR exhaust gas compositions can be validated

3.4.2 XRF Data Evaluation

Solid samples taken from the pilot plant at certain operation points, the Ni-carrier and the ilmenite samples have been analysed using the XRF glass bead technique. Once the chemical composition is known, the problem is to characterize each mixture by the mass fractions of ilmenite and Ni-carrier present. Table 7 shows the chemical compositions of the pure materials as gained from XRF analysis (without oxygen content). Whereas the Ni-carrier almost exclusively contains Al and Ni (the oxygen is not visible in the XRF), the main components contained in ilmenite are as expected Fe and Ti (with traces of Al, Ca, Mg, Na, Si and V). The ilmenite also contains traces of Ni (0.15% corresponding to 0.12 wt% NiO). In the following discussion these measured compositions will be denoted as XRF derived (calculated) compositions (XRFCM) and regarded as a vector. In the following, methods will be described how the measured compositions of Ni-carrier and ilmenite can be used to calculate compositions of known and unknown mixtures of ilmenite and Ni-carrier.

Element	[Ni19γAl ₂ O ₃]=wt%	[Ilmenite]=wt%
Al	65.36	0.82
Ca	0.15	0.76
Cl	0.74	0.29
Со	0.00	0.00
Cr	0.02	0.11
Cu	0.04	0.04
Fe	0.00	49.51
K	0.21	0.27
Mg	0.27	3.32

 Table 7: Chemical composition of Ni-Carrier and ilmenite

Element	[Ni19yAl ₂ O ₃]=wt%	[Ilmenite]=wt%
Mn	0.08	0.29
Мо	0.00	0.00
Na	3.10	1.18
Nb	0.00	0.01
Ni	29.74	0.15
Р	0.00	0.02
Pb	0.00	0.00
S	0.02	0.04
Si	0.13	3.21
Sr	0.00	0.00
Ti	0.13	38.50
V	0.00	1.42
Zn	0.01	0.03
Zr	0.00	0.03
Sum	100.00	100.00

Method 1: Linear Combination of XRFCM

If we assume that we have physical mixtures of ilmenite with Ni-carrier (i.e. mixtures without any chemical interactions between the compounds of each component), it can be concluded that the composition of such a mixture must be a linear combination of the compositions of the pure substances. The linear combination coefficients (α and β) are the masses (or mass fractions) of the pure substances in the mixture. These masses can be obtained from a mass balance over the whole experimental setup (including filter box inventory) considering solids loss by attrition and solids sampling as well as solids addition the actual chemical looping reactor system inventory (see Subsection 4.1). When solving this mass balance for ilmenite and Ni-carrier their masses and thus their weight fractions in the mixture can be derived corresponding to a specific (operation) point. The calculated XRF derived composition is denoted as XRFCC. The XRFCC is calculated according to (33) by weighting all components of the XRFCM with the same linear combination coefficients.

$$(\overrightarrow{XRFCC})_{n,calc} = \frac{\alpha_n \cdot (\overrightarrow{XRFCM})_{ilmenite} + \beta_n \cdot (\overrightarrow{XRFCM})_{Ni-Carrier}}{\alpha_n + \beta_n}$$
(33)

For a particular XRF derived composition the deviation between XRFCC and XRFCM for the individual elements (in mass percent) can be given. It can be shown that these deviations are below 3% in all cases (over the whole investigated concentration range) for all elements (irrespective of their absolute content), which is an indication that there is no bias in the XRF spectra measurements. Also the assumption of a linear attrition model for ilmenite as well as Ni-Carrier with individual attrition rates (see Subsection 4.1) seems to be justified. This is interesting to note as usually more than one operation point with different operation parameters (T, Fuel Power, point duration, inventory etc.) will lie within the region where the linear model is applied.

Table 8 to Table 10 show the measured and calculated XRF derived compositions for three operation points. Column 1 of these tables contains the list of chemical elements taken into account. Before a linear combination is calculated the values for Na and Cl are set to zero in the XRF vectors for ilmenite and the Ni-carrier, since these two values have the biggest fluctuations and the samples are most prone to contamination with these elements. The

resulting vectors are then renormalized so that the sum of all mass percentage values again yields 100%. The same procedure is applied to the XRFCM vector for the sample taken at the upper loop seal (ULS) and the lower loop seal (LLS). Then the arithmetic average of both is taken. If further trace elements are removed again a renormalized to 100% according to equation (33) is necessary. This yields the values in column 2 (AV). Column 3 (LC) contains the XRFCC values calculated according to equation (33). In column 6 and 7 the absolute differences between the calculated and the measured values (Abs Δ = LC-AV) and the square of these differences is calculated. Column 8 contains the relative differences i.e. the absolute difference related to the averaged value AV. The calculation of one component of the XRFCM vector is done according to:

$$(XRFCM)_{n,i,averaged} = \frac{0.5 \cdot \left[(XRFCM)_{n,i,ULS} + (XRFCM)_{n,i,LLS} \right]}{\sum_{1}^{j} (XRFCM)_{n,j}}$$
(34)

Table 8 to Table 10 contain the results for three operation points. If the relative or absolute differences exceed the value of 1%, those values are highlighted in red. For the linear inventory mass values refer to Table 17 and Table 18 in Subsection 4.2.

Element	[AV] =wt%	[LC] =wt%	[Abs ∆] =%	$[\Delta^2] = \%^2$	[Rel ∆] =%
Al	1.04	1.04	0.00529	0.00003	0.00509
Ca	0.52	0.77	0.25123	0.06312	0.48336
Cl	0.00	0.00	0.00000	0.00000	
Со	0.00	0.00	0.00004	0.00000	
Cr	0.11	0.11	-0.00128	0.00000	-0.01130
Cu	0.00	0.05	0.04504	0.00203	
Fe	49.47	50.09	0.62183	0.38667	0.01257
K	0.12	0.27	0.14693	0.02159	1.18545
Mg	3.11	3.36	0.25199	0.06350	0.08100
Mn	0.28	0.29	0.00716	0.00005	0.02526
Mo	0.00	0.00	0.00000	0.00000	
Na	0.00	0.00	0.00000	0.00000	
Nb	0.00	0.01	0.01247	0.00016	
Ni	0.23	0.25	0.02770	0.00077	0.12260
Р	0.00	0.02	0.02245	0.00050	
S	0.00	0.04	0.03871	0.00150	
Si	2.46	3.25	0.78738	0.61997	0.32028
Sr	0.00	0.00	0.00000	0.00000	
Ti	41.23	38.95	-2.28296	5.21192	-0.05537
V	1.43	1.44	0.00491	0.00002	0.00343
Zn	0.00	0.03	0.02996	0.00090	
Zr	0.00	0.03	0.03117	0.00097	
Sum	100.00	100.00	0.00000	6.37369	2.17238

 Table 8: XRFCM (AV) and XRFCC (LC) for operation point 2.5 (according to method 1)

Element	[AV] =wt%	[LC] =wt%	[Abs ∆] =%	$[\Delta^2] = \%^2$	[Rel ∆] =%
Al	2.18	1.99	-0.175338	0.030743	-0.080309
Ca	0.69	0.76	0.074949	0.005617	0.109117
Cl	0.00	0.00	0.000000	0.000000	
Со	0.09	0.00	-0.094486	0.008928	
Cr	0.11	0.11	0.001311	0.000002	0.011952
Cu	0.03	0.05	0.010921	0.000119	
Fe	49.03	49.36	0.318253	0.101285	0.006491
K	0.15	0.27	0.123285	0.015199	0.849939
Mg	3.63	3.32	-0.317676	0.100918	-0.087409
Mn	0.31	0.29	-0.028487	0.000811	-0.090529
Мо	0.00	0.00	0.000000	0.000000	
Na	0.00	0.00	0.000000	0.000000	
Nb	0.00	0.01	0.012282	0.000151	
Ni	0.78	0.73	-0.038690	0.001497	-0.049810
Р	0.01	0.02	0.007199	0.000052	
S	0.00	0.04	0.036013	0.001297	
Si	3.70	3.20	-0.496413	0.246426	-0.134288
Sr	0.00	0.00	-0.004790	0.000023	
Ti	37.89	38.38	0.482126	0.232445	0.012724
V	1.32	1.41	0.093890	0.008815	0.071139
Zn	0.03	0.03	-0.001488	0.000002	
Zr	0.03	0.03	-0.002861	0.000008	
Sum	100.00	100.00	0.000000	0.754340	0.619017

Table 9: XRFCM (AV) and XRFCC (LC) for operation point 2.15 (according to method 1)

Table 10: XRFCM (AV) and XRFCC (LC) for operation point 3.10 (according to method 1)

Element	[AV] =wt%	[LC] =wt%	[Abs ∆] =%	$[\Delta^2] = \%^2$	[Rel ∆] =%
Al	9.72	9.60	-0.12187	0.01485	-0.01253
Ca	0.60	0.69	0.08801	0.00775	0.14627
Cl	0.00	0.00	0.00000	0.00000	
Со	0.09	0.00	-0.08543	0.00730	
Cr	0.10	0.10	0.00039	0.00000	0.00390
Cu	0.04	0.05	0.00830	0.00007	
Fe	43.58	43.50	-0.07831	0.00613	-0.00180
K	0.32	0.25	-0.06765	0.00458	-0.21403
Mg	3.43	2.95	-0.47615	0.22672	-0.13895
Mn	0.27	0.25	-0.02058	0.00042	-0.07544
Мо	0.00	0.00	0.00000	0.00000	
Na	0.00	0.00	0.00000	0.00000	
Nb	0.00	0.01	0.01083	0.00012	
Ni	4.80	4.55	-0.24892	0.06196	-0.05183
Р	0.02	0.02	0.00116	0.00000	
S	0.02	0.04	0.01412	0.00020	
Si	3.16	2.84	-0.32014	0.10249	-0.10127
Sr	0.00	0.00	0.00000	0.00000	
Ti	32.59	33.85	1.25866	1.58423	0.03862
V	1.20	1.25	0.04332	0.00188	0.03602
Zn	0.03	0.03	-0.00600	0.00004	
Zr	0.03	0.03	0.00027	0.00000	
Sum	100.00	100.00	0.00000	2.01873	-0.37105

The absolute deviations Abs Δ are usually very low, but may be up 3% for some elements. The sum of all absolute deviations is zero, whereas the sum of the squares of the absolute deviations may be up to 7%. The relative deviations for the elements vary from 0.001 to 0.1. The values for Ti seem to be outliers, which may have to do with an insufficiently adapted background correction method for this element used in the XRF spectra error correction procedure (see Figure 28). However, it can be concluded that the measured compositions as well as those calculated with this method are in good agreement and yield reasonable values.

This is also confirmed by the plots of the element mass fraction vs. the Ni-Carrier content, which show linear correlations for all elements (see Figure 31, Figure 32). The element mass fraction is the XRFCM, whereas the Ni-carrier content is calculated by solving the mass balance in the attrition model (see Subsection 4.1). In accordance with expectation the curves for Al and Ni increase strongly with increasing content (concentration effect), whereas the curves for Fe and Ti decrease strongly (dilution effect). The dilution effect can also be observed for the other elements (Ca, Si and V) whose curves are slightly decreasing. The Mg curve is an exception, since it is slightly increasing. The reason for this may be that the measurement error for light chemical elements using XRF is higher than for heavy elements (see 3.3.2 for a more detailed discussion). The slope of the Ni-curve is about half the slope of the Al-curve which is in accordance with the absolute concentration relation of these elements in the Ni-carrier (see Table 7).



Figure 31: Plot of element mass fraction vs. Ni-carrier content (1)



Figure 32: Plot of element mass fraction vs. Ni-carrier content (2)

<u>Method 2: Least Squares Fit (LSQF) of single Elements of measured XRF Spectra and Extrapolation</u>

Another option for calculating chemical compositions of the mixtures is to apply a (linear or non linear) least squares fit to the measured values of mass fractions of a single element as a function of the added Ni-Carrier content. The Ni-carrier content is calculated before by calculating the mass balance according to equation (42) of Subsection 4.1. This allows for applying different weights to different chemical elements. Using a *linear least squares fit* the construction of the XRFCC vector proceeds in the following way:

1) In Excel a table of Ni_carrier content values (x_i -values) vs. measured mass fractions of the desired element (y_i -values) is set up and the deviations from the mean values are calculated:

$$x_i^* = x_i - \overline{x}$$
 and $y_i^* = y_i - \overline{y}$ (35)

2) Then the coefficients α_0 and α_1 are calculated, whereby

$$\alpha_0 = \overline{x} - \alpha_1 \cdot \overline{y} \tag{36}$$

$$\alpha_{1} = \frac{\sum x_{i}^{*} \cdot y_{i}^{*}}{\sum (x_{i}^{*})^{2}}$$
(37)

3) The desired y_i-values are gained by:

$$y_i = \alpha_0 + \alpha_1 \cdot x_i \tag{38}$$

- 4) The steps 1) to 3) are for the all other elements (different y_i -values) to construct the XRFCC vector for a specific Ni-carrier content (x_i -value)
- 5) Finally the vector is renormalized in order to ensure that the sum of all values equals 100%

It shall be noted that when doing extrapolation or interpolation, y_i -values from XRFCM vectors with a medium (or high) Ni-Carrier content taken yield the best values, since at low

Ni-carrier content the fluctuations of the mass fraction values of elements are high and this distorts the (extrapolation) curve. This can be observed in Figure 33 to Figure 38. At least 4 y_i -values shall be taken for an extrapolation (interpolation) in order to have sufficient accuracy and confidence.

For the construction of the XRFCC vector using a *quadratic least squares fit* the Excel solver function can be used in the following way:

1) An excel table is set up, which contains the mass fractions (from XRF) of a desired element (y_i -values) as a function of the Ni-carrier content values (x_i -values) whereby:

$$y_i = \alpha_0 + \alpha_1 \cdot x_i + \alpha_2 \cdot x_i^2 \tag{39}$$

- 2) Reasonable starting values for the coefficients α_0 , α_1 and α_2 have to be found such that the equation (39) is fulfilled
- 3) The residua y_i* are calculated for all values and the squares of the residua are summed up to yield the sum of residua according to

$$y_i^* = y_i - \overline{y} \tag{40}$$

$$RSS = \sum (y_i^*)^2 \tag{41}$$

- 4) The solver is started and the value of RSS is entered as target value to be minimized, whereby the changeable cell values are the coefficients α_0 , α_1 and α_2 and the side condition is e.g. that all y_i -values must be positive
- 5) Further side conditions can be added (e.g. that the relation between two y_i -values must have a certain value), if appropriate. This is necessary, if the calculated y_i -values are e.g. negative or not physically not sensible.
- 6) Furthermore solver parameters (maximum time for calculation in seconds, maximum number of iterations, accuracy, tolerance in % and convergence) as well as the estimation method (e.g. linear, forward Newton method) can be entered
- 7) Then the solver is started and refined values for the coefficients α_0 , α_1 and α_2 are calculated
- 8) The desired y_i -values for a specific x, value can be calculated by applying equation (39)
- 9) The steps 1) to 8) are repeated for the all other elements to construct the XRFCC vector
- 10) The XRFCC vector is renormalized in order to ensure that the sum of all y_i -values equals 100%

It shall be noted that the use of a non-linear least squares fit (resulting in a non-linear correlation of elemental mass fraction and Ni-carrier content) at first sight does not seem to be physically justified as we expect purely physical mixtures with a linear correlation between the concentrations of ilmenite and Ni-carrier. The mixtures however, also represent the operation points and operation conditions and thus also some non equidistant points in time. If, however, ilmenite and Ni-carrier (or their components) are attrited rather differently in the periods between operation points, non-linearities may arise. This may also be the case, if the (effective) attrition rate is a function of the current inventory mass, the current particle size and other physical parameters (like temperature, pressure etc.). Indeed it may also be the case, that components of a substance (e.g. Fe_2O_3 in ilmenite, Al_2O_3 and NiO in Ni-Carrier) may undergo faster attrition than others (e.g. SiO_2 and MgO in ilmenite). Thus with increasing Ni-carrier content the elemental mass fraction of faster abraded components (e.g. Al_2O_3 and NiO) slightly decreases, whereas that for others (e.g. SiO_2 and MgO) stays constant. This effect is

of course overlaid by the dilution effect, but is an explanation of what is actually observed in Figure 33 to Figure 38 below. As a check for the fit the mass fraction of the desired element y_i -value at higher and lower Ni-carrier contents (corresponding to different operation points) is calculated. A comparison is made in Table 11 to Table 14.

Moreover it can also be observed from the figures below, that there can be considerable deviations from the linear least squares fit at points with lower Ni-carrier content. The increase of Si and Mg content with increasing Ni-carrier concentration can be explained by the fact that the points at low Ni-carrier content distort the the linear curve (which actually should have a negative slope for these elements due to dilution). Three indications can be used for the verification of an extrapolation (interpolation) curve:

- 1) If extrapolating a component of the XRFCC vector for zero Ni-carrier content, the extrapolated value shall be close to the value of component the XRFCM vector of pure ilmenite
- 2) If extrapolating a component of the XRFCC vector for a certain (measured) Ni-carrier content, the extrapolated value shall be close to the value of component the XRFCM vector
- 3) If extrapolating a component of the XRFCC vector for that Ni-carrier content, where 100% or a certain conversion value is expected, these value can be compared e.g. with the value as obtained by Method 1.



Figure 33: Al mass fraction as a function Ni-carrier content



Figure 34: Ni mass fraction as a function Ni-carrier content



Figure 35: Fe mass fraction as a function Ni-carrier content



Figure 36: Ti mass fraction as a function Ni-carrier content



Figure 37: Mg mass fraction as a function Ni-carrier content



Figure 38: Si mass fraction as a function Ni-carrier content

The quality of the fit (of the XRFCM) can be estimated from a diagram, where the fitted mass fraction of an element is plotted vs. the XRF derived mass fraction. If the fit were ideal, the curve should be close to the straight green line which originates from the origin of coordinate system. Figure 39 shows this plot for the element Ni. At low as well as at high mass fractions for both fits the deviations from the experimental values are in the same order of magnitude. However, the behavior may be different for different elements (refer to Figure 40 to Figure 42, where the same plots are given for Fe, Al and Ti). The largest deviations in both fits occur for the element Ti, which is again an indication for the lower quality of the Ti values.



Figure 39: Fitted mass fraction vs. measured mass fraction for Ni



Figure 40: Fitted mass fraction vs. measured mass fraction for Fe



Figure 41: Fitted mass fraction vs. measured mass fraction for Al



Figure 42: Fitted mass fraction vs. measured mass fraction for Ti

A comparison between Method 1 and Method 2 is presented in Table 11 to Table 14. The tables present the (linear or quadratically) extrapolated and interpolated mass fraction values of the essential chemical elements calculated with Method 2 and Method 1. For both methods the measured XRF spectra are taken as reference. Summarizing it can be seen that the quadratic LSQF according to method 2 provides the best fit to the experimental XRF spectra for medium to high Ni-Carrier contents. The sum of the squares of the deviations is taken as a criterion for the quality of the fit. At low Ni-Carrier contents (opPt 2.1 and opPt 2.5) Method 1 provides the better fit, which is not surprising, since the relative weight of the (experimental) XRF derived Ni-Carrier contents the absolute errors of linear combined values for elements (Δ (LC-XRF) in Table 11 to Table 14) are between 1 and 4%. Therefore (and due to the much simpler calculation) it seems justified to use the values gained with Method 1 as a basis for some further discussions.

Table 11: Comparison of measured and fitted XRF compositions obtained with Method 1 and Method 2 (opPt2.1)

opPt2.1	[XRF]=%	[LSQF lin]=%	Δ^2	[LSQF quadr]=%	Δ^2	[LC]=%	Δ^2	Δ (LC-XRF)
Al	0.83	1.72	0.79	-0.10	0.87	0.83	0.00	0.00
Fe	50.25	49.83	0.18	50.79	0.29	50.25	0.00	0.00
Mg	3.37	3.68	0.10	3.12	0.06	3.37	0.00	0.00
Ni	0.15	0.32	0.03	-0.08	0.05	0.15	0.00	0.00
Si	3.26	3.62	0.13	3.12	0.02	3.26	0.00	0.00
Ti	39.07	38.12	0.90	39.70	0.39	39.07	0.00	0.00
others	3.07	2.71	0.13	3.46	0.15	3.07	0.00	0.00
sum	100.00	100.00	2.26	100.00	1.84	100.00	0.00	
opPt2.5	[XRF]=%	[LSQF lin]=%	Δ^2	[LSQF quadr]=%	Δ^2	[LC]=%	Δ^2	Δ (LC-XRF)
---------	---------	--------------	------------	----------------	------------	--------	------------	-------------------
Al	1.04	1.90	0.73	0.25	0.62	1.04	0.00	0.01
Fe	49.47	49.70	0.05	50.55	1.18	50.09	0.39	0.62
Mg	3.11	3.68	0.32	3.17	0.00	3.36	0.06	0.25
Ni	0.23	0.42	0.04	0.06	0.03	0.25	0.00	0.03
Si	2.46	3.61	1.32	3.15	0.48	3.25	0.62	0.79
Ti	41.23	38.00	10.45	39.40	3.36	38.95	5.21	2.28
others	2.47	2.71	0.06	3.41	0.89	3.06	0.35	0.59
sum	100.00	100.00	12.97	100.00	6.55	100.00	6.63	

Table 12: Comparison of measured and fitted XRF compositions obtained with Method 1 and Method 2(opPt2.5)

Table 13: Comparison of measured and fitted XRF compositions obtained with Method 1 and Method 2(opPt3.10)

opPt3.10	[XRF]=%	[LSQF lin]=%	Δ^2	[LSQF quadr]=%	Δ^2	[LC]=%	Δ^2	Δ (LC-XRF)
Al	9.72	8.88	0.72	9.33	0.16	9.60	0.01	0.12
Fe	43.58	44.49	0.84	44.19	0.38	43.50	0.01	0.08
Mg	3.43	3.49	0.00	3.64	0.05	2.95	0.23	0.48
Ni	4.80	4.40	0.16	4.54	0.07	4.55	0.06	0.25
Si	3.16	3.18	0.00	3.32	0.02	2.84	0.10	0.32
Ti	32.59	32.81	0.05	32.32	0.07	33.85	1.58	1.26
others	2.72	2.76	0.00	2.67	0.00	2.71	0.00	0.01
sum	100.00	100.00	1.77	100.00	0.75	100.00	2.00	

 Table 14: Comparison of measured and fitted XRF compositions obtained with Method 1 and Method 2 (opPt3.20)

opPt	[XRF]=%	[LSQF lin]=%	Δ^2	[LSQF quadr]=%	Δ^2	[LC]=%	Δ^2	Δ (LC-XRF)
3.20								
Al	8.72	11.43	7.35	10.08	1.86	12.73	16.11	4.01
Fe	44.09	42.59	2.25	43.40	0.47	41.09	9.00	3.00
Mg	3.55	3.42	0.02	3.15	0.16	2.80	0.57	0.75
Ni	3.62	5.86	4.99	5.41	3.20	6.13	6.28	2.51
Si	3.52	3.02	0.25	2.78	0.55	2.69	0.68	0.83
Ti	33.82	30.91	8.45	32.23	2.52	31.98	3.38	1.84
others	2.68	2.78	0.01	2.94	0.07	2.58	0.01	0.10
sum	100.00	100.00	23.32	100.00	8.82	100.00	36.02	

4 Results and Discussion

4.1 Attrition Model

As already mentioned a linear attrition model was constructed using inventory data. For the construction of the model it is assumed that each of the two mixture components (ilmenite and Ni-Carrier) has its individual attrition rate. For the attrition model it is necessary to know exactly the points of time where material is added to the reactor. These points can be determined from the drops and spikes in the temperature curves. Besides the temperature in the fuel reactor at a measurement point 1 (TIR FR1) and the air reactor (TIR AR1), the fuel power, the active solids inventory in the fuel reactor and the air reactor as well as the total active solid are depicted. In order to ensure comparability between different operation runs, the active solids inventory is an important parameter. An overview of a typical experiment is depicted in Figure 44. When the height, the diameter of the reactor (or the reactor cross section $A_{reactor}$) and the pressure drop Δp are known, it is possible to calculate the bed mass in the reactor using the following formula:

$$m_{bed} = \Delta p_i \cdot A_{reactor} \tag{42}$$

This bed mass in the reactor is referred to as the active inventory. In the course of an experiment the effective solids inventories are determined by pressure (difference) measurement at some points in the reactors. The pressure profiles in the reactors for two different operation points (2.1 and 2.15) are depicted in Figure 43 below.



Figure 43: Pressure profiles of two operation points; left: 2.1, right: 2.15



Figure 44: Overview on MOEXC2

The total active solids inventory is the sum of the active inventories of both reactors. The total mass of solids (TMS) contained in the pilot plant includes the mass of solids contained in the loop seals, the downcomer etc. At the start of an experiment the TMS is determined. Whenever masses are added to the system or extracted from the system (e.g. by solid sampling, attrition) this is taken into account in the mass balance. Moreover at the end of the experiment, the content of the filter-box is weighed in order to determine the total discharge. This total discharge is equal to the masses that have been entrained from the reactors. Thus the mass balance can be written as:

$$m_{bed}^{eff} = m_{init} + \sum m_{i,added} - \sum m_{j,sampling} - \sum \Delta m_{k,attrition}$$
(43)

The drops visible in the temperature curves (corresponding also to spikes in the power curves) in Figure 44 indicate the addition of large masses (bed material). The attrition model is taking into account the well known amounts of masses added. Also the weight of all samples as a function of time is determined. This leads to the attrition curves for the experiments as depicted in Figure 45 and Figure 46 below. It shall be noted that a direct comparison with Figure 44 is not possible, since a large fraction of the total solid discharge from the active solids is directly proportional to the attrition. An overview on the inventory masses at different operation points derived from the attrition model can be found in Subsection 4.2. There it is also shown that XRF derived Ni concentrations and the attrition model derived values are in good agreement.

The curves depicted in Figure 45 and Figure 46 allow to calculate piecewise overall attrition rates. When taking into account the Ni-carrier contents of the filterbox and the mass delta by sampling as a linear background over the whole time of the experiment, the individual attrition rates of the Ni-carrier and the ilmenite can be calculated.

The procedure is as follows:

- 1) The compositions of the filter box content are determined by XRF measurements.
- 2) The weight of the filter box is determined after the experiment. It is a measure for the total mass discharge during the experiment.
- 3) Now the chemical composition of the filter box is approximated by a linear combination of the XRFCM of ilmenite and Ni-carrier in such a way, that the sum of the least squares deviations over all elements is a minimum. The linear combination coefficients (α and β) are the masses of ilmenite and Ni-carrier which have been elutriated from the reactors. Reasonable starting values (α_0 and β_0) for these coefficients have to be chosen.
- 4) Using the Excel solver these coefficients can be calculated by entering the desired total elutriated mass as a target value and starting values as changeable parameters with the side condition that for some elements (e.g. Ni) the least square deviation shall be lower than a chosen value.
- 5) If there is more than one solution, the number of solutions can be reduced by choosing reasonable side conditions and that solution is taken, which has the minimal overall sum of least square deviations.
- 6) It is crucial that the entrained mass is evaluated based on the change of ∆p based total solids inventory for constant fluidization conditions. Since the entrained mass of Ni-carrier is now known, it is possible to calculate the specific Ni-carrier attrition rate. By subtracting the fraction of mass of the Ni-carrier entrained in a certain time interval

from the total mass out bed material entrained within that interval the dragged out ilmenite can be estimated and thus the attrition rate for ilmenite within this period becomes available. The overall ilmenite attrition rate can be calculated using the difference between the total entrained bed mass and the Ni-carrier mass entrained.



Figure 45: Mass fluctuation of total inventory and ilmenite in MOEXC2



Figure 46: Mass fluctuation of total inventory and ilmenite in MOEXC3

Figure 45 and Figure 46 depict the total mass fluctuation and the ilmenite mass fluctuation for MOEXC2 and MOEXC3. In MOEXC2 the ilmenite curve closely follows the total curve and the slopes of the two curves are the same. Two periods with a steep descent (period 1 from 13:24 to 16:12 and period 2 from 17:52 to 20:12) are followed by a step ascents (at 16:12 and 20:12), when 10 and 15 kg of ilmenite are added, respectively (green and orange shaded areas in Figure 45). During period 1 there are four operation points (opPt2.5, opPt2.7-2.9) with 120 kW fuel power and also during period 2 there are two more operation points with 100 kW (opt 2.11 and opt 2.14) followed by one further operation point with 120 kW fuel power (opt 2.15). More details about the operation points can be found in Subsection 4.2. During these periods also the air-preheater was used extensively for temperature stabilization and temperature recovery after insertion of material. For this purpose an air stream of about 170 m³/h at 300°C was injected, which is outside the values specified for the air reactor (see Table 3). The resulting higher gas velocities surely also contribute to the increased attrition.

The more Ni-carrier is added, the larger the gap between the total and the ilmenite curve becomes. Whereas from the start of MOEXC3 (10:58) until about 15:00 the two curves are parallel, in the period between 15:00 and 17:07 (green shaded area in Figure 46) the slope of the ilmenite curve is steeper than the slope of the total curve. During this period 6.8 kg of Ni-carrier in batches of approximately 0.9 kg are added to the ilmenite. Since the added Ni-carrier has a much lower attrition rate than the ilmenite, the total curve stays more or less constant, while the ilmenite curve goes down with the same slope. During the last period of MOEXC 3 (from 17:07 to 21:20 approximately) the ilmenite curve and the total curve are again parallel. The increase of the curves at 21:20 marks the addition of the last portion of Ni-carrier (2.7 kg).

Particle properties					rates] = kg/h
Component	[Particle size] = µm	$[\rho] = g/cm^3$	[Crushing strength] = N	MOEXC1	MOEXC2
Ilmenite (I)	$180^{(3)}$	4.7 ⁽³⁾	2.39 (1)	-3.90	-2.81
Ni-Carrier (II)	100-300 ⁽²⁾	1.7 (2)	2.60 ⁽²⁾	-0.04	-0.04
			Overall:	-3.94	-2.74
			(I)/(II):	97.75	75.96

Table 15: Particle properties and overall attrition rates for P=120 kW

References: ⁽¹⁾ [86]; ⁽²⁾ [31]; ⁽³⁾ [24]

Table 15 summarizes particle properties and calculated overall attrition rates for the mixture components in the experiments MOEXC1 and MOEXC2 using all operating points. It can be seen that the ilmenite has an attrition rate which is 75 to 100 times higher than the attrition rate of the Ni-carrier (despite of the similar crushing strength and the similar particle size). This leads to the conclusion that – in first approximation - the particle density is responsible for the differences in the attrition rate. It can also be seen, that the overall attrition rate decreased from MOEXC1 to MOEXC2. This is in accordance with expectation, because in MOEXC1 the average of fuel power and thus the circulation rate taken over all operation points is higher than in MOEXC2 (see Subsection 4.2 for details).

It remains now to say some words about attrition and scale-up. In a simple model the contributions to the attrition rate of a particle is dependent on several factors:

- The mechanical fragmentation
- The fluid mechanical properties
- The particle properties
- The particle concentrations
- The chemical changes of particle properties

The mechanical fragmentation depends on the number of collisions between particles and with the wall. The fluid mechanical properties are the gas velocities, the gas densities, the particle densities and the surface/volume relation of the reactor etc. Further particle properties are the particle surface and particle hardness. This is also a function of the chemical reactions at particles which may lead to a change of particle properties, such as surface and size (compare shrinking particle model in [69]). Also the concentration of particles in the reactor influences the attrition rate. From what was said above it becomes clear that these factors are not independent of each other and change with the varying conditions in the reactor. It is therefore difficult to say, which term dominates in the system ilmenite/Ni-carrier. In a rough first guess, the following assumptions can be made:

- 1) all attrition contributions and the fluid dynamic properties of the reactor remain the same, when the reactor is scaled up
- 2) In order to achieve 1 MW fuel power instead of 120 kW the inventory volume has to be about 8 times larger thus we have about 720 1000 kg inventory
- 3) If we assume the same attrition rate of 3-4 kg/h, which is about 3-5%/h, we arrive at 20 50 kg/h attrition for a 1MW reactor.

This relative high attrition rate requires high solids inventories. Minimum solids inventories have been estimated and are in the range of 25-1000 kg/MW_{th} [15]. Lyngfelt et. al suggested that solid mass inventories of less than 500kg/MW_{th} might be reasonable [17]. This makes it questionable, whether ilmenite can be used in a scaled-up plant as oxygen carrier. This has however to be taken with some caution:

- a. The pilot plant dimensions and gas velocities have not been optimized for ilmenite.
- b. The surface/volume ratio becomes better, when the reactor is scaled up.
- c. The long-term effect of chemical reactions (repeated oxidation and reduction reactions usually cause an increase in particle surface and fragmentation) has not been taken into account.

Whereas (a) and (b) may help to reduce the attrition rate e.g. by optimizing the incoming gas velocities and thus reducing the jet effect, (c) counteracts and may become more dominant with time. The question on how many oxidation and reduction cycles have taken place during an experimental campaign can be determined in the following way: The mean global solids mass flow at a fuel power of 120 kW is between 11000 and 15000 kg/h. This means that the bed material makes 130-180 cycles/h, which results in a total of 1300 to 1800 cycles per experimental campaign in a typical 10h campaign (Note: A cycle in this context means the complete exchange of the bed mass in the reactors). If it is assumed that a steady state attrition rate is achieved after a certain number of cycles (since smaller particles experience lower attrition and fragmentation), the question is whether this is already the case after the above number of cycles.

4.2 Overview on Operation Points, Parameters and Results

Table 16 to Table 18 below provide an overview on the operation points, the operation parameters, such as the ilmenite inventory masses, the Ni-carrier inventory masses and the NiO mass fractions, fuel power, fuel reactor temperature and effective air/fuel ratio. When not noted otherwise the inventory masses (in column 2 and 3) were calculated using the attrition model as described in Subsection 4.1. The NiO weight fraction [NiO] in column 4 was calculated by relating the value in column 3 to the value in column 2 and assuming that 19 wt% of added Ni-carrier mass is NiO. The NiO fraction (0.12 wt %) from the ilmenite is additively taken into account. Column 4 [NiO_{XRF}] contains the weight fraction of NiO as derived from the XRF spectra. The values for the fuel power and the temperature values are the measured values as recorded by the PLS. The effective air/fuel ratio λ_{eff} in column 8 is calculated according to equation (32).

OpPt	[Ilm] = kg	[Ni19] = kg	[NiO] = wt%	[NiO _{XRF}] =wt%	[P]=kW	$[T_{FR}] = C$	λ_{eff}	Fuel
1.1	85.00 ¹⁾	0.00	0.120	0.120	81.5	911.6	1.1	SYNG
1.2	85.00	0.00	0.120	0.120	81.6	912.5	1.2	SYNG
1.3	85.00	0.00	0.120	0.120	81.6	909.3	1.2	SYNG
1.4	85.00	0.00	0.120	0.120	81.1	960.2	1.2	SYNG
1.6	85.00	0.00	0.120	0.120	121.8	959.7	1.2	SYNG
1.9	85.00	0.00	0.120	0.120	121.4	963.5	1.1	NG
1.8	85.00	0.00	0.120	0.120	100.9	964.5	1.1	NG
1.7	85.00	0.00	0.120	0.120	82.2	964.7	1.1	NG
1.16	85.00	0.00	0.120	0.120	62.1	967.3	1.1	NG
1.10	85.00	0.00	0.120	0.120	123.2	963.2	1.0	NG
1.17	85.00	0.00	0.120	0.120	125.0	963.3	0.7	NG
1.11	85.00	0.00	0.120	0.120	114.9	963.7	1.2	NG
1.12	85.00	0.00	0.120	0.120	119.4	964.1	1.1	NG
1.13	85.00	0.00	0.120	0.120	80.5	913.1	1.1	NG
1.14	85.00	0.00	0.120	0.120	100.9	912.6	1.1	NG
1.15	85.00	0.00	0.120	0.120	122.2	913.2	1.0	NG
Average					100.0	944.1	1.1	

Table 16: Operation points, parameters and results from Mixed Oxides Campaign 1

¹⁾ The ilmenite masses for ilmenite benchmark were calculated from the total inventory.

OpPt	[Ilm] = kg	[Ni19] = kg	[NiO] = wt%	[NiO _{XRF}] =wt%	[P]=kW	$[T_{FR}] = C$	λ_{eff}	Fuel
2.1	85.00	0.00	0.120	0.120	120.9	971.6	1.1	NG
2.2	84.49	0.00	0.120	0.149	120.9	968.2	1.1	NG
2.3	84.10	0.12	0.147	0.149	100.8	964.6	1.1	NG
2.4	83.78	0.09	0.141	0.149	81.1	963.6	1.1	NG
2.5	83.52	0.27	0.181	0.184	125.2	966.1	1.1	NG
2.6	80.79	0.24	0.176	0.184	81.2	965.1	1.1	NG
2.7	80.52	0.60	0.261	0.467	121.6	963.4	1.1	NG
2.8	78.34	0.58	0.259	0.467	121.3	964.4	0.7	NG
2.9	76.34	0.56	0.258	0.467	126.1	962.7	0.5	NG
2.10	79.93	1.39	0.444	0.548	120.8	967.3	1.1	NG
2.11	78.54	1.38	0.446	0.548	101.6	966.2	1.1	NG
2.12	76.95	1.36	0.449	0.548	81.2	966.1	1.1	NG
2.13	74.10	1.33	0.454	0.548	79.9	911.9	1.1	NG
2.14	72.90	1.32	0.457	0.548	100.4	917.1	1.1	NG
2.15	70.85	1.30	0.460	0.630	120.2	914.4	1.1	NG
Average					106.9	955.5	1.1	

 Table 17: Operation points, parameters and results from Mixed Oxides Campaign 2

 Table 18: Operation points, parameters and results from Mixed Oxides Campaign 3

OpPt	[I lm] = kg	[Ni19] = kg	[NiO] = wt%	[NiO _{XRF}] =wt%	[P]=kW	$[T_{FR}] = C$	λ_{eff}	Fuel
3.1	78.00	3.36	0.900	1.024	81.2	966.1	1.1	NG
3.2	76.62	6.51	1.599	2.666	80.7	967.4	1.1	NG
3.3	74.78	6.49	1.627	2.666	118.3	967.5	1.1	NG
3.4	73.89	6.48	1.642	2.666	101.7	966.8	1.1	NG
3.5	72.50	6.46	1.665	2.666	60.6	969.4	1.1	NG
3.6	71.01	6.44	1.690	2.666	81.1	957.7	1.2	SYNG
3.7	72.92	7.58	1.898	1.889	81.1	966.7	1.1	NG
3.8	72.03	8.37	2.086	2.451	80.9	965.9	1.1	NG
3.9	70.49	9.15	2.290	2.860	81.0	962.1	1.1	NG
3.10	69.10	10.74	2.659	3.871	80.3	962.7	1.1	NG
3.11	67.51	13.12	3.192	4.078	79.8	964.2	1.1	NG
3.12	66.56	13.10	3.225	4.078	100.6	967.0	1.1	NG
3.13	65.71	13.09	3.255	4.078	120.3	966.3	1.1	NG
3.14	64.91	13.07	3.285	4.078	123.7	967.7	0.9	NG
3.15	64.03	13.06	3.318	4.078	122.0	963.4	0.7	NG
3.16	62.50	13.04	3.379	4.078	80.5	910.5	1.1	NG
3.17	61.06	13.02	3.438	4.078	101.5	914.2	1.1	NG
3.18	60.72	13.01	3.452	4.078	120.3	917.2	1.1	NG
3.19	59.57	13.00	3.502	4.078	123.5	915.7	0.9	NG
3.20	58.13	12.98	3.566	2.914	130.8	912.4	0.8	NG
Average					97.5	952.5	1.1	

It shall be noted that the difference between the columns 3 and 4 is in most cases less than 1%. This shows that the attrition model is in good accordance with the XRF derived NiO values. Exceptions are the values at operation points 3.2. to 3.4 and 3.10. At the operation points 3.2 to 3.6 the XRF derived NiO values seem to be too high, since at operation points with higher Ni carrier content (3.7 and 3.8) lower XRF derived NiO values are measured and also the values derived from the attrition model are lower. The XRF derived value at 3.20 seems to be too low, since the NiO values at operation points 3.11 to 3.19 are already higher and also the value in column 4 is higher. It shall further be noted that the average of the fuel power taken over all operation points was lowest in campaign 3 and highest in campaign 2. This explains the lower attrition rate in campaign 3.

4.3 Conversions and Yields

4.3.1 Discussion of Conversion Curves

When plotting the CH_4 conversion or the CO_2 yield against the Ni-carrier content, it is reasonable to expect a sigmoid, exponential (or parabolic) curve. The different types of curves are depicted below in Figure 47. The sigmoid curve is typical for autocatalytic reactions. These are reactions, in which one of the reactants is also product. In the case of CH_4 conversion, this could be the H_2 .



Figure 47: Curve types and phases of CH4 conversion as function of Ni-carrier concentration

A sigmoid curve is characterized by a lag phase (P1) in the first section of the curve: due to the small amount of NiO present there is also a small amount of Ni which catalysis the reforming reaction necessary for conversion. The lag phase is then followed by a (positive) acceleration phase (P2), when the amount of free Ni is increasing. The more CH₄ is cracked, the more H₂ (and CO) are generated and this allows reducing more NiO (logarithmic phase, P3). If there is a rate determining step which limits the maximum velocity of the overall reaction and no further NiO is delivered, there is a decrease of conversion the de-celeration

phase starts (P4). Finally a <u>stationary phase</u> (P5) is reached, if all CH_4 delivered immediately is converted. An *exponential (a parabolic or even a linear) curve* are most probably indiscernible from the sigmoid curve in the lag phase. Therefore it is necessary to add enough Ni-carrier to reach the acceleration phase or the following phases.

4.3.2 Effect of Ni-carrier Addition

Figure 48 and Figure 49 depict the CH_4 conversion and the CO_2 yield as a function of the Ni-Carrier content for NG fuel powers of 80-120 kW. Instead of the expected non-linear increase with Ni-carrier concentration a linear increase over a wide concentration range is observed. An explanation for this behaviour is given in Subsection 4.3.7 below.



Figure 48: CH₄ conversion as function of Ni-Carrier content for fuel power P = 80-120 kW (NG), T_{FR}=965°C, λ_{eff} =1.1



Figure 49: CO₂ yield as function of Ni-Carrier content for fuel power P = 80-120 kW (NG), T_{FR} =965°C, λ_{eff} =1.1

Moreover, with increasing fuel power the conversion efficiency is decreasing. The points at 0% Ni-carrier depict the conversion and yield values for pure ilmenite. This means an increase of conversion of approximately 7.5 % pts or 15% with respect to the pure ilmenite performance. The difference between the CH_4 conversion and the CO_2 yield allows calculating the CO fraction which allows closing the carbon balance (Figure 50). It can be seen that the differences in the CO yields are less than 1%. Since there is no significant increase in the CO generation, it can be concluded, that the excess CO can be fully converted by ilmenite and the ilmenite is not limiting the CO conversion.



Figure 50: CO yield as function of Ni-Carrier content for fuel power P = 80-120 kW (NG), T_{FR} =965°C, λ_{eff} =1.1

4.3.3 Effect of Fuel Power

Figure 51 and Figure 52 show the CH_4 conversions and the CO_2 yields as a function of the fuel power for different constant values of Ni-carrier content. The conversions and yields decrease with increasing fuel power. It can be seen that the Ni-carrier content has the most pronounced effect of all factors on the CH_4 conversion. For a NG fuel power of 80 kW there is an increase of about 10% in the conversion, when going from pure ilmenite to 14 wt% Ni-carrier.

It can also be seen is that between 0.0 % (ilmenite) and 1.7 wt% Ni-carrier the conversion curves are close together. This can be interpreted such that the conversion mechanism in this range is independent of the Ni-carrier content or in other words that a certain threshold value of Ni-carrier content is required, in order to start the reaction. The CO_2 yield curves even remain up to 7.2 wt% Ni-carrier close together. It is also observed, that the slope of the decreasing curves seems to be slightly steeper when going to a Ni-carrier content above 7.2%.



Figure 51: CH₄ conversion as function of fuel power P = 80-120 kW (NG), T_{FR}=965°C, λ_{eff} =1.1



Figure 52: CO₂ yield as function of fuel power P = 80-120 kW (NG), T_{FR}=965°C, λ_{eff} =1.1

4.3.4 Effect of Air/Fuel Ratio Variation

For CLC it is possible to define a global air/fuel ratio which is usually greater than 1. Since it was observed, that the conversion level of CH_4 was below expectations, several experiments were performed, where the air/fuel ratio was reduced below stoichiometric requirements. The motivation for this was to reduce a larger amount of ilmenite and consequently also of the Ni-carrier to metallic Ni in order to trigger the catalytic steam reforming and CO shift reactions. This, however, could not be achieved.

Figure 53 shows that the conversion levels and the yields decrease with decreasing air/fuel ratio. When the Ni-carrier concentration is low, the conversion levels and the yields are close to values for pure ilmenite, although the effect of Ni is already noticeable at low concentrations. A parallel upward shift of the curves takes place with increasing Ni-carrier concentration.



Figure 53: CH4 conversion and CO₂ yields as a function of air/fuel ratio variation for various Ni-Carrier contents at T_{FR}=965°C

4.3.5 Effect of Temperature

Figure 54 shows the dependency of the CH₄ conversion and the CO₂ yield on the Ni-carrier content at a fuel power of 120 kW and λ_{eff} =1.1 for two fuel reactor temperatures (T_{FR}= 910°C and T_{FR}= 965°C). The effect of temperature on the conversion is very pronounced. A temperature increase of about 55°C increases the conversion efficiency by 10%. This is equivalent to the addition of about 17 wt% of Ni-carrier to pure ilmenite.

Again the purely linear dependency on Ni increase of Ni-carrier concentration is observed. It is known, that ilmenite as other oxygen carriers performs worse at lower temperatures. These effects account for the observed yield reduction.



Figure 54: CH₄ conversion and CO₂ yield as function of Ni-carrier content for fuel power P = 120 kW (NG), and T_{FR} =965°C and T_{FR} =910°C, λ_{eff} =1.1

4.3.6 Syngas Conversion Performance

Figure 55 shows the conversion levels for H_2 and the CO₂ yields for a 1:1 mixture of CO/H₂ at T=965°C.



Figure 55: H₂ conversion and CO₂ yields as a function of Ni-Carrier contents at T=965°C

With increasing Ni-carrier concentration the H_2 concentration should also increase, since more H_2 is produced by the reforming reaction. This is however not observed, which is also an indication that the reforming reaction is inhibited or not catalyzed sufficiently. Whereas the H_2 level stays almost constant and is almost identical to the value for pure ilmenite, the CO_2 yield is (slightly) decreasing with increasing Ni-carrier concentration.

4.3.7 Explanations for the linear Conversion Behaviour

In principle five possible explanations (or a combination of these) may theoretically account for the deviation from the expected sigmoid or exponential behaviour of the conversion:

- 1. **Oxide layer or combined oxide formation**: "inhibition" of the added Ni-carrier by ilmenite or some compounds contained therein e.g. by formation of a stable oxide layer covering the Ni-carrier particles or by combined oxide formation. This results in slowing down or even preventing reduction to Ni in the fuel reactor.
- 2. **Insufficient residence/contact time**: Due to the large excess of ilmenite in comparison to Ni-Carrier present (and the unfavourable surface relation) the probability of a CH_4 molecule (or the CH_3 radical) meeting a reduced Ni, being adsorbed and further cracked may be reduced. In addition the low gas/solid contact time may be an adverse condition for the reaction.
- 3. **Stable (inert) spinel:** high stability of the spinel entered in the CLC plant under the reducing atmosphere of the fuel reactor thus preventing formation of metallic Ni
- 4. **Segregation**: rapid elutriation of a considerable fraction of the lighter Ni-Carrier (solid density $\rho = 1.7 \text{ gcm}^{-3}$; ilmenite for comparison has a solid density of $\rho = 4.72 \text{ gcm}^{-3}$) and accumulation in regions (e.g. in the loop seals) where they can only react with a small portion of CH₄.
- 5. Unfavourable oxidation potential: according to Figure 10, Ni (II) cannot be reduced as long as Fe (III) (e.g. in Fe_2O_3) is present. Since ilmenite is present in large excess this may prevent the Ni-carrier from being reduced (see also Subsection 2.6.3).

4.3.8 Tradeoff between Explanations

The following section provides a first analysis of the explanations for the linear CH_4 conversion as given above:

Oxide Layer Formation or combined Oxide Formation

This explanation cannot be totally excluded without closer investigation of the particle probes by e.g. XRD analysis, chemical analysis or preparation of thin section slides in order to get insight into particle structure and composition. However, from a first optical inspection of the solid samples it was evident that the blue Ni-carrier (spinel) particles which have been entered into the pilot plant are clearly visible. Since the surface color of the particles should change through oxide formation, this possibility is very likely to be excluded. Moreover the formation of an oxide layer (a solid/solid reaction) would probably require more time.



Figure 56: Solid Samples from operation point 2.10; left: ULS, right: LLS



Figure 57: Solid Samples from operation point 3.11; left: ULS, right: LLS

Insufficient Residence/Contact Time

Cracking and reforming of CH_4 over Ni proceeds via a multistep mechanism involving adsorption, desorption and surface reactions (compare e.g. [87]). In addition excess steam supports the completion of the reaction and prevents coke formation. Thus the surface ratios of the ilmenite and the added NiO may indeed play an important role (if e.g. CH_4 are adsorbed at the ilmenite surface, which increases through attrition, and thus become unavailable within the residence time in the fuel reactor for reaction with metallic Ni). The ilmenite reacts slowly with CH_4 . Moreover, a change in the conversion slope (indicating a change in reaction mechanism) was not observed in this study and remains to be proven by further experiments at higher Ni-carrier concentrations.²

Stable (inert) Spinel

According to the XRD spectrum presented in [31] the NiAl₂O₄ is the major crystalline phase of the fresh Ni-carrier. Traces of NiO which may be still present will also be converted to NiAl₂O₄ under the conditions in the air reactor, since there is an excess of γ -Al₂O₃. As the NiAl₂O₄ is more stable than NiO from a thermodynamic point, of view this option would allow explaining the conversion behaviour (see also the discussion in Subsection 2.6.3). However, according to [31] the spinel reacts very quickly in a reductive atmosphere and under the conditions of TGA analysis.

² Experiments with up to approximately 45% Ni-carrier content were performed in the meantime. However, no deviation from the linear conversion behavior was observed. Thus this possibility can be excluded.

Segregation

The density difference between Ni-Carrier and ilmenite could lead to the phenomenon of segregation i.e. the Ni-Carrier particles are "swimming" on top of the ilmenite "lake" in the reactor. However, a (more or less) **immediate rapid elutriation** of Ni-Carrier particles can also be excluded, as in the solid samples the blue spinel particles are still visible. Secondly, as the bed and the filter box material after each experiment have been analysed and contain an increasing amount of Ni comparable to the last operation point. No spinel particles are visible (see Figure 58). As an example the chemical composition values for operation point 2.15 are presented in Table 19. Thus, the option of segregation can be excluded.

Element	[LLS 2.15]=wt%	[ULS 2.15]=wt%	[bed] =wt%	[fbox] = wt%
Al	2.40	1.96	2.33	1.75
Ca	0.69	0.68	0.49	0.23
Cl	0.07	0.00	0.26	0.00
Со	0.09	0.10	0.09	0.09
Cr	0.10	0.12	0.12	0.13
Cu	0.03	0.03	0.03	0.04
Fe	48.38	49.56	49.54	51.15
K	0.14	0.15	0.14	0.00
Mg	3.82	3.44	3.53	2.92
Mn	0.32	0.31	0.30	0.31
Na	0.17	0.00	1.12	0.20
Ni	0.81	0.74	0.96	0.84
Р	0.02	0.01	0.01	0.01
S	0.00	0.00	0.02	0.03
Si	3.97	3.42	2.86	0.94
Ti	37.60	38.09	36.69	39.85
V	1.32	1.32	1.39	1.45
Zn	0.03	0.03	0.04	0.03
Zr	0.03	0.04	0.04	0.02
Sum	100.00	100.00	100.00	100.00

Table 19: Comparison of chemical compositions of filterbox and bed material in MOEXC2





Figure 58: Solid Samples; left: Bed material between MOEXC2 and MOEXC3 right: Filterbox content after MOEXC3

Unfavourable Redox Potential

In the following, some considerations and a brief discussion of chemical reactions with the Ni- 19γ -Al₂O₃ which could account for the low increase of conversion with increasing Ni concentration are given. It has been stated that the reforming reaction (R20), which is catalyzed by metallic Ni, seems to be the critical reaction step in the reaction cycle. Therefore, it seems to be useful to look at the reduction reactions which can occur in the fuel reactor and could lead to the formation of metallic Ni, FeTiO₃, Fe₃O₄, FeO or even Fe. In particular these are the already mentioned reactions (R9)-(R12), (R27)-(R28). Furthermore the following reactions shall be considered:

$$CO + NiAl_2O_4 \rightarrow CO_2 + Ni + Al_2O_3$$
(R29)

$$H_2 + NiAl_2O_4 \rightarrow H_2O + Ni + Al_2O_3$$
(R30)

$$CO + Fe_3O_4 \rightarrow CO_2 + 3FeO$$
 (R31)

$$H_2 + Fe_3O_4 \rightarrow H_2O + 3FeO \tag{R32}$$

$$CO + FeO \rightarrow CO_2 + Fe$$
 (R33)

$$H_2 + FeO \rightarrow H_2O + Fe$$
 (R34)

$$CO + Fe_2O_3 + 2TiO_2 \rightarrow CO_2 + 2FeTiO_3$$
 (R35)

$$H_2 + Fe_2O_3 + 2TiO_2 \rightarrow H_2O + 2FeTiO_3$$
(R36)

An overview on the redox systems which may play a role in the fuel reactor and the reducing gases is presented in Table 20:

Redoxsystem	CO	H_2
NiO/Ni	R27	R28
NiAl ₂ O ₄ /Ni	R29	R30
Fe ₂ O ₃ /Fe ₃ O ₄	R11	R12
Fe ₃ O ₄ /FeO	R31	R32
FeO/Fe	R33	R34
Fe ₂ TiO ₅ /FeTiO ₃	R9	R10
Fe ₂ O ₃ /FeTiO ₃	R35	R36

Table 20: Relevant redoxsystems and reactions in the FR

The following figures depict the temperature dependency of the reactions listed in Table 20. Figure 59 depicts the reactions with H₂; Figure 60 depicts the reactions with CO. The dashed red line marks the fuel reactor temperature of T_{FR} =960°C. It can be seen that NiO and NiAl₂O₄ will thermodynamically be reduced only when all Fe(III) species (Fe₂O₃ and Fe₂TiO₅) are reduced. It is also evident that the reduction to FeO or to metallic Fe requires high H₂ or CO partial pressures, respectively and is, thermodynamically, not expected to happen in CLC fuel reactors.



Figure 59: T-Dependency of partial pressure ratio p_{H2}/p_{H20} for redox reactions in fuel reactor (data from HSC6.2, see [90])



Figure 60: T-Dependency of partial pressure ratio p_{CO}/p_{CO2} for redox reactions in fuel reactor (data from HSC6.2, see [90])

5 Conclusions and Outlook

The performance results for increasing content of Ni-19 γ Al₂O₃ catalyst show that

- 1. Ni- $19\gamma Al_2O_3$ seems to have but a slightly higher CH_4 reforming activity than ilmenite under the conditions investigated
- 2. Ni- 19γ Al₂O₃ has a lower reactivity for conversion of CO to CO₂ compared to ilmenite
- 3. An increase of temperature of about 55°C results in an increase of CH₄ conversion of about 10 % points
- 4. The CH_4 conversion level and the CO_2 yields decrease (only) linear with decreasing air/fuel ratio.
- 5. With syngas the H_2 conversion level stays close to the level of ilmenite, while the CO_2 yield slightly decreases.
- 6. Ilmenite shows a relatively high attrition rate of 3-4 kg/h which is about 3-5% of the inventory, whereas Ni-19 γ Al₂O₃ shows a considerably lower attrition rate of 0.04 kg/h. This corresponds to an estimated inventory/fuel power relation of about 1t/1 MW (whereas the best Ni-based oxygen carriers have an inventory of 25-50 kg/MW).
- 7. The ilmenite attrition rate shows an increase with increasing fuel power (circulation rate).

It is therefore justified to conclude that $Ni-19\gamma Al_2O_3$ could not develop its catalytic properties. This is very likely because reduction to metallic Ni did not take place in the FR despite the fact that CO/CO₂ and H2/H₂O ratios in the FR off-gas would emphasize reduction of NiO thermodynamically.

Possible reasons for not reducing NiO are:

- The presence of NiO as Ni- $19\gamma Al_2O_3$ exhibiting slow reduction kinetics compared to the low mean residence time in the reactor.
- Locally low CO/CO₂ and H2/H₂O ratios because of the presence of Fe_2O_3/Fe_3O_4 and $Fe_2TiO_5/FeTiO_3$, leading to a competition for the CO and H₂ respectively.

As a general conclusion, catalysts which exhibit highest steam reforming reactivity at fully reduced conditions are not necessarily suitable as rate promoters in mixed oxide CLC.

In order to clarify, whether the missing reforming capability is a behaviour which also can be observed at higher contents of Ni-19 γ -Al₂O₃, or if there are other mechanisms or formation of chemical compounds, which inhibit the reforming the following suggestions for further work are made:

- 1) At least one further experiment with a higher content of Ni- 19γ -Al₂O₃ (equal to e.g. 10% NiO) shall be performed to have further evidence for the extrapolated conversion curve progression.
- 2) The particles in the bed material shall be investigated with respect to their particle size distribution, particle structure (using polished sections) and particle composition (e.g. using XRD) and their particle surface (e.g. using BET adsorption measurements).
- 3) Measures shall be taken in the reactor in order to enable a longer gas/solids contact time

- 4) The (linear) attrition model shall be further refined (e.g. taking into account influence of temperature, circulation rate etc.) and results from particle analysis shall be taken into account. Methods for investigation of particle attrition under high temperatures shall be developed and e.g. applied to (the components of) a mixture before doing experiments in the pilot plant.
- 5) The extrapolation methods based on XRF results shall be further elaborated and their applicability to other mixed oxide systems shall be verified. Further extrapolation methods shall be developed and the accuracy of all methods shall be tested in order to allow reducing the number of operation points in an experiment.
- 6) The influence of other (particle) parameters such as particle size, particle hardness (crushing strengths) etc. on attrition shall be systematically investigated.
- 7) Methods for clarification and elucidation of the differences in reaction mechanisms of CH₄ conversion on mixed oxides shall be developed and applied. In order to reach a deeper understanding of the changes in reaction mechanisms when mixing metal oxides probably also ab-initio calculations shall be applied.

Alternatively, other mixed oxide combinations based on Ni-materials which exhibit better CH_4 conversion performance even in oxidized state can be considered and investigated.

6 Acronyms and Abbreviations

AET	Advanced Energy and Technology (Library)
AR	Air Reactor
AR _{fg}	Air reactor flue gas
AV	Average
BET	Brunauer, Emmett, Teller (Adsorption Isotherm)
CCS	Carbon Capture and Storage
CLC	Chemical Looping Combustion
CLOU	Chemical Looping Oxygen Uncoupling
DCFB	Dual Circulating Fluidized Bed
DLL	Dynamic Link Library
ECBM	Enhanced Coal Bed Methane Recovery
EOR	Enhanced Oil Recovery
EU	European Union
FR	Fuel Reactor
FR _{pg}	Fuel reactor product gas
FTB _{og}	Fire tube boiler off-gas
GHG	Green House Gases
IEA	International Energy Agency
IR	Infrared (Radiation)
LC	Linear Combination
LLS	Lower Loop Seal
LSQF	Least Squares Fit
MCA	Multi Channel Analyser
MDK	Model Development Kit
MOEXC1	Mixed Oxides Experimental Campaign 1 (Ilmenite Benchmark)
MOEXC2	Mixed Oxides Experimental Campaign 2
MOEXC3	Mixed Oxides Experimental Campaign 3
NDIR	Non Dispersive Infrared
NG	Natural Gas
OECD	Organisation for Economic Cooperation and Development
PTFE	Polytetrafluoroethylene
SRES	Special Report on Emission Scenarios
TGA	Thermogravimetric Analysis
TMS	Total Mass of Solids
ULS	Upper Loop Seal
UV	Ultraviolet (Radiation)
wt	Weight
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence
XRFCC	XRF Derived Compositions (Calculated)
XRFCM	XRF Derived Compositions (Measured)
YSZ	Yttrium Stabilized Zirconia

7 Symbols, Notation and Units

Greek Symbol	Notation	Unit
$\alpha_0, \alpha_1, \alpha_2$	Coefficients according to equation (35), (36) and (38)	[-]
α_n, β_n	Linear combination coefficients (masses) in equation (32)	[kg]
3	Porosity	[-]
θ	Angle between incident ray and atomic layer	[°]
λ	Air/fuel ratio	[-]
λ	Wave length	[m]
$\lambda_{e\!f\!f}$	Effective air/fuel ratio	[-]
μ_g	Dynamic viscosity	[Pa.s]
v	Frequency	$[m^{-1}]$
v_i	Stoichiometric coefficient	[-]
$ ho_f$	Fluid density	[kgm ⁻³]
$ ho_g$	Gas density	[kgm ⁻³]
ρ_p	Particle density	[kgm ⁻³]
ρ_s	Solid density	[kgm ⁻³]
φ_p	Particle sphericity	[-]
Ω	Dimensionless gas velocity expression in Reh diagram	[-]

Roman Symbol	Notation	Unit
AD_{AR}	Air demand in AR	$[m^3s^{-1}]$
A_p	Particle area, particle cross section	[m ²]
Ar	Archimedes Number	[-]
A _{reactor}	Reactor cross section	[m ²]
С	Velocity of light (299792458 ms ⁻¹)	$[ms^{-1}]$
C_w	Drag coefficient	[-]
d	Distance between atomic layers in equation (25)	[m]
d_p^*	Dimensionless particle size	[-]
D	Diameter	[m]
d_p	Particle diameter	[m]
Ē	Energy	[W]
Fr	Froude number	[-]
Fr_p	Particle specific Froude number	[-]
g	Standard gravity (9.80665 ms ⁻²)	[ms ⁻²]
Н	(Reactor) Height	[m]
h	Planck's Wirkungsquantum (6.62606957*10 ⁻³⁴ Js)	[Js]
K _{MOx}	Equilibrium constant in pressure units	$[bar^{\Delta v_1}]$
L _{tot}	Total volume stream of air	$[m^3 s^{-1}]$
L _{tot}	Total volume stream of air	$[m^3 s^{-1}]$
m	Mass	[kg]
M	Molar mass (e.g. $M_{Fe_2O_3}$ molar mass of Fe ₂ O ₃)	[kgmol ⁻¹]
$m_{bed}^{e\!f\!f}$	Effective bed mass	[kg]
m _{init}	Initial (bed) mass	[kg]
m _{bed}	Bed mass in reactor	[kg]
<i>m</i> _{i,added}	Mass added to the reactor during mixed oxides campaign	[kg]
<i>m</i> _{i.attrition}	Mass entrained from the reactor due to attrition	[kg]

Roman Symbol	Notation	Unit
m _{i,sampling}	Mass subtracted from reactor for sampling	[kg]
m _{ox}	Mass of fully oxidized material	[kg]
moxides	Mass of oxides	[kg]
<i>m</i> _{oxides_red}	Mass of reduced oxides	[kg]
m _{red}	Mass of fully reduced material	[kg]
'n	Molar flow rate of CO	[mols ⁻¹]
р	Pressure	[Pa]
p_{CH_4}	Partial pressure of CH ₄ (analog p_{CO_1} , p_{CO_2} , p_{H_2})	[Pa]
Р	Power	[kW]
Δp	Pressure difference	[Pa]
R_0	Oxygen transport capacity	[kg/kg]
Re	Reynolds Number	[-]
Re_p	Particle specific Reynolds Number	[-]
RSS	Sum of residua	[-]
Т	Temperature	[K]
t_AR	Mean residence time in the air reactor	[s]
t_FR	Mean residence time in the fuel reactor	[s]
T_{FR}	Fuel reactor temperature	[K]
U	Superficial gas velocity	[ms ⁻¹]
U^*	Dimensionless velocity	[-]
U_{mb}	Minimum bubbling velocity	[ms ⁻¹]
U_{mf}	Minimum fluidization velocity	$[ms^{-1}]$
<i>u</i> _t	Terminal velocity	$[ms^{-1}]$
Wox	Weight fraction of oxide	[-]
$X_{s,ox}$	Solids conversion level for oxidation	[-]
X _{CH4}	Methane conversion (analog X_{H_2} , X_{CO} , X_{CO_2})	[-]
<i>x</i> _{<i>CH</i>₄}	Volume fraction of dry methane in exhaust gas (analog x_{CO_2}	[vol%]
	and x_{co})	
$Y_{CO_2,methane}$	Carbon dioxide yield with methane fuelling	[-]
$Y_{CO_2,syngas}$	Carbon dioxide yield with syngas fuelling	[-]
XRFCC	XRF derived calculated composition vector	[-]
(XRFCM) _{ilmenite}	XRF derived measured composition vector e.g. for ilmenite	[-]
<i>x</i> [*] <i>x</i> [*]	Deviation of Ni carrier content value from mean value	[kg/kg]
	(residuuiii)	[]ra/!ra]
X _i		[kg/kg]
\overline{x}	Mean Ni carrier content value	[kg/kg]
y_i^*	Deviation of element mass fraction value from mean value (residuum)	[kg/kg]
y _i	Element mass fraction value	[kg/kg]
\overline{y}	Mean element mass fraction value	[kg/kg]

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