

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Using affordable materials from metallurgical industries in Oxygen Carrier Aided Combustion and Chemical-Looping Combustion

FELICIA ELIASSON STÖRNER

Department of Space, Earth and Environment

CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2022

Using affordable materials from metallurgical industries in Oxygen Carrier Aided Combustion and Chemical-
Looping Combustion
FELICIA ELIASSON STÖRNER

© FELICIA ELIASSON STÖRNER, 2022.

Department of Space, Earth and Environment
Chalmers University of Technology
SE-412 96 Gothenburg
Sweden
Telephone + 46 (0)31-772 1428

Department of Space, Earth and Environment
Gothenburg, Sweden 2022

Abstract

Oxygen carriers are solid oxides of transition metals that can be used to convert fuel in the absence of gaseous oxygen in a process called Chemical-Looping Combustion (CLC). The use of oxygen carriers makes it possible to produce undiluted CO₂ without expensive gas separation. High-concentration CO₂ is a requirement in carbon capture and storage (CCS), which is considered a promising path for climate change mitigation. Oxygen carriers can also be used as bed material in fluidized bed conversion, and in that case provides enhanced oxygen distribution in the furnace. The concept is called Oxygen Carrier Aided Combustion (OCAC), and has been implemented in several existing biomass-, or municipal solid waste-fired boilers with ilmenite as oxygen carrier.

This thesis examines utilizing oxygen carriers for the conversion of biomass and waste-derived fuels. Such fuels contain reactive ash species, which cause operational problems in the boiler such as corrosion, bed agglomeration, and slagging. Historically, much of the CLC-research has been on synthetic oxygen carriers with high reactivity. However, since the lifetime is expected to become quite low due to contamination of ash, they are likely not economically viable with these low-grade fuels. Here, the focus instead is on low-cost materials. The situation in Sweden is quite unique, since affordable metal oxide particles are produced in large quantities in our metallurgical industries. Several products and by-products from these industries are potential oxygen carriers. This thesis summarizes and discusses the large-scale utilization of oxygen carriers for OCAC in Sweden. Ilmenite is the most studied oxygen carrier for this purpose, but some other low-cost materials have also been tested in semi-industrial scale. The general findings are that implementing OCAC in already existing fluidized bed boilers is possible and enables a decrease in air-to-fuel ratio.

Since biomass and waste fuels have complex and reactive ash compositions, they react with, and affect the lifetime of oxygen carriers. This thesis, therefore, also discusses ash interactions with some low-cost materials. Potassium is considered the most problematic ash element. Potassium is reactive with bed material and causes deposit formation and corrosion on the boiler, among other problems. Fixed bed interaction experiments have been conducted in this work with different potassium salts and oxygen carriers to study the changes in the materials with respect to composition and reactivity. Two by-products from steelmaking (LD-slag and iron mill scale) were studied in fixed bed interactions experiments. Also, as part of the work, a new lab-scale method which allows for improved experiments in a fluidized bed reactor has been developed. The method was used to study the effect of the accumulation of potassium on reactivity and fluidization of oxygen carriers. The study was conducted with ilmenite as oxygen carrier and K₂CO₃ as ash model compound. The addition of K₂CO₃ caused defluidization in ilmenite and diffusion of K into the particles.

Acknowledgments

I want to thank Magnus for always taking time to discuss the work and helping me understand when to continue planning and when to get going with stuff. You seem to always trust what we're doing and that makes me feel calm and happy. Not to mention our lunch discussions which are like a roller coaster of discussion topics (in an enjoyable, thrilling and mind-boggling kind of way!)

Many warm thanks to my supervisors Pavleta and Fredrik. Meetings with Pavleta always makes me excited for what's ahead. Fredrik welcomed me to my PhD studies in a very warm way and made me feel like this will be something doable and fun. Thank you Tobias for being an excellent examiner and teacher, you are always thorough and help me out with the details. I'm looking forward to continue working with all of you for another couple of years.

A lot of time with this thesis has been spent in the lab. Work in the lab can sometimes feel like being trapped in a maze (full of glowing hot steel, carbon monoxide and anxiety). Fortunately there are some real heroes out there that always take time to help me out with grumpy pressure transducers and various other problems. Thank you Rustan, Johannes, Fredrik, Tomas, Ivan, Victor, Viktor and Daofeng for that. I hope that I can give back to the lab community now that you've taught me so much (mainly patience!!!). Thank you also to Henrik for sharing your knowledge about experimental methods and keeping my mood up. And for introducing me to oxygen carriers in the first place!

I'm very grateful for the social environment created by my colleagues at Energiteknik and Chemistry. It feels like an honor to be working with such intelligent, interesting, enthusiastic, considerate, witty, hilarious, resolute, resourceful people. I'm having fun every day, and having fun is one of my biggest interests!

Many hugs and thank yous to my family for being my best friends and always encouraging me to be creative and believe in myself. Thank you morfar for reading and being interested in my work and for taking me to Universeum as a kid. Thank you Roland for all your love and for taking care of me during the last weeks of writing this thesis.

Felicia Eliasson Störner
Göteborg, November 2022

List of publications

This thesis is based on the following publications:

- I. Störner F, Hildor F, Leion H, Zevenhoven M, Hupa L, Rydén M. Potassium ash interactions with oxygen carriers steel converter slag and iron mill scale in Chemical-Looping Combustion of biomass – experimental evaluation using model compounds. *Energy & Fuels* 2020; 34:2304-2314.
- II. Störner F, Lind F, Rydén M. Oxygen Carrier Aided Combustion in Fluidized Bed Boilers in Sweden—Review and Future Outlook with Respect to Affordable Bed Materials. *Applied Sciences* 2021;11:7935.
- III. Störner F, Knutsson P, Leion H, Mattisson T, Rydén M. A new experimental method for studying ash interactions with oxygen carriers in a bubbling fluidized bed – CLC experiments with ilmenite, methane, and K_2CO_3 . To be submitted for publication 2022.

Felicia is the main author of all three papers. Felicia has done the experimental work and the data evaluation for Paper I and Paper III, and taken a major role in the planning of the experimental work.

Table of contents

Chapter 1: Introduction.....	1
Aim and Scope of the thesis	2
Publications	3
Chapter 2: Theory and background.....	5
Solid fuel CLC	6
Oxygen Carrier Aided Combustion (OCAC).....	7
Oxygen carriers	9
Biomass ash and interactions in the boiler.....	10
Chapter 3: Methodology.....	15
Fixed bed experiments (Paper I).....	15
Thermogravimetric analysis (Paper I)	16
Fluidized bed experiments (Paper III)	17
Materials.....	19
Material analysis.....	21
Literature review (Paper II)	21
Chapter 4: Results and discussion	23
Review of OCAC activities (Paper II)	23
Review of bed material flows (Paper II)	25
Ash interactions (Paper I and III)	28
Chapter 5: Conclusions.....	37
Chapter 6: Future studies.....	38
References	39

Chapter 1: Introduction

To limit global warming, novel ways to reduce CO₂ emissions to the atmosphere are sought. Since fossil fuels are the main energy source globally, it is necessary to not just reduce but to eliminate or even reverse emissions, to keep within the limits stated in the Paris agreement. Carbon Dioxide Removal (CDR) is identified as central in limiting global warming to 1.5°C, according to the IPCC special report on global warming published in 2018 [1]. One measure for obtaining net negative CO₂ emissions is to capture CO₂ from the combustion of biomass. This is referred to as Bio-Energy Carbon Capture and Storage (BECCS, or Bio-CCS). Direct air capture, reforestation, and storage of biochar are other suggested pathways to bind CO₂ from the air and store it in carbon sinks [2].

Several different carbon capture and storage (CCS) strategies have been suggested. Most of them are based on so-called post-combustion carbon capture. The flue gas from a combustion process contains CO₂, N₂, and some oxygen, but CCS requires pure CO₂. In post-combustion CCS, the CO₂ is therefore extracted from the flue gas by means of for example absorption. Post-combustion CCS is energy intensive. Thus, it will typically reduce the overall energy efficiency of the combustion plant. Another option is oxy-fuel combustion, where the combustion air is replaced by pure oxygen. This requires air separation (for oxygen production) which also is an energy-intensive process. A way to make CCS more attractive is to find an efficient technology for separating CO₂ from the other flue gas components without large energy penalties. Chemical-Looping Combustion (CLC) is one such technology that has shown promising preliminary results.

CLC utilizes a type of material called oxygen carriers. The idea of using oxygen carriers for the production of pure CO₂ from fossil fuels was first patented in the 1950s by Lewis and Gilliland [3]. They suggested using an oxygen carrier based on copper oxide and performing the conversion in either a fluidized or moving bed. The concept is illustrated in Figure 1, and Ishida et. al later named the process Chemical-Looping Combustion [4].

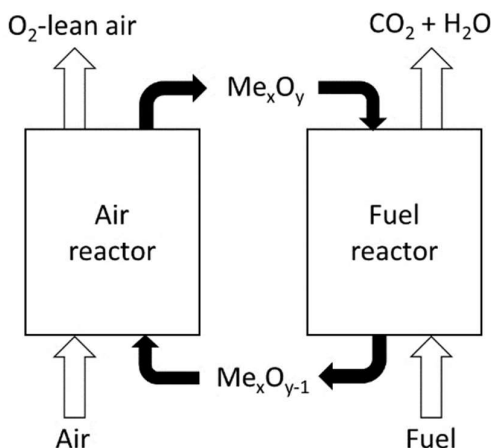
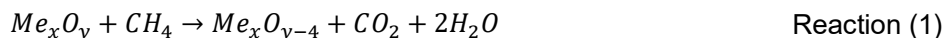


Figure 1: Illustration of the CLC concept (Figure from Paper II)

In the CLC process, the fuel is added to and converted inside a separate fuel reactor. The fuel is oxidized to CO₂ and H₂O through a reaction with the oxygen carrier, in which the oxygen carrier becomes reduced. The reaction is exemplified in Reaction (1) with a general, oxidized oxygen carrier Me_xO_y and methane as fuel.



The reduced oxygen carrier Me_xO_{y-4} is transported to the air reactor and is there re-oxidized according to Reaction (2) (air nitrogen is inert and therefore left out from the balance).



The overall reaction and enthalpy of the process are the same as for conventional methane conversion, Reaction (3).



The oxygen carrier is transported back and forth between the reactors to facilitate fuel conversion. The oxidation of the oxygen carrier (Reaction 2) is strongly exothermic, and the reaction with the fuel (Reaction 1) is mildly endothermic for most combinations of fuel and oxygen carriers. The circulation rate of the oxygen carrier must be adjusted to transport both oxygen and heat from the air reactor to the fuel reactor. There are several possible advantages of CLC, compared to conventional combustion. The main advantage is that the flue gas stream from the fuel reactor is free from air. That means that carbon capture from the technology is, in theory, simple and that CCS could be realized without expensive gas separation processes. CLC is one of several chemical-looping technologies presented so far. Gasification is another, similar process that can be run as a chemical-looping process to make use of the inherent separation between conversion products and air [5].

In parallel with developing chemical-looping technologies, the idea of using oxygen carriers directly in Fluidized Bed Combustion (FBC) has emerged. The concept has been named Oxygen Carrier Aided Combustion (OCAC) [6] and has been implemented in a few biomass and waste boilers. Conventional FBC suffers from some non-ideal mixing and fuel-oxygen contact, which results in uneven temperature profiles and emissions of unconverted fuel components. The introduction of oxygen carriers to FBC enhances the process by increasing the availability of oxygen in the boiler. Industrial OCAC operation is not only desirable from an operational point of view. OCAC could also create a market for oxygen carriers and experience in using them. This potentially lowers the threshold for implementing CLC at a later stage.

Aim and Scope of the thesis

This thesis aims to facilitate the introduction and utilization of oxygen carriers on an industrial scale for the conversion of biomass and waste fuels. Many previous studies have been done to develop new materials, but the focus here is on using materials that are more or less readily available on the market.

The goal was to both map out available products and investigate some performance parameters of such materials experimentally. Since the primary area of interest is for utilization with solid biomass and waste fuels, the experimental study aimed to better understand ash interactions with a focus on potassium, which is considered the most problematic ash element in the targeted plant types.

Publications

The work presented in this thesis is published/submitted as three publications, listed in Table 1. Papers I and III are based on lab-scale experimental work that aims at understanding the interactions between ash-forming species and oxygen carriers on a detailed level. Paper II is a review of large-scale oxygen carrier aided combustion and oxygen carrier production and utilization.

Table 1: Content of papers included in this thesis.

Paper I

Paper I is an experimental study of alkali ash interactions with two waste-derived oxygen carriers. The paper evaluates how some potassium compounds interact with the oxygen carriers in a fixed bed under reducing conditions and discusses ash interaction aspects such as agglomeration and deactivation.

Paper II

Paper II is a review and future-oriented paper. The aim was to discuss oxygen carrier utilization from a broader perspective, taking into account practical issues like transportation, procurement, and cost of oxygen carriers. Large-scale OCAC operation was reviewed, and different sources of potential low-cost oxygen carriers were discussed with a focus on Sweden and the Nordics.

Paper III

Paper III aimed at developing an improved method for investigating alkali interactions with oxygen carriers. The methodologies for ash interaction experiments have previously been mainly fixed-bed interactions with model compounds or sampling from large-scale combustion. A reactor was manufactured for measuring both fuel conversion and fluidization in a controlled environment. Experiments were performed with ilmenite and a potassium salt to simulate the accumulation of fuel potassium.

Chapter 2: Theory and background

CLC as a combustion technology has been subject to research during the last 25 years and several pilot-scale experiments have been conducted. The most common technological solution for CLC is to connect two fluidized bed reactors in which the oxygen carrier makes up the bed material of the two reactors, as suggested by Lyngfelt, Leckner & Mattisson [7]. The air reactor is typically a circulating fluidized bed (CFB) in which the oxygen carrier is entrained with the fluidizing gas (air). After being separated from the gas in cyclones, the oxygen carrier falls into the fuel reactor, which is typically a bubbling fluidized bed (BFB). On its way through the reactor system, the oxygen carrier passes through loop seals (a fluidized u-shaped passage) which hinders air from escaping to the fuel reactor and vice versa. There are many different suggested setups and technological solutions to enhance the conversion and CO₂-capture efficiency [8],

CLC of solid fuel in a continuous, pilot-scale reactor was first demonstrated in 2008 in a 10 kW unit at Chalmers [9]. The demonstration was done with coal as fuel and ilmenite as oxygen carrier. The scale of demonstration with biomass is in the size range of 1-100 kW [10]. The Chalmers 12 MW_{th} research boiler has been operated in what can be described as a CLC/CLG mode with spruce wood pellets as fuels [11]. However, this operation resulted in relatively low operational parameters like CO₂ capture efficiencies and fuel conversion, because the unit is not built for chemical-looping operations. A coal-fired demonstration unit of up to 4 MW thermal capacity is currently being constructed in China in a collaboration between European and Chinese actors [12].

Techno-economical evaluations of CLC have found that the cost of capturing CO₂ with CLC could be somewhere between 10-30 €/ton, including the cost for CO₂ compression to 110 bar [13]. In comparison, a recent case study indicates a range of 45-125 €/ton CO₂ for post-combustion (via amine absorption) from biogenic sources in combined heat and power plants in Sweden [14] (including transport to the nearest harbor, making up roughly 10% of the calculated cost).

CLC has yet to be demonstrated at a truly industrial scale. OCAC, on the other hand, has been successfully demonstrated and implemented with more or less no adaptation of existing boilers [15]. OCAC was first demonstrated in 2012 in Chalmers 12 MW CFB-type research boiler with ilmenite [6]. The concept has since then been implemented in several industrial boilers in Sweden [16]. The general findings are that there are several advantages when it comes to boiler load and emissions. A simplified overview of the development from conventional combustion to CLC is illustrated in Table 2. When there is an oxygen carrier in the bed, there are additional reaction mechanisms between the fuel and oxygen compared to when the bed is silica sand.

Table 2: Overview of the development from FBC to CLC

Fluidized Bed Combustion (BFB/CFB)	Oxygen Carrier Aided Combustion (OCAC)	Integrated Gasification Chemical-Looping Combustion (iG-CLC)
Conventional setup	Fundamental design change Oxygen carrier constitutes the bed material	Fundamental design change Conversion is separated into fuel reactor and air reactor
	Retrofit of existing FBC plants	Fundamentally new design
	Boiler effects (main) Additional heterogenous (solid-gas) oxygen-fuel reaction Oxygen buffering in time and space Enhanced fuel conversion	Boiler effects (main) Inherent separation of CO ₂ from other flue gases
	Large-scale effects Lowered CO emissions Increased efficiency Increased boiler load	Large-scale effects Zero or negative CO ₂ -emissions when connected to CO ₂ -storage

Solid fuel CLC

Review studies show that much of the early CLC research was done with gaseous fuels, but work with solid fuels has been done more recently [17], [18], [19]. There are significant conceptual differences between solid fuel and gaseous fuel CLC units. Gaseous fuels can be injected in the bottom of the fuel reactor and make up the main part of the fluidizing gas. The fuel is in immediate contact with the oxygen carrier and is directly converted to the combustion products. Solid fuels, on the other hand, have a more complex conversion path in the boiler. This is because solid-solid reactions have a low probability to occur. The fluidizing gas in the fuel reactor is steam or a mixture of steam and CO₂ to enable the gasification of the fuel char [17].

Solid fuels consist of four main components; moisture, volatiles, char, and ash-forming matter. The conversion steps with solid fuels are illustrated in Figure 2. When the fuel is inserted in the boiler it heats up, which initiates the drying process and the moisture is released as steam. The volatiles fraction then evaporates quickly from the fuel and contains hydrocarbons that are converted by reacting with the oxygen carrier. In the absence of gaseous oxygen (like in CLC without oxygen release from the oxygen carrier), there is no direct char combustion. The char particle remains in the bed and is gasified by steam and CO₂. This is referred to as in-situ Gasification-CLC (iG-CLC). Some oxygen carriers have the property that they release gaseous oxygen in under reducing conditions, and can be used in a process called Chemical-Looping Oxygen Uncoupling (CLOU) [20]. In CLOU, the char is converted directly via char combustion. Alternative configurations with external gasification are also suggested, but will not be considered further in this work. The gasification reactions create CO and H₂ and these, in turn, are converted by the oxygen carrier into combustion products. Char gasification is by far the most time-consuming step in solid fuel CLC [21], [22]. The slow gasification step is replaced by a faster char combustion step when using oxygen carriers with CLOU-properties.

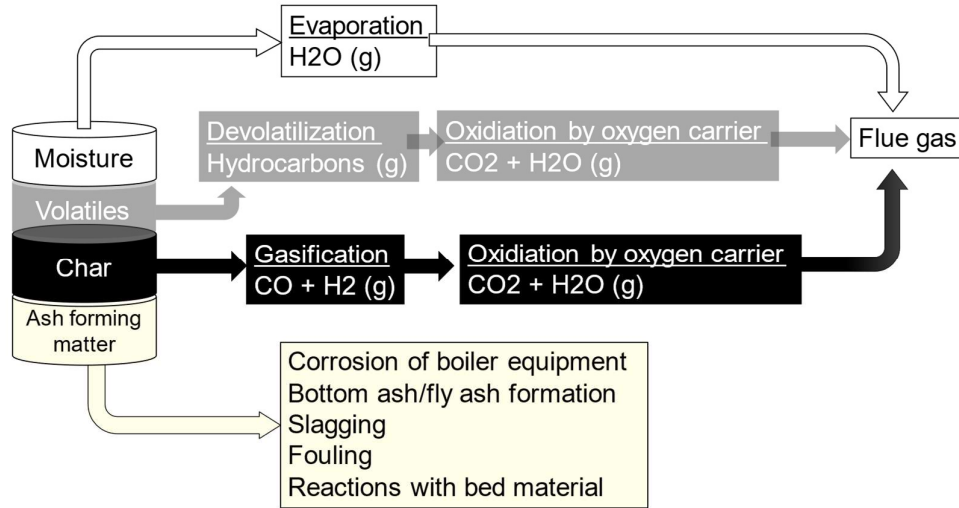


Figure 2: Solid fuel conversion mechanisms in a CLC process.

The ash-forming matter is the remaining fraction, and it undergoes several transformations in the boiler, finally ending up as ash. The release and reactions with the ash in the boiler are complex and will be discussed in more detail later.

Different solid fuels have different distributions of the four fuel components presented in Figure 2, as well as different compositions within the volatiles, char, and ash fractions. Biomass fuels, which are the focus of this study, have a relatively large share of volatiles and moisture compared to coal. Further, biomass char is more reactive and more readily gasified compared to coal char. This has a significant impact on the choice of conversion parameters like solids residence time. A too-low residence time of solids results in unconverted char particles being transferred to and converted in the air reactor. At the same time, a sufficiently high recirculation of the bed materials is required to transport enough heat and oxygen from the air reactor. Unit designs and process parameters will not be further discussed in this thesis but have been discussed extensively elsewhere (Adánez et al. [23], Lyngfelt & Leckner [24], Lyngfelt et al. [13] and Lyngfelt [18] to mention a few).

Oxygen Carrier Aided Combustion (OCAC)

Sweden has a long history of combusting residues from the forestry industry as well as various other wastes, both for waste handling and energy production purposes. The complex nature of solid biomass and waste-derived fuels has made FBC a particularly useful combustion technology in Sweden [25], [26], [27]. Some of the advantages of fluidized beds over other combustion technologies are summarized in Table 3. There are currently around 120 FBC boilers in Sweden.

Table 3: The main advantages of fluidized bed combustion

High thermal inertia in the bed

Sudden variations in fuel composition can be expected when feeding solid fuels, especially waste or waste-derived fuels. A bed with high thermal inertia can keep the temperature and heat transfer in the boiler stable, also during sudden changes in moisture and heating value.

Bed material can absorb volatile ash components

Alkali from ash, and especially KCl, is very corrosive. A part of the released alkali is captured by the bed material and this can reduce the risk of high-temperature corrosion in exposed areas such as the superheater.

Temperature is relatively low

Thermal NO_x formation and severe high-temperature corrosion can be avoided.

Co-combustion of different fuels is possible

A challenge that remains with conventional FBC is that there are limitations in the mixing of fuel, bed, and air. The ideal case is a completely mixed bed where all the fuel is converted and all the heat is released evenly across the bed. In reality, this ideal case is difficult to approach. Insufficient mixing between oxygen and fuel results in unconverted species in the flue gas. Uneven distribution of fuel and oxygen across the boiler results in uneven heat release and, in turn, cold and hot spots in the boiler. This is undesirable for the boiler efficiency and heat transfer equipment (due to thermal stress). In hot spots of the boiler, the temperature also can be high enough for thermal NO_x formation. This is compensated for by having a high air-to-fuel ratio. A high air-to-fuel ratio, however, requires that the equipment is built for handling high flows of gases which is expensive. Large flue gases also result in large heat losses in the stack.

Introducing oxygen carriers in the boiler (OCAC) improves the oxygen distribution across the boiler and the oxygen-fuel contact. The concept was first demonstrated on large scale in the Chalmers boiler in 2012 where 40% of the silica sand was replaced with ilmenite [6]. The conclusions were that the combustion process was enhanced by the enhanced oxygen distribution. The CO emissions decreased by 80% and the NO emissions decreased by 30%. A significant advantage of using oxygen carriers is that the air-to-fuel ratio can be decreased without experiencing problems with increased emissions of unconverted species. The air flow is what typically limits the thermal capacity of the boiler. When a lower air ratio is required, the thermal load of the boiler can be increased without increasing the air flow or changing anything in the boiler setup. A lower air-to-fuel ratio also means a higher CO₂ concentration in the flue gas, which could be important for certain post combustion CO₂-capturing technologies.

Since the initial demonstrations, OCAC has been subject to experiment with several different oxygen carriers and applied to boilers in Sweden with promising results. Large-scale OCAC has been reviewed and will be discussed in more detail in the results chapter of this thesis.

Oxygen carriers

Studying oxygen carriers is a central aspect of CLC and OCAC research. For the CLC and OCAC concepts to be viable, suitable oxygen carriers are required, preferably with a cost that is comparable to that of silica sand. The required properties for an oxygen carrier to be suitable for OCAC or CLC are summarized in Table 4.

Table 4: General requirements for oxygen carriers.

Reactivity with fuel and oxygen

Both conversion and re-oxidation of the oxygen carrier are crucial reaction processes and reactivity should be maintained over many cycles.

Mechanically and chemically stable

During operation the particles are exposed to mechanical stresses, high temperatures, and some cases, reactive ash components in the reactor. Attrition and agglomeration must be on acceptable levels, to limit loss of material and risk for defluidization.

Environmentally friendly

The oxygen carrier should be free from toxic components. Environmental factors should be considered both in the production of the oxygen carriers and for handling of the bottom ash.

Material properties are suitable for fluidized beds

Properties like particle size distribution and density should be suitable for fluidized bed particles. Crushing and sieving processes can be done but are cost- and energy intensive.

Economically feasible

The acceptable cost per kg depends on the application, and the expected lifetime of the material.

These requirements are general. The specific requirements will differ depending on the applications, like choice of fuel. For example, the economic viability of the oxygen carrier is based on the lifetime the material can be expected to have in the boiler. This depends on (among other factors) how the bed material interacts with ash. Biomass and waste CLC and OCAC are assumed to have high ash accumulations and need for high bed material regeneration [10], i.e. that significant amounts of fresh material needs to be added with regular intervals. Thus, the cost of the material becomes very important, as well as the ability of the material to withstand degradation by the ash. It also becomes important to consider things like whether the material can be separated from the ash and recirculated to the boiler, how to handle the bottom ashes and if the rejected material can be utilized elsewhere.

Historically, the oxygen carriers studied the most are synthetic particles with oxides of Fe, Cu, Mn, and Ni [17]. In many cases, the pure metal oxide in itself has a high reactivity but can't sustain good mechanical properties at combustion conditions. The active metal oxide is

therefore mounted on some inert support material. This can potentially produce very powerful materials in terms of fuel and oxygen reactivity. However, the production cost is high and a very long lifetime is required for making them viable. Synthetic oxygen carrier are not further considered in this thesis. They are not likely to be economically viable in combustion of biomass and waste fuels [10], [8].

The materials in focus in this thesis are instead low cost options, which are based on naturally occurring minerals or by-products from metallurgical industries. One well studied such material is ilmenite, which is a titanium-iron oxide that is industrially mined and concentrated for the production of TiO_2 . Ilmenite has been successfully used as bed material in FBC and has properties in line with the requirements in Table 4. Many experimental hours of lab-scale and pilot-scale CLC has been conducted with ilmenite [8]. The other materials that are discussed in this thesis are based on by-products from the steel and copper industries. There are unique prerequisites for utilizing oxygen carriers for combustion in Sweden. There is a widespread utilization of FBC for solid fuel conversion and there are also well-established metallurgical industries producing large amounts of by-products containing iron oxides.

Biomass ash and interactions in the boiler

The ash-forming matter in the fuel plays a significant role in the boiler and the combustion process. The elemental composition of ash-forming matter differs largely from different fuels. Some examples are provided in Figure 3, where the composition is presented as oxides (although the actual composition will contain several different anions). The figure is adapted from *Åbo Akademi University Chemical Fractionation Database* [28].

The chart for coal shows mainly oxides of Si, Al, Fe, and Ca. The ash-forming elements in coal are typically not very reactive in combustion and can accumulate in the fluidized bed without necessarily causing any operational problems. The challenges with coal combustion instead lie in the inherent production of fossil CO_2 , formation of particulate matter, and SO_x emissions.

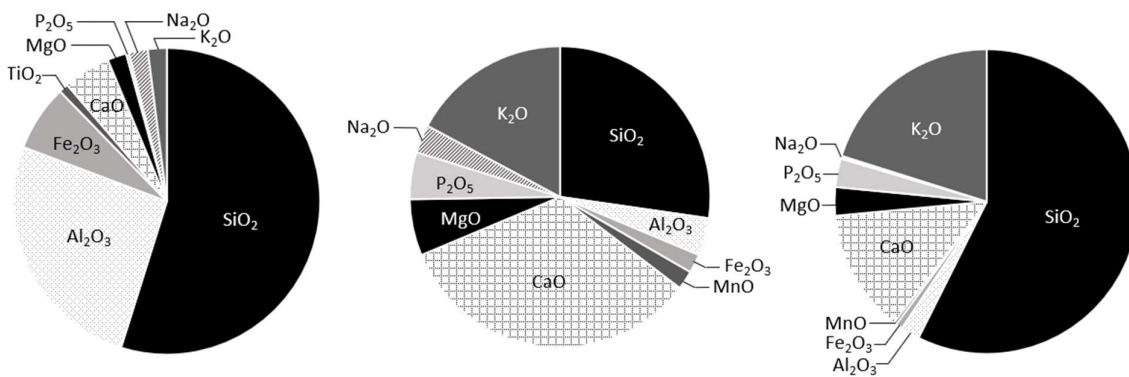


Figure 3: Composition of (from left to right) coal ash, wood ash, straw grasses ash (wt.-%). The components are presented as oxides. [28]. The figure is from Paper III

On the other hand, the charts for woody biomasses and straw grasses show large fractions of K, Si, and Ca, as well as some Na and P. Especially K, Na, and P take place in many reactions in the boiler potentially resulting in slagging, fouling and corrosion on boiler surfaces [29], [30].

The presence of reactive ashes therefore limits the temperature in the boiler. Not visible in the figure is Cl, which also exists in biomass and plays an important role in the ash chemistry of the fuel. Another fuel fraction that is of great importance in the Swedish energy system is waste, which is a broad term and covers many different material streams. Waste can be both renewable and fossil material.

When entering the boiler with the fuel, alkalis are mainly released in the gas phase as hydroxides, sulfates, and chlorides [29], [31]. An overview of possible release and deposit paths in the boiler is given in Table 5. Note that the table is not exhaustive but there are many other factors influencing the final path of the K- and P-species in the boiler [32]. In FBC with silica sand bed material, gaseous K-species attack the silica sand particles which results in a sticky melt formation on the surface of the particles [33]. Other species such as Ca are then incorporated into the melt, which changes the composition of the initial layer. The formation of sticky layers results in agglomeration of bed particles. Many studies have been done to understand the mechanisms of agglomeration and how it can be avoided [33], [34], [35], [36], [37], [38]. However, some build-up of alkali on the particles can also have a positive effect on the conversion due to the catalytic effect that K has on the char gasification [39].

To avoid the negative effects that fuel alkali has on the process, there is a significant replacement of bed material when using biomass and waste as fuels. The overall mineral balances in coal and biomass FBC are illustrated in Figure 4 (and in Paper II in this thesis). The amount of ash forming matter (*fuel minerals*) in coal is high (on for example a weight fraction basis), and bottom ash extraction is required to keep the bed surface at a stable level. The concentration of fuel minerals in the bed can be allowed to be quite high. In biomass combustion, on the other hand, bottom ash extraction is high even though the amount of ash forming matter in the fuel is relatively low. The reason for this is to only allow for a small amount of accumulated ash in the bed, for the reasons discussed earlier. To close the material balance over the unit, the required bed material make-up flow (typically in the form of added silica sand) is high in biomass and waste combustion.

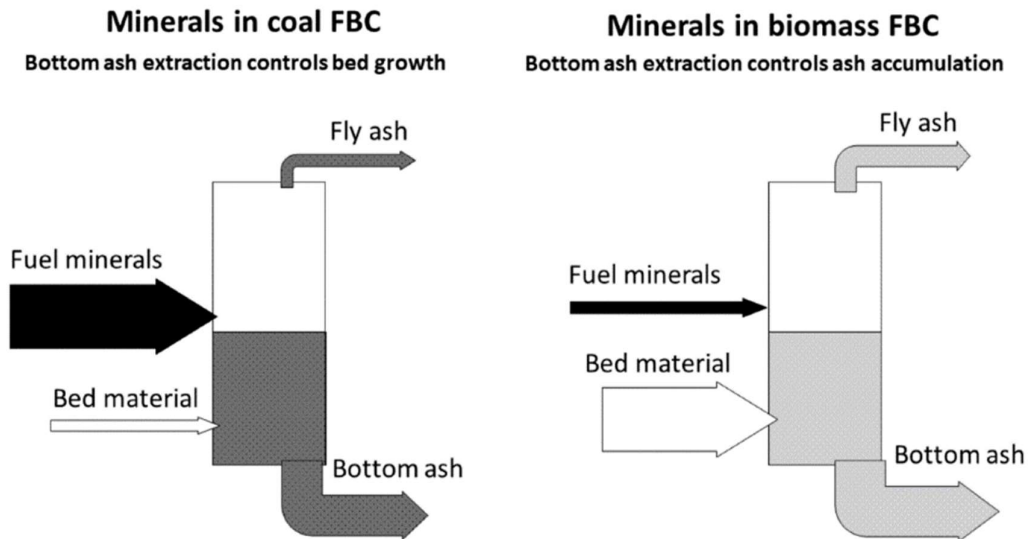


Figure 4: Mineral balance in the boilers (Figure from Paper II)

Table 5: Possible release and deposit formation of K and P, species in boiler conditions.
The table is non-exhaustive.

Presence in biomass				
K	Organically bound			
	Ionic form (aq)			
	Bound to Si	K-silicate	Stable, inert. For example in feldspar	
P	Organically bound			
	Inorganic			
Phosphorous interactions				
Alkali present?	Alkali phosphates		Eutectic mixture	Melts. Deposits on surfaces, causes agglomeration
Ca present?	Calcium phosphates		-	-
Vaporization K(s)/(l)/(aq) -> (g)				
Cl present?	Yes		KCl(g)	Very corrosive
	No	Ox	KOH(g)	
	No	Red	K(g)	
Condensation of KOH(g) and K(g)				
S present?	Yes		K ₂ SO ₄	Forms aerosols in the fly ash
	No	<860°C	K ₂ CO ₃ (s)	
	No	>860°C	K ₂ CO ₃ (l)	
Condensation of KCl(g)				
S present?	Yes		K ₂ SO ₄	Extremely corrosive. Lowers the melting point of fly ash and makes it sticky.
	No	<770°C	KCl(s)	
	No	>770°C	KCl(l)	

Ash interactions with oxygen carriers

Understanding the ash interactions with oxygen carriers in OCAC and CLC is crucial for the processes. Ash interactions and particle aging can have a large impact on the process and the economic viability of different oxygen carriers. The interactions cannot easily be generalized, since the resulting interactions depend on the compositions of both the bed material and the ash [29].

A well-studied oxygen carrier in industrial settings is ilmenite. Some major morphological and chemical differences were found between fresh particles and particles used as bed material in OCAC with biomass as fuel [40], [41]. Ash species accumulated on the particle surface and K and Ca were the components most visibly forming layers on the particles after a few days of operation. K was found to diffuse into the ilmenite and become evenly distributed across the particles. The formation and stability of both $\text{KTi}_8\text{O}_{16}$ and $\text{KTi}_8\text{O}_{16.5}$ have been reported by means of XRD analysis of spent material [41] and thermodynamic calculations [42]. Wiinikka et al. have also concluded that fuel K was retained to a larger extent in the bed instead of evaporating when TiO_2 was added to the fuel [43]. Agglomeration in ilmenite has not been observed, as opposed to silica sand that must be replaced at a high rate in the boiler because of agglomeration [16].

Apart from studying particles from biomass combustion, several studies have been done on interactions between oxygen carriers and ash model compounds. Some of the recent studies are listed in Table 6. Most of the interaction experiments in these studies are performed in fixed beds. Fixed bed experiments are simple and are important for testing extreme conditions. A drawback, however, is that they don't take into account the movements in the bed and don't give realistic conditions for the ash-bed material contact. One of the studies in Table 6 is done with a fluidized bed with dry air as fluidizing gas [44]. Since the gas is air, the study doesn't take into account the influence of the reducing conditions in CLC and OCAC processes. A new method was developed in this work, to combine the effects of fluidization and reducing atmosphere in the combustion process.

Table 6: List of previous experimental studies of interactions between oxygen carriers and ash model compounds

Study	Oxygen carrier	Model compound	Experiment	Atmosphere	Temp
Zevenhoven et al. [44]	Ilmenite	K ₂ CO ₃	Fluidized bed, continuous feeding	Dry air	850°C
		K ₂ SO ₄			950°C
		KCl	Fixed bed, mixtures	Dry air	850°C
		KH ₂ PO ₄			
Hildor et al. [45]	Ilmenite	K ₂ CO ₃	Fixed bed, mixtures	Wet reducing	850°C
		K ₂ SO ₄		Dry reducing	
		KCl			
		KH ₂ PO ₄			
			TGA	Wet cycles Dry cycles	850°C
Staničić et al. [46]	Ilmenite (synthetic) Hausmannite Hematite	CaCO ₃	Fixed bed, mixtures	Dry air	900°C
		K ₂ CO ₃		Wet reducing	
		SiO ₂			
Staničić et al. [47]	Combined Mn-oxides	CaCO ₃ K ₂ CO ₃ CaHPO ₄	Fixed bed, mixtures	Dry air Wet reducing Inert	900°C
Yilmaz and Leion [48]	Pure Fe-oxide	Several Na- and K-based oxides and synthetic ash mixtures	Fixed bed, mixtures	Dry air Wet reducing	950°C

Chapter 3: Methodology

An overlook of the methods used in the work encompassed by this thesis is presented in Table 7. The work includes two separate experimental studies resulting in two publications. The work also includes a literature review providing a general outlook concerning the way forward for utilizing oxygen carriers in Sweden. The review study resulted in a published review paper.

Table 7: Overview of the methods used in this thesis

Paper I – Experimental study	Oxygen carriers	K-salts
Fixed bed experiments to study the possible interactions between 2 waste derived oxygen carriers and some K-salts during CLC conditions. Mixtures of oxygen carrier and a salt were subject to reduction and TGA. Subsequent material analysis to determine changes in material composition.	Waste derived Iron mill scale Steel slag (LD-slag)	K ₂ CO ₃ KCl KH ₂ PO ₄ K ₂ SO ₄
Paper II – Review study Review of industrial scale testing and utilization of oxygen carriers in Sweden. Summarizing of flows of potential oxygen carriers produced in metallurgical and mining industries in Sweden. Thorough discussion of the main practical aspects of utilizing those such as transports, processing, and costs.		
Paper III – Method development and experiments	Oxygen carrier	K-salt
Development of a new method for ash interaction experiments in a lab-scale fluidized bed. The novelty lies in the possibility to combine gas fuel CLC simulation (fuel cycles) with live addition of alkali ash components. Experiments with ilmenite and addition of two alkali salts.	Commercial Ilmenite	K ₂ CO ₃

Fixed bed experiments (Paper I)

Fixed bed interaction experiments were conducted, during which an oxygen carrier and a potassium salt were thoroughly mixed and exposed to wet, reducing conditions at a high temperature for several hours. The experiments aimed to investigate possible interactions between two waste-derived oxygen carriers and four potassium salts. Waste-derived oxygen carriers are interesting for economic reasons but their behavior in combustion settings is not yet well understood. The setup used for the fixed bed experiments consisted of a horizontal, tubular furnace in which a reactor was placed. An illustration is presented in Figure 5.

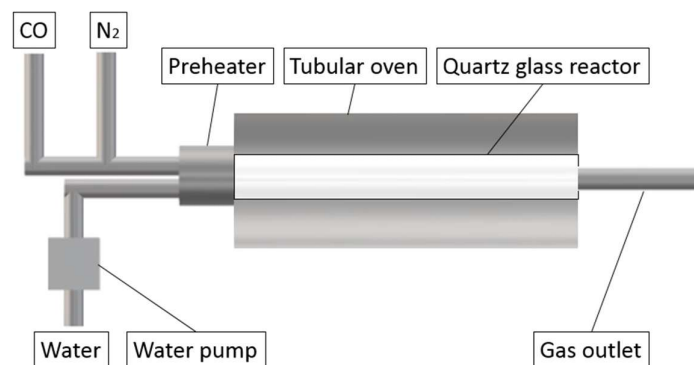


Figure 5: Experimental setup for the fixed bed interaction experiments presented in Paper II

The reactor was a cylindrical quartz glass vessel and gas lines were connected to both ends of the reactor. The inlet gases were fed together with water into a preheater where the water evaporated and the resulting gases were mixed and heated to around 300°C. The solid mixtures were prepared by mixing the oxygen carrier with a potassium salt so that the K-content in the mixture was 4 wt.-%. The mixtures were prepared so that there would be close solid-solid contact between the two components. The sample (1g of oxygen carrier-salt mixture) was placed in a ceramic crucible and placed in the glass vessel. After placing the sample in the reactor, the temperature was increased, and the CO and steam were included in the gas mixture when the reactor reached 850°C. The gas mixture used in the experiments was 50% steam, 45% N₂, and 5% CO. The reducing, hot conditions were kept for a duration of 6 hours and the reactor was subsequently cooled down overnight with a flow of N₂. The samples were then subject to material analysis.

Thermogravimetric analysis (Paper I)

Mixtures of oxygen carrier and an ash model component were subject to thermogravimetric analysis (TGA). In TGA, the weight of a small sample is continuously measured while the conditions (such as temperature and atmosphere) vary. The current analysis was done to quantify the reduction and oxidation of the oxygen carriers while reacting with the ash model compounds. The program used in the TGA is presented in Table 8. The analysis started with heating the system to 850°C. The sample was then reduced, oxidized, and reduced once more. The analysis ended with colling down the sample in inert atmosphere (N₂).

Table 8: Program used in the thermogravimetric analysis (TGA)

Heating	Flushing	Reduction	Flushing	Oxidation	Flushing	Reduction
N ₂	N ₂	N ₂	N ₂	N ₂	N ₂	N ₂
1000mL/min	1000mL/min	450mL/min	1000mL/min	800mL/min	1000mL/min	450mL/min
		CO		O ₂		CO
		50mL/min		200mL/min		50mL/min
		H ₂ O				H ₂ O
		500mL/min				500mL/min
45 min	15 min	60 min	5 min	30 min	30 min	60 min

Fluidized bed experiments (Paper III)

The reactor used for the experiments presented in Paper III was a lab-scale fluidized bed reactor with a system for adding solid particles during the experiment. Solid K_2CO_3 was fed into the reactor during the experiment to simulate the accumulation of fuel-K in the bed. The reactor was designed and constructed specifically for this work. The setup was constructed to be flexible with respect to bed material and ash components. When using potassium in the experiment, (and in the future, possibly, other model compounds), it's important to have a construction that is corrosion-resistant and can be properly cleaned. Interactions between alkali and reactor walls for experimental setups have been observed and studied experimentally by Andersson et al. [49]. High temperature steel of the material 253MA was chosen for the design. A schematic view of the reactor is presented in Figure 6.

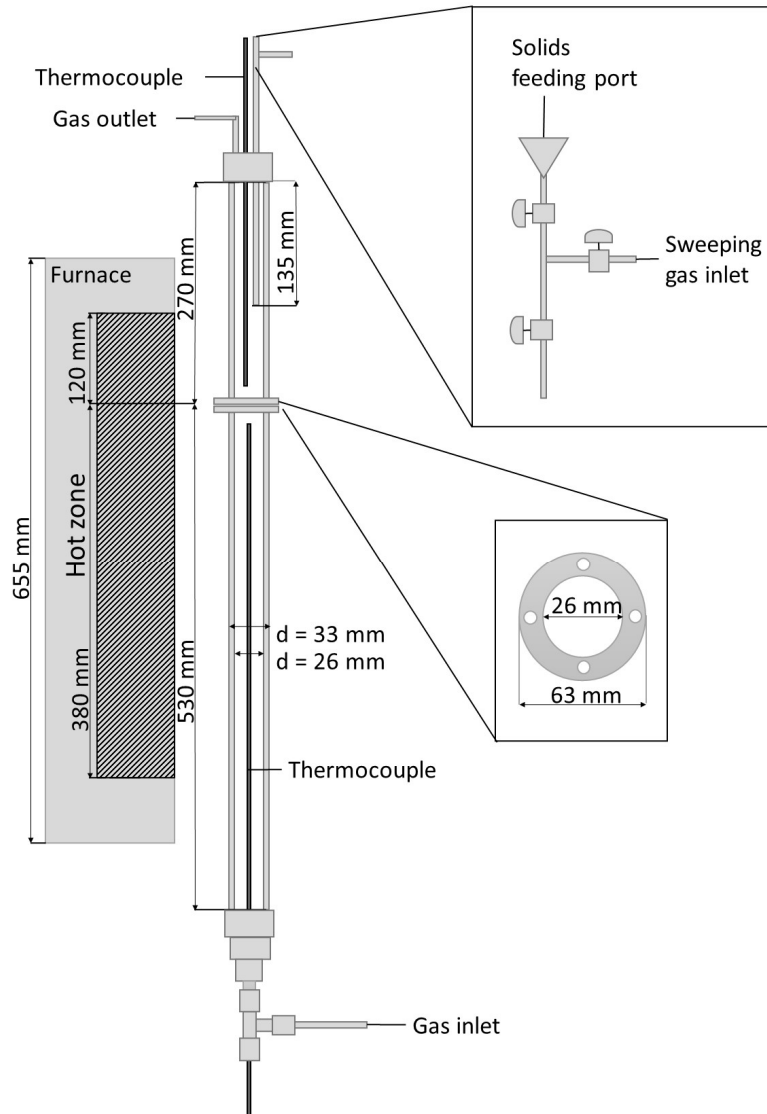


Figure 6: Schematic drawing of the lab-scale fluidized bed reactor

Two steel pipes (with 26mm inner diameter) are connected in series. The top and bottom pipes are 270 and 530mm long. A distribution plate is placed between them. The distribution plate

is a perforated stainless-steel plate. The pipes are connected with flanges and screws, and it's possible to open and clean the reactor and replace the distribution plate when needed.

The reactor was placed in a furnace in a larger experimental infrastructure explained in detail by Leion et al. [50]. The reactor inlet was connected to a line for gas feeding. The gas flow was controlled by mass flow controllers and magnetic valves were opened and closed for seamless changes between different gas mixtures. The magnetic valves were controlled according to a preset program for the changes in conditions (i.e. oxidizing, inert, and reducing) to simulate CLC cycles. The redox cycles used to simulate CLC operation are presented in Table 9. The program started with heating the reactor to the experimental temperature with diluted air as fluidizing gas. The CLC cycles started with reduction. The material was then oxidized with diluted air and then the cycle restarted with reduction. Inert gas was passed through the reactor between the different reactive atmospheres to not allow mixing between oxidizing and reducing gas. In the experiments with salt addition, the salt was added during the last inert period, as indicated in Table 9.

Table 9: Program used in the experiment with salt addition during CLC cycles.

Period	Gas flow (NmL/min)	Gas composition	Time
Heating	1000 NmL/min	Air in N ₂ (12.4% O ₂)	
Inert	1000 NmL /min	N ₂	180 s (approx.)
Start of experimental cycles			
Reduction	400 NmLmin	CH ₄	40 s
	500 NmL/min	N ₂	
Inert	1000 NmL /min	N ₂	60 s (approx.)
Oxidation	1000 NmL/min	Air in N ₂ (12.4% O ₂)	Until CO _{2, out} = CO _{2, in}
Inert*	1000 NmL /min	N ₂	180 s (approx.)

* K₂CO₃ was added to the bed during this inert period preceding the reduction.

The bed initially consisted of pure ilmenite, and K₂CO₃ was added seven times into the bed during CLC simulation cycles. The addition was done according to Table 10, presenting the timing (cycle number) and the amount of added salt.

Table 10: Details of the additions of K₂CO₃ during the experiments

Cycle no.	Addition (mg)	Accumulated (mg)	Wt.-% salt added to the bed	Wt.-% K added to the bed
6	100	100	0.5	0.3
8	100	200	1.0	0.6
10	300	500	2.4	1.4
12	400	900	4.3	2.4
14	400	1300	6.1	3.5
16	500	1800	8.3	4.7
18	500	2300	10.3	5.8

Data evaluation

The gas concentrations in the reactor outlet were analyzed to quantify the fuel conversion. The fuel conversion is here presented as the mass-based conversion of the oxygen carrier. The mass-based conversion is defined according to Equation (1), where m is the mass of the oxygen carrier at a given time, and m_{ox} is the mass of the oxygen carrier when it's fully oxidized.

$$\omega = \left(\frac{m}{m_{ox}} \right) \times 100 [\%] \quad \text{Equation (1)}$$

The mass-based conversion for the redox cycle was calculated according to Equation (2):

$$\omega = \omega_i - \left(\int_{t_0}^{t_1} \frac{\dot{n}M_o}{m_{ox}} (4x_{CO_2} + 3x_{CO} - x_{H_2}) dt \right) \times 100 [\%] \quad \text{Equation (2)}$$

ω_i is the mass-based conversion at the beginning of the reducing period (at t_0 , immediately after oxidation). The oxygen carrier was assumed to be fully oxidized after oxidation. Thus, $\omega_i = 1$. M_o is the molar mass of oxygen and x are the concentrations. $\dot{n}$ is the molar flow (moles/second).

The yield of CO_2 in the cycle was calculated according to Equation (3), where n_{CO_2} is the number of moles of CO_2 formed in the cycle, calculated according to Equation(4).

$$\gamma_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{CO} + n_{CH_4}} \quad \text{Equation (3)}$$

$$n_{CO_2} = \int_{t_0}^{t_1} \dot{n}x_{CO_2} dt \quad \text{Equation (4)}$$

The yields of CO and CH_4 are calculated in the same way, according to Equations (5) and (6)

$$\gamma_{CO} = \frac{n_{CO}}{n_{CO_2} + n_{CO} + n_{CH_4}} \quad \text{Equation (5)}$$

$$\gamma_{CH_4} = \frac{n_{CH_4}}{n_{CO_2} + n_{CO} + n_{CH_4}} \quad \text{Equation (6)}$$

Materials

Three different oxygen carriers have been studied in the experimental work for this thesis: ilmenite concentrate, LD-slag, and iron mill scale. All three materials are produced in industrial processes. Ilmenite is a mineral mined for its titanium content and is usually processed to TiO_2 . The ilmenite used in this study is mined in Norway and refined into a concentrate by Titania A/S. LD-slag and iron mill scale are by-products of steel production. Table 11 presents the materials and their composition, origin, and how they have been pretreated in the studies presented in this thesis. All three oxygen carriers have previously been studied in CLC/OCAC experiments. Ilmenite is the most studied one and has been subject to many hours of both lab-scale and industrial-scale operation.

Table 11: Oxygen carriers studied in the experimental work in this thesis.

Oxygen carrier	Industrial process	Composition	Origin	Preparation	Previous research***
Ilmenite concentrate	Mined for Ti-production	*Fe(36.46) Ti(26.89) Mg(2.16) Si(0.93) Al(0.34) Ca(0.23) Mn(0.19) K(0.02)	Titania A/S	Calcination Sieving Activation	[6], [51], [52],
LD-slag	By-product from steel converting	**Ca(49.5) Fe(24.0) Si(10.2) Mg(6.5) Mn(3.6) V(3.3) Al(1.3) Ti(1.1)	SSAB Merox	Calcination Grinding	[53], [54], [55], [56],
Iron mill scale (Glödsdal B)	By-product from steel processing	**Fe (95.1) Si(4.0) Mn(0.9)	SSAB Merox	Calcination Grinding	[22], [57], [58]

Composition is on oxygen free basis.

* = data is from the producer (Titania A/S).

** = Oxygen free composition. Data is from SEM/EDS analysis on a cross-section of many particles.

*** = The list is non-exhaustive

The model compounds that were used to simulate ash presence in the bed are listed in Table 12. They are all potassium salts. For the fixed bed experiment and the thermogravimetric analysis, LD-slag and iron mill scale were used as oxygen carriers. KCl, K₂CO₃, K₂SO₄ and KH₂PO₄ were used as ash model compounds. One oxygen carrier was mixed with one model compound so that the K-content in the sample was 4 wt.-%.

Table 12: Ash model compounds used in the experimental work in this thesis

Compounds	Melting temperature	
K ₂ CO ₃	891	Decomp., releases CO ₂ (g)*
K ₂ SO ₄	1069	Decomp., releases S-oxide (g)*
KH ₂ PO ₄	253	Decomp., releases H ₂ O*
KCl	776	Evaporation*

* = expected decomposition at experimental conditions

For the fluidized bed interaction experiments, ilmenite was used as oxygen carrier and K₂CO₃ was used as model compound. According to thermodynamic calculations, K₂CO₃ is very stable in the experimental temperatures, except for at very low CO₂ partial pressures. Lehman et al. [59] studied the stability of K₂CO₃ close to its melting temperature while varying the CO₂ concentration between 0 and 100%. They concluded that the rate of decomposition into K₂O and CO₂ is strongly dependent on the CO₂-pressure, but that weight loss from K₂CO₃ was detected for all gas concentrations. They also concluded that the melting temperature of K₂CO₃ is between 900 and 905°C depending on the gas composition. In inert atmosphere, during which the salt was introduced in the reactor in the current experiments, it was assumed that some decomposition of the K₂CO₃ would occur and that the vapor pressure of K would be low. When methane was converted in the reducing period, the steam formed would likely react with the K and to some extent form KOH, which has a higher vapor pressure. It can therefore be assumed that the contact of K with the oxygen carrier would be a combination of solid-

liquid-, and gas-solid in varying fractions depending on the temperature. This is discussed further in the results section, and in Paper III.

Material analysis

SEM/EDS

Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDS) was used for analyzing the structure and the elemental distribution of the particles. For particle surface analysis, the particles were mounted on a stub with carbon tape. For analyzing the cross-section of particles, they were placed in a mold together with epoxy and subsequently the epoxy slab was polished to obtain a cross-section.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used for analyzing the reduction and oxidation behavior of the sample. A small amount of sample was placed in a ceramic alumina sample holder. The sample holder hangs in a scale placed in a furnace. During the experiment, the temperature or the composition of the atmosphere in the testing chamber is altered, during which the weight of the sample is recorded. By altering between oxidizing and reducing conditions, it can be determined how much the sample is oxidized and reduced and how the redox behavior differs with ash model components. The method is commonly used for determining the oxidation states of oxygen carriers in different atmospheres and temperatures.

Literature review (Paper II)

The utilization of oxygen carriers on a large scale in OCAC creates a space for developing the production, infrastructure, and recycling of oxygen carriers, as well as gaining experience in operation. A literature review was published in this work to summarize the work performed so far on large-scale oxygen carrier utilization. The review encompasses both previously published material and previously unpublished information. Some of the information is first-hand, from plant operators via the co-authors of the paper. While previous publications focus mainly on the experimental results from the studies, the publication in this work (Paper II) goes further to also discuss aspects such as bed material processing and transportation, as well as estimated costs and potential market solutions.

Another part of the study was to identify and quantify flows of potential oxygen carrier materials in the industrial sector in Sweden. These include raw materials such as ores, as well as products and by-products generated in the Swedish metallurgical industries. Reports and statistics from the producing companies were reviewed to gather data on production. Further data and information were gathered by contacting the companies in some cases. The production of potential oxygen carriers in metallurgical and related industries were then compared to current consumption of FBC bed materials.

Chapter 4: Results and discussion

Selected results from the work included in this thesis are briefly presented and discussed. The related papers are referred to, for further details.

Review of OCAC activities (Paper II)

An overview of large scale OCAC activities are presented in Table 13. 18 instances of OCAC operation were identified (out of which three were operation that could be described as CLC/CLG mode) which had resulted in 19 publications (as of 2021). Seven instances of OCAC operation had not resulted in any publications in scientific literature. OCAC operation has been performed in six CBF-boilers and two BFB boilers in the size range 12-170 MW thermal capacity. Since the publication of Paper II, Stockholm Exergy has also reported that they have been using ilmenite in their 400 MW_{th} CFB biomass boiler during 2022 [60]

Table 13: Overview of large scale OCAC operations identified in Paper II.

Oxygen Carrier	Facility	Description	Ref
Rock Ilmenite	Chalmers (12 MW _{th} CFB)	OCAC proof of concept study	[6], [41]
Rock Ilmenite	Chalmers (12 MW _{th} CFB)	Various OCAC research activities	[40], [61], [62], [63], [64], [65], [66]
Sand ilmenite	Chalmers (12 MW _{th} CFB)	OCAC research activities	[64]
Rock Ilmenite	Chalmers (4 MW _{th} gasifier)	CLC/CLG proof of concept	[11]
Rock Ilmenite	Händelö P14 (75 MW _{th} CFB)	OCAC in a commercial boiler	[67], [68]
Rock Ilmenite	Händelö P15 (85 MW _{th} CFB)	OCAC in a commercial boiler	[68]
Rock Ilmenite	Örtofta (115 MW _{th} CFB)	OCAC in a commercial boiler	[15], [66]
Rock Ilmenite	Eskilstuna (50 MW _{th} CFB)	OCAC in a commercial boiler	NA
Rock Ilmenite	ÖrebroP5 (170 MW _{th} CFB)	OCAC of a commercial boiler	NA
Rock Ilmenite	Sollefteå (19 MW _{th} BFB)	OCAC in a commercial boiler	NA
Rock Ilmenite	Borås (20 MW _{th} BFB)	OCAC in a commercial boiler	NA
LD-slag	Chalmers (12 MW _{th} CFB)	OCAC proof of concept study	[55], [69], [70]
LD-slag	Chalmers (4 MW _{th} gasifier)	CLC/CLG proof of concept	[71]
LD-slag*	Sävenäs HP2 (95 MW _{th} BFB)	OCAC in a commercial boiler	NA
Sibelco Mn-ore	Chalmers (12 MW _{th} CFB)	OCAC proof of concept study	[72], [73]
Sibelco Mn-ore	Chalmers (4 MW _{th} gasifier)	CLC/CLG proof of concept	[11]
Elwaleed C Mn-ore**	Chalmers (12 MW _{th} CFB)	OCAC research activities	NA
Foundry slag	Lidköping Energi (13 MW _{th} BFB)	OCAC in a commercial boiler	[74], [75]

* LD-slag inventory was only about 7% due to problems with the pneumatic transport of LD-slag.

**lasted only one day due to extensive elutriation of bed material.

Six different bed materials with oxygen carrying properties had been used in large scale OCAC operation and are presented in Table 14. The table presents two types of ilmenite, two slags, and two manganese ores.

Table 14: Materials used in commercial/semi-commercial scale OCAC

Rock ilmenite Produced by the company Titania A/S in Norway. The ore has been crushed and sorted to increase the ilmenite concentration to 85-90%. The crushed ilmenite is sieved and dried. Transported by pressure discharge trucks.	Composition* [64] Fe(34) Ti(28) Mn(0.5) Mg(0.4) Al(0.2) Si(0.2)
Sand ilmenite Provided from Australia by the mineral trading company Sibelco. The material was used as received.	[64] Fe(33) Ti(24) Mg(1.8) Si(0.9) Al(0.3) Ca(0.3) Mn(0.1)
LD-slag Originating from SSAB, processed and provided by SSAB Merox. Some problem with pneumatic transport arose, probably because of excess amounts of fine material.	Merox, (product specification sheet) CaO(43) FeO(22) SiO ₂ (10) MgO(9) MnO(3) V(1.5) TiO ₂ (1.3) Al ₂ O ₃ (1.1)
Manganese – two different ores One ore was provided by Sibelco as large chunks. The other one was a low-grade ore provided by Elwaleed. Both ores were processed into suitable particles by UVR-FIA GmbH. The particles were produced by multistage grinding and sieving with horizontal shaker and wind sifter.	Sibelco [11] SiO ₂ (7.95) Al ₂ O ₃ (6.42) Fe ₂ O ₃ (7.36) TiO ₂ (0.4) MgO(0.4) MnO ₂ (59.7) CaO(2.6) K ₂ O(1.2) Elwaleed [76] Mn(11.54) Fe (51.74) Si (4.59) Al (1.27) Ti (0.07) Ca (0.82) K (0.26) Mg (0.39) Ba (0.43) Na (0.30)
Foundry slag Originating from Sandvik SRP AB and processed and provided by Sibelco. Processing was crushing, drying and sieving.	[74] Mn(18) Mg(14) Si(9.0) Ca(8.9) Fe(5.7) Al(2.7) Ti(1)
* Some of the compositions are presented as oxides, some as elements. Balance is mainly oxygen.	

Out of the instances of OCAC operation presented in Table 13, 11 were with ilmenite as oxygen carrier. Furthermore, all continuous commercial OCAC operation has been with ilmenite as bed material. The general experience from these studies was that with ilmenite as oxygen carrier, the excess air (or air-to-fuel ratio) could be reduced without a negative influence on the fuel conversion. Lowering the excess air would otherwise result in less complete combustion causing increased CO emissions. The oxygen buffering ability of the oxygen carrier compensated for the inadequate mixing in the bed and ensured a high fuel conversion also with excess air flows [61], [62]. A successful lowering of excess air by between

14 and 30% was observed in some studies (out of which one is unpublished) [15], [67] (*Successful* refers to a possible decrease in excess air flow without reaching unacceptable levels of CO in the flue gas). With a lowered air-to-fuel ratio there is room to increase the thermal load of the boiler. 7% and 13% increase in thermal load was accomplished in two boilers [15], [67]. 3-8% increase in thermal load was seen in two cases of previously unreported industrial OCAC operation.

The properties of ilmenite were suitable for the continuous combustion of biomass and waste fuels. It was found to perform a long time inside the boiler without either agglomerating or otherwise being destroyed by the chemical and mechanical stresses in the boiler. Apart from ilmenite, LD-slag, manganese ores, and foundry slag are other oxygen-carrying materials that had been tested in large-scale FBC. LD-slag operation in the 12 MW_{th} research boiler with wood chips resulted in enhanced fuel conversion throughout the furnace but increased CO emissions, presumably due to poor burnout in the cyclone [55]. The increased CO-emissions were suggested to be from the relatively poor ability of LD-slag to absorb and stabilize alkali. Some problems were also experienced with increased fly ash generation and large amounts of fines. LD-slag operation was also attempted in a 95 MW_{th} BFB. The campaign was not successful and had to be aborted because the transport of the material into the bed material silo did not work properly. Large amounts of fines in the fresh material were thought to be the reason for the problems. Foundry slag was added to a municipal solid waste-fired BFB and the addition of the slag was seen to lower the CO-emissions by 80%. Further, the thermal output could be increased by 15% and the agglomeration risk was determined to be low [74].

Review of bed material flows (Paper II)

The current situation for most FBC units in Sweden is that silica sand is used as bed material. It has quite a short lifetime in the boiler because it quickly becomes degenerated by ash interactions. By means of calculations and well-grounded assumptions about the bed material consumption in fluidized bed boilers, the size of total annual bed material consumption in Sweden was estimated to be 160-180 kton. This has also been confirmed with Sibelco, which is the mineral trading company responsible for providing most of the silica sand to Swedish boilers (although the precise size of the market was not disclosed). Notably, this means that sand consumption in fluidized bed boilers corresponds to approximately 20% of the total Swedish quartz sand production. The Swedish quartz sand production was between 579 and 783 kton between the years 2008 and 2018 according to the Geological Survey of Sweden [77].

The bed material consumption on the basis of thermal load for some CBF and BFB biomass boilers is presented in Figure 7. The data for the operation with sand is from a study by Öhman et. al [78]. The regeneration differs greatly between different plants. Silica sand is relatively cheap and a large marginal can be employed to ensure a low risk of agglomeration and defluidization of the bed. However, reducing the use of virgin sand and gravel is a sub goal of one of Sweden's environmental goals and should be pursued.

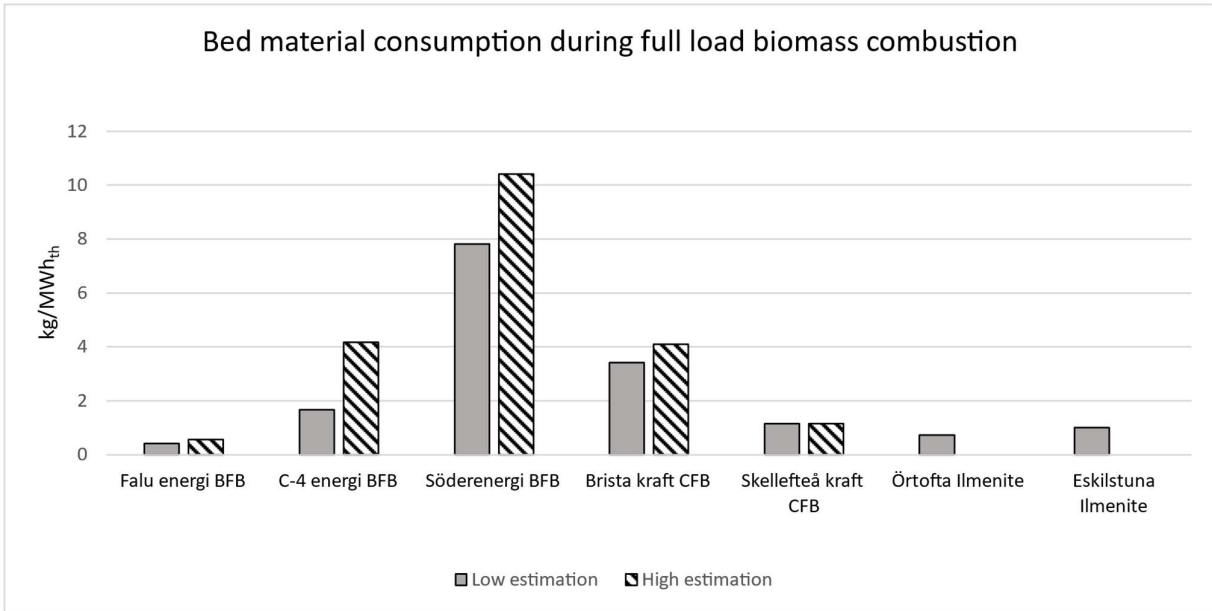


Figure 7: Bed material consumption (kg/MWh_{th}) in some biomass-fired boilers. Five of the entries are for operation with sand. The last two are for operation with ilmenite.

Figure 7 also presents bed material consumption during two instances of operation with ilmenite. The data for ilmenite consumption in Örtöfta is from Moldenhauer et al. [15] and the data for Eskilstuna is previously unpublished. Unpublished data from a CFB unit in Händelö showed that 3 kg/MWh was possible with municipal solid waste as fuel and ilmenite as bed material. The consumption could be decreased to 0.8 kg/MWh when a recycling system based on magnetic separation (explained in [66]) was introduced. Ilmenite has a long lifetime in the boiler and can enhance the combustion process. However, a drawback is that ilmenite is also a virgin material produced by mining and utilized in many industrial processes.

While the ilmenite is mined for being used as bed material, there are already large amounts of potentially suitable by-products being produced in metallurgical industries in Sweden. Some of these are more or less viewed as a waste. There are for example slags and tailings that could have oxygen carrying properties since they contain iron oxides. The idea of using oxygen carriers that already exist as material flows in the industry has some clear advantages when it comes to scaling up. The production processes and properties of these materials are well known. Facilities for processing, transportation, etc. are already in place. Further, since the utilization degree of some of those materials is low, the cost could also be quite low. There are several materials with seemingly suitable properties that could be utilized more or less directly from the source. This is illustrated in Figure 8, where the green arrows represent utilizing available materials in the industrial system. All materials here can be classified as by-products, except for iron ore fines. An estimation of production and utilization potential is presented in Figure 9.

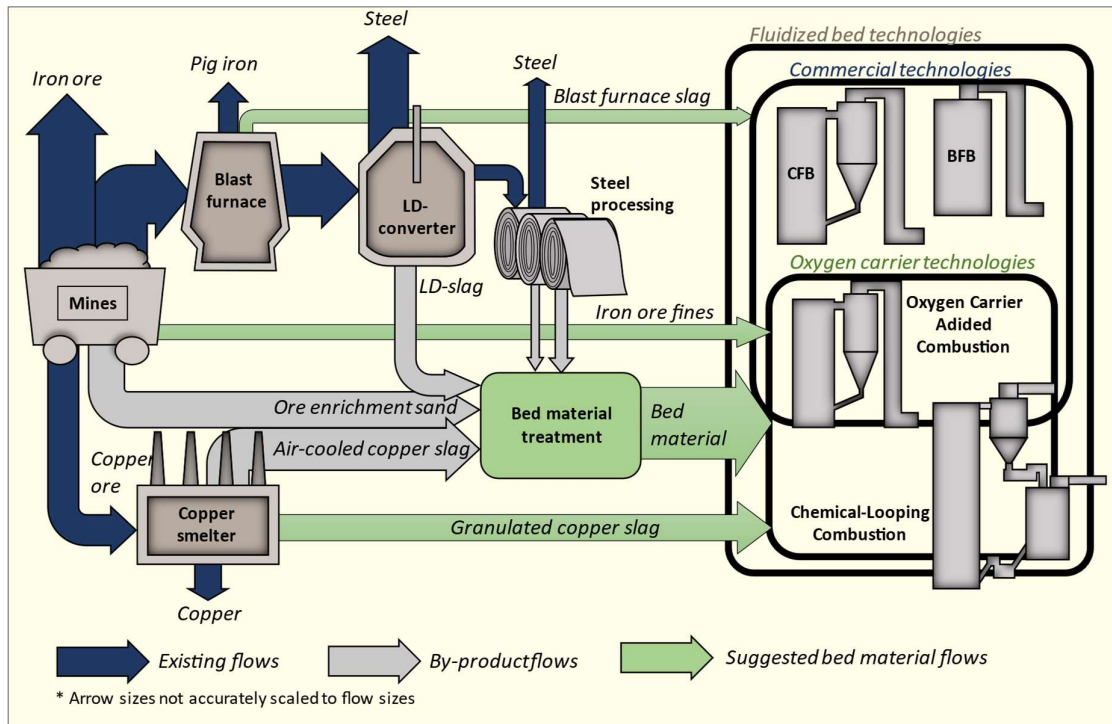


Figure 8: Suggested utilization of by-products in the Swedish metallurgical industries (Iron ore fines is not a by-product). Some materials require treatment, but some can be utilized more or less directly. (Figure is from Paper II)

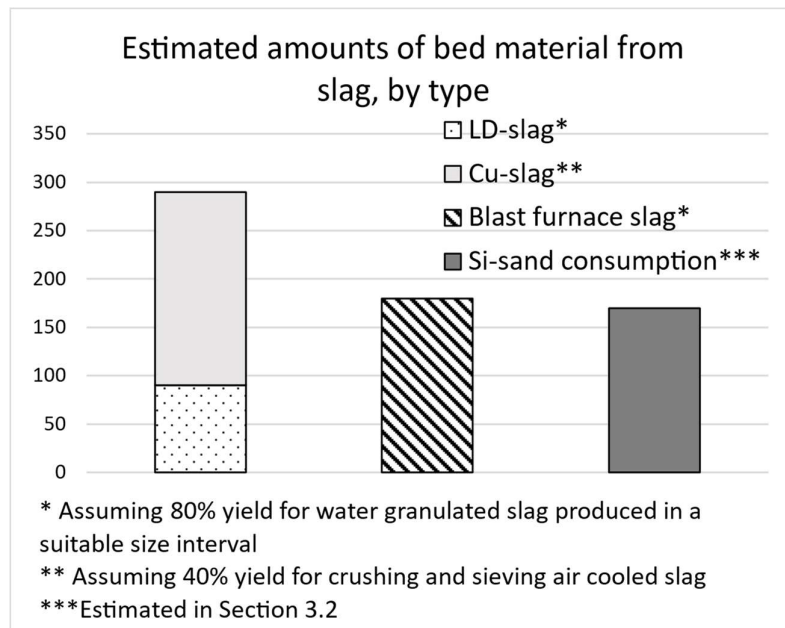


Figure 9: The estimated potential to produce bed materials from slag-based materials. Left: Oxygen carriers copper slag and LD-slag. Middle: Blast furnace slag (not an oxygen carrier). Right: Current estimated silica sand consumption. "Section 3.2" refers to the section in Paper II.

Ash interactions (Paper I and III)

Interactions with iron mill scale and LD-slag in fixed bed experiments

The mixtures between the two oxygen carriers and four potassium salts were subject to TGA and fixed bed interaction experiments. The presented material analysis was done on samples from the latter. The results from the TGA of iron mill scale (Glödskal) and mixtures between iron mill scale and a potassium salt are presented in Figure 10. The upper graph shows 2 curves: the iron mill scale without any salt present, and the mixture between iron mill scale and KH_2PO_4 . The analysis showed that mixing iron mill scale with KH_2PO_4 drastically reduced the rate of weight decrease during reducing conditions. The oxidation also seemed to be slower with KH_2PO_4 present. The curve for the mixtures with K_2CO_3 and K_2SO_4 are presented in the lower graph. K_2SO_4 did not affect the rate of weight change in either reducing or oxidizing conditions. K_2CO_3 , on the other hand, increased the rate of reduction. The changes in weight recorded for KH_2PO_4 and K_2CO_3 at the heating period related to decomposition of the potassium salts (K_2CO_3 released CO_2 , KH_2PO_4 released water).

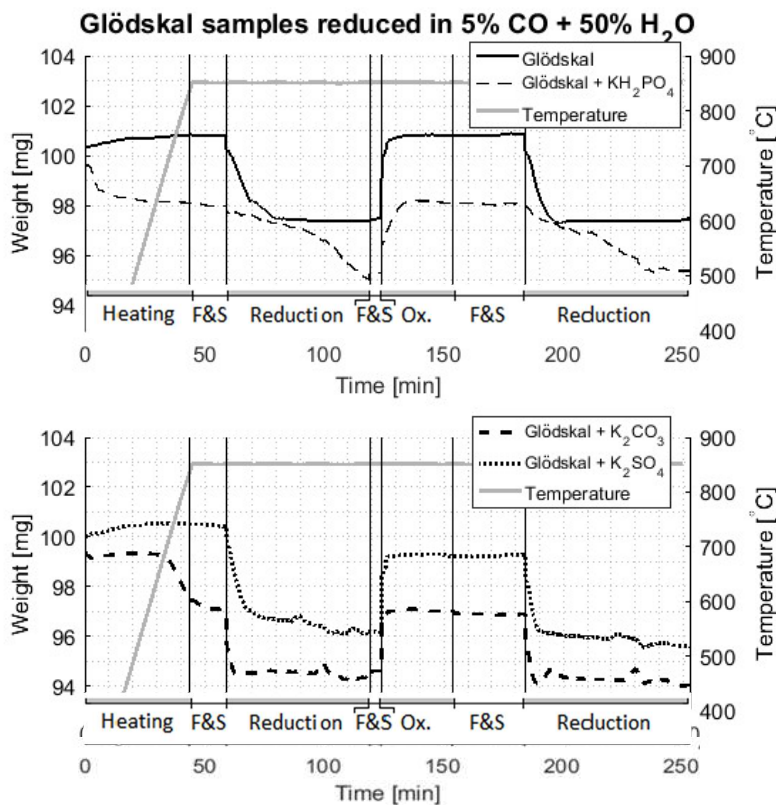


Figure 10: TGA results with Glödskal (iron mill scale) and mixtures of Glödskal and a potassium salt. The timeline underneath the graphs explains the change in conditions, (F&S = Flushing and Stabilizing; Ox. = Oxidation)

The changes in reactivity were explained by findings in the material analysis. The SEM analysis of iron mill scale that had been mixed with KH_2PO_4 and reduced for 6h showed that particles in the sample had agglomerated. This was also apparent from the way the sample looked in the sample holder. The whole sample was stuck together like a slab. This was very unlike the samples of the pure oxygen carrier and the other mixtures which were soft and could easily be removed from the sample holder. The agglomeration between some particles can be seen in Figure 11. The images to the left show (upper) the cross-section and (lower) the surface of some particles glued together to one solid structure. It was seen that particles were glued together and that the surface of the particles was covered. The SEM/EDS analysis on the cross-section further showed that the phase between the particles consisted of Fe, K and P in similar atomic concentrations. This is presented by the elemental maps of Fe, K and P and quantitative analysis of 2 points in the sample (seen in Figure 11). The conclusions were that the KH_2PO_4 decomposed into KPO_3 and H_2O , and the KPO_3 formed a sticky melt that got stuck on the particles and absorbed some of the Fe from the particles. The release of H_2O was visible in the TGA results as an initial weight decrease in the beginning of the heating period. With a layer of molten Fe-K-P compound on the particle surface, the contact with the reducing gas was impaired, which in turn caused the rate of reduction to decrease.

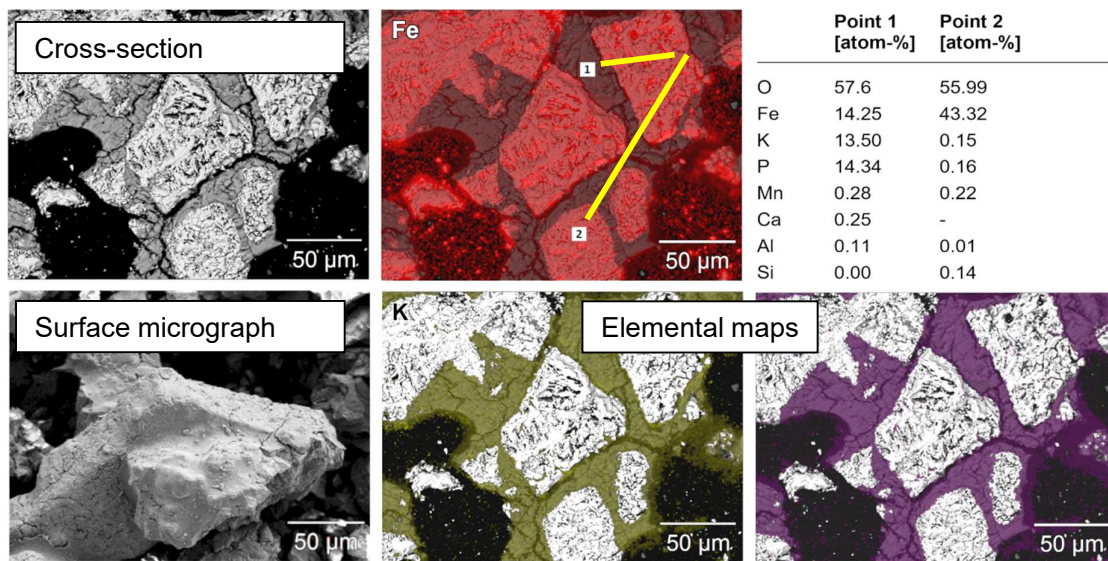


Figure 11: Material analysis (SEM/EDS) of reduced iron mill scale- KH_2PO_4 mixture. The figure presents a cross-section micrograph, a surface micrograph, the elemental maps of Fe (red), K (yellow), and P (purple), and a concentration analysis of 2 points/spots in the sample.

For the iron mill scale mixed and reduced together with K_2CO_3 , on the other hand, no agglomeration was seen. Instead, the surface of the particles seemed to have a more cracked surface, as seen in Figure 12. If the particle surface was more porous, this could have been the reason for the increased reduction rate, because of better gas-solid contact. The SEM/EDS analysis of the cross-section displayed no/only very low presence of K both on the surface and inside the particles.

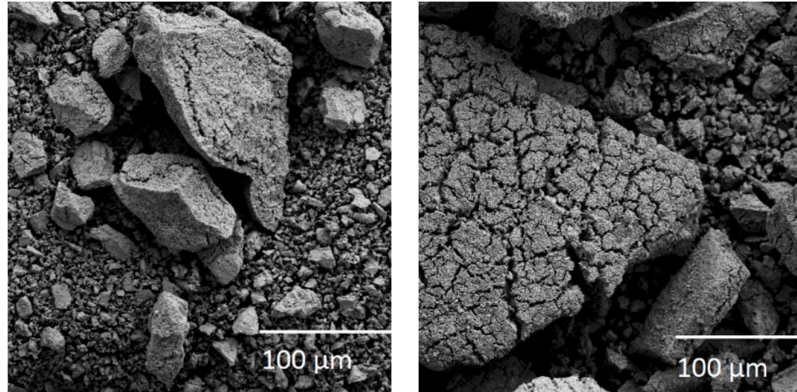


Figure 12: Micrographs of the surface of sample particles. Left: Iron mill scale reduced without any salt present. Right: Iron mill scale reduced in the presence of K_2CO_3 .

The TGA results with LD-slag as oxygen carrier are presented in Figure 13. The weight curves for LD-slag without salt present and the LD-slag mixed with KH_2PO_4 are presented. Contrary to what was seen with iron mill scale, the presence of KH_2PO_4 did not affect the reduction and oxidation rates of LD-slag.

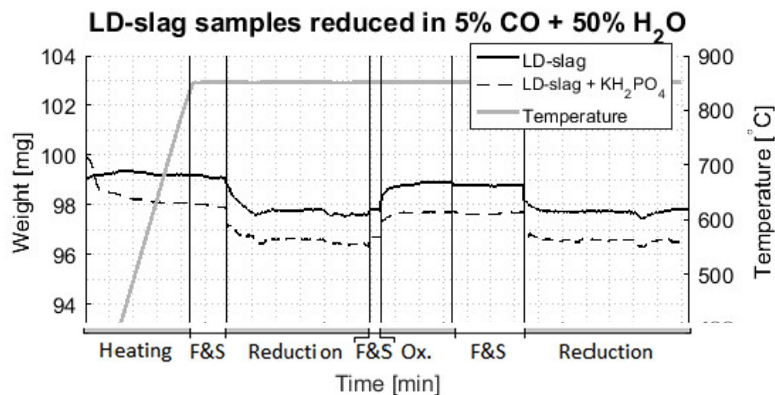


Figure 13: TGA results with LD-slag and a mixture of LD-slag and KH_2PO_4 . The timeline underneath the graphs explains the change in conditions, (F&S = Flushing and Stabilizing; Ox. = Oxidation)

The SEM/EDS analysis of LD-slag was in general more complicated since LD-slag is inhomogeneous and contains many different phases. A phase analysis was therefore done to identify different phases in the sample. (The term “phase” is here used not in the strict chemical definition but refers to a specific elemental composition, as seen in Figure 14). A cross-section analysis is presented in Figure 14. One of the identified phases was found to contain most of the K. The composition of this formed phase is presented to the left in Figure 14. The K-P salt added to the mixture interacted with the material and this resulted in a phase consisting of K, P, and Ca in similar atomic concentrations. Some agglomeration was observed when the sample was taken out of the sample holder, although the binding between the particles was not as strong as in the iron mill scale mixed with KH_2PO_4 . It was concluded that the Ca together with K and P formed a compound with high melting temperature since the agglomeration was soft and the particle surfaces were not covered with melt.

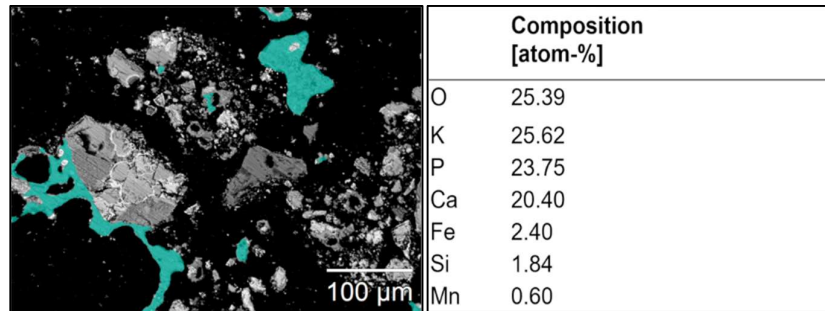


Figure 14: Material analysis (SEM/EDS) of reduced LD-slag- KH_2PO_4 mixture. The area marked in blue contained most of the K and had the concentration presented in the table to the right.

The TGA results of LD-slag mixed with K_2CO_3 and mixed with K_2SO_4 are presented in Figure 15. The results showed a drastically changed behavior with K_2CO_3 compared to the pure LD-slag. The weight changed slowly during reducing conditions, and no clear increase or decrease in weight was seen in the consecutive oxidation and reduction.

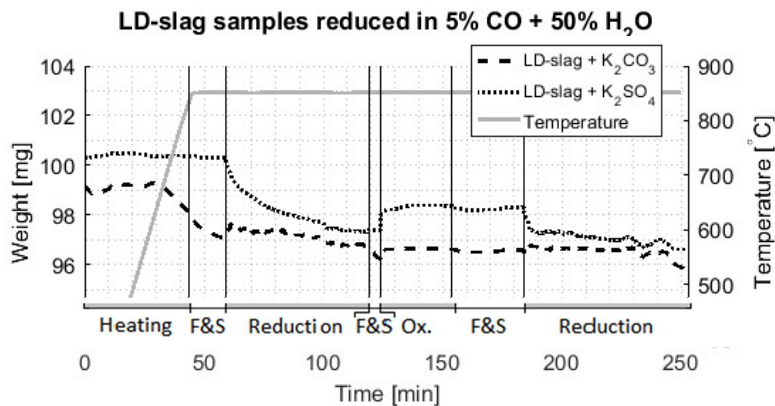


Figure 15: TGA results with mixtures of LD-slag and a potassium salt. The timeline underneath the graphs explains the change in conditions, (F&S = Flushing and Stabilizing; Ox. = Oxidation)

The SEM/EDS analysis of the cross-section of particles from the sample is presented in Figure 16 and shows the elemental distributions of Fe, K and V. Some K was present in the particles, mainly close to the surface. The K-rich areas were also rich in V and Ca which are inherent to the slag. The behavior seen in TGA with K_2CO_3 could not easily be explained by the findings from the material analysis. Fe, which is assumed to be an active oxygen carrying compound in LD-slag, seemed to be available for interactions according to the cross-section analysis, but it's difficult to say for sure from this analysis. The interaction with K_2SO_4 didn't affect the redox curves in TGA. The cross-section analysis of LD-slag reduced in the presence of K_2SO_4 (not presented here) showed that K had diffused into the particles. Some K was included in the particle structure, together with V.

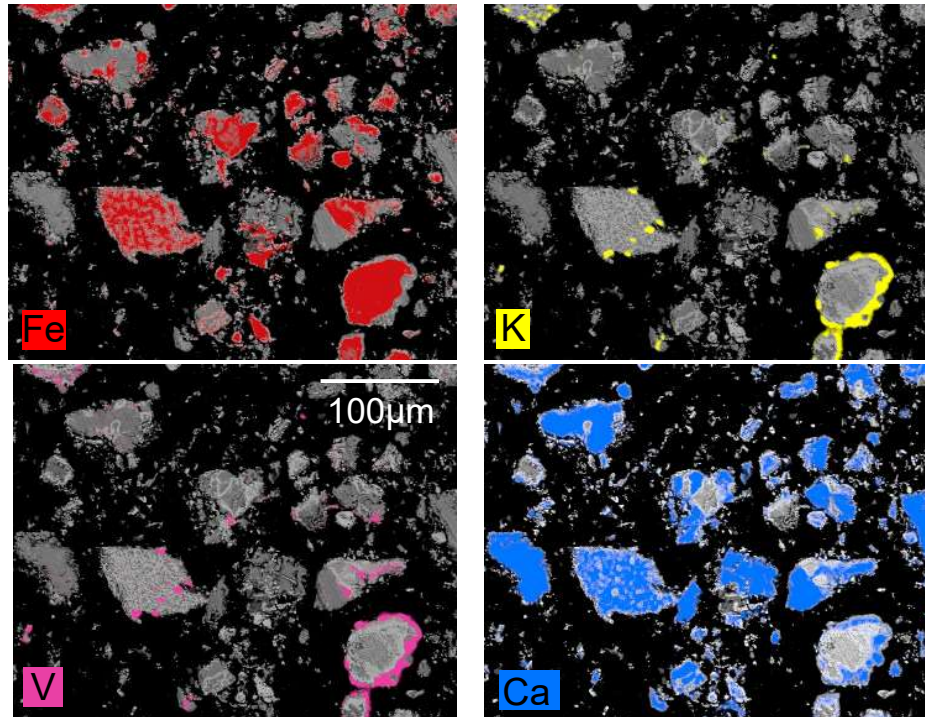


Figure 16: SEM/EDS results. Cross-section of particles from the reduced LD-slag- K_2CO_3 mixture. The elemental maps of Fe (red), K (yellow), V (pink) and Ca (green) are presented.

Interactions with ilmenite in fluidized bed experiments

Interactions between ilmenite and K_2CO_3 were studied in a lab-scale fluidized bed reactor simulating CLC conditions. The performance of ilmenite was studied at an increasing load of K_2CO_3 with respect to fuel conversion and fluidization.

One finding from the fluidized bed experiments with the addition of K_2CO_3 was that the bed defluidized at 950°C after the addition of 900mg of K_2CO_3 . This is seen as a sharp decrease in pressure drop and pressure drop fluctuations in cycle 12 in the right-hand graph in Figure 17.

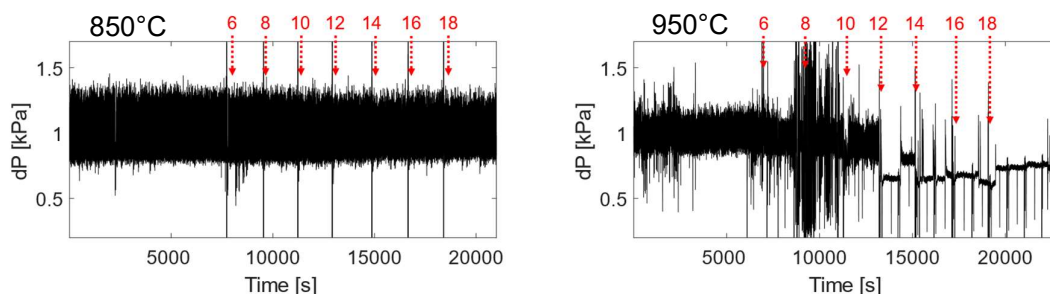


Figure 17: Pressure drop over the bed recorded during the fluidized bed experiments with the addition of K_2CO_3 . The left graph shows the experiment at 850°C and the right graph shows the experiment at 950°C (displays defluidization). The red arrows indicate cycle numbers with K_2CO_3 addition.

A visual examination of the sample collected after the 950°C experiment confirmed that lumps of bed material of varying shapes and sizes had formed in the bed and were the cause for the defluidization. This is seen in the right image in Figure 18. At 850°C, on the other hand, no effect on the fluidization was seen (left graph in Figure 17). The sample also didn't show the formation of lumps in the bed, and it was found that salt existed as white grains in the sample. These are seen in the left image in Figure 18. It therefore seemed like the K_2CO_3 interacted with the bed material at 950°C but not at 850°C. No defluidization or lump formation was observed when the experiment was conducted without salt addition.



Figure 18: Photos of samples collected after the experiments with the addition of K_2CO_3 . Left: the sample from the experiment at 850°C showing the presence of white grains. Right: the sample from the experiment at 950°C showing lumps of agglomerated particles.

A material analysis was done on the agglomerated particles to describe the agglomeration mechanism. The diffusion of K into the interior of the ilmenite was found in many of the studied particles, as was the migration of Fe to the surface, as seen in Figure 19. Contrary to what was first expected, the agglomeration was not found to be because of alkali sticking to the surface of the particles. The agglomeration was instead suggested to be from solid-sintering of the Fe-oxide phases, as can be seen in Figure 20. Enhanced Fe-migration in the presence of K has been concluded in previous studies [40], [45], in a process similar to alkali roasting [79]. No signs of melt formation on the surface were seen in the material analysis. As was discussed previously, the behavior of K_2CO_3 at elevated temperatures is complex and strongly dependent on the atmosphere in the reactor. Solid-solid interactions are not expected to be significant at fluidized conditions, and therefore it can be assumed from these results that the K has diffused into the particles from the gas-phase. This is further supported by the finding that an even, low concentration of K was found when analyzing the surface with SEM/EDS.

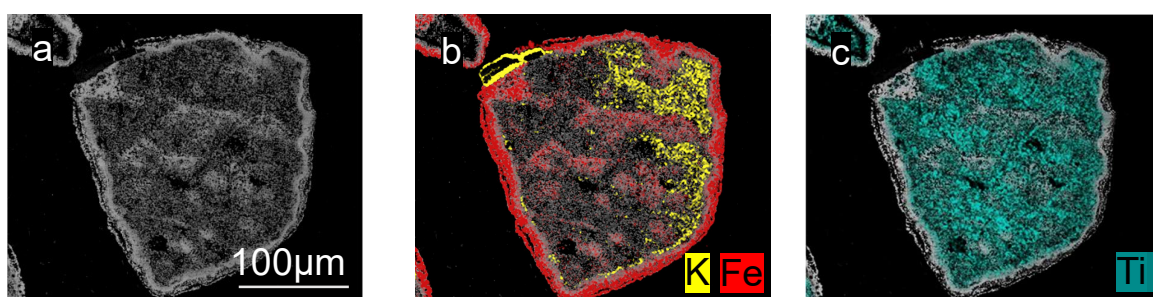


Figure 19: Elemental distribution obtained with SEM/EDS analysis. The sample is from the experiment at 950°C with addition of K_2CO_3 . a) Micrograph, b) distribution of Fe in red and K in yellow, c) distribution of Ti in blue.

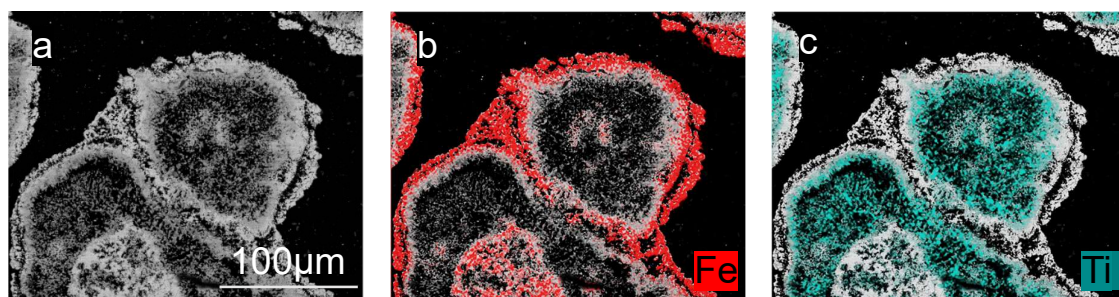


Figure 20: Elemental distribution obtained with SEM/EDS analysis. The sample is from experiment at 950°C with addition of K_2CO_3 . a) Micrograph, b) distribution of Fe in red, c) distribution of Ti in blue.

The methane conversion was also evaluated during the experiment. The methane conversion is displayed as a function of the cycle number in Figure 21. The data is presented as the mass-based conversion of the ilmenite and the yields of CO₂, CH₄, and CO as explained in *Data evaluation*. The ilmenite had been activated before the experiments. The first five points show the stable conversion in the beginning of the experiment, before addition of K₂CO₃.

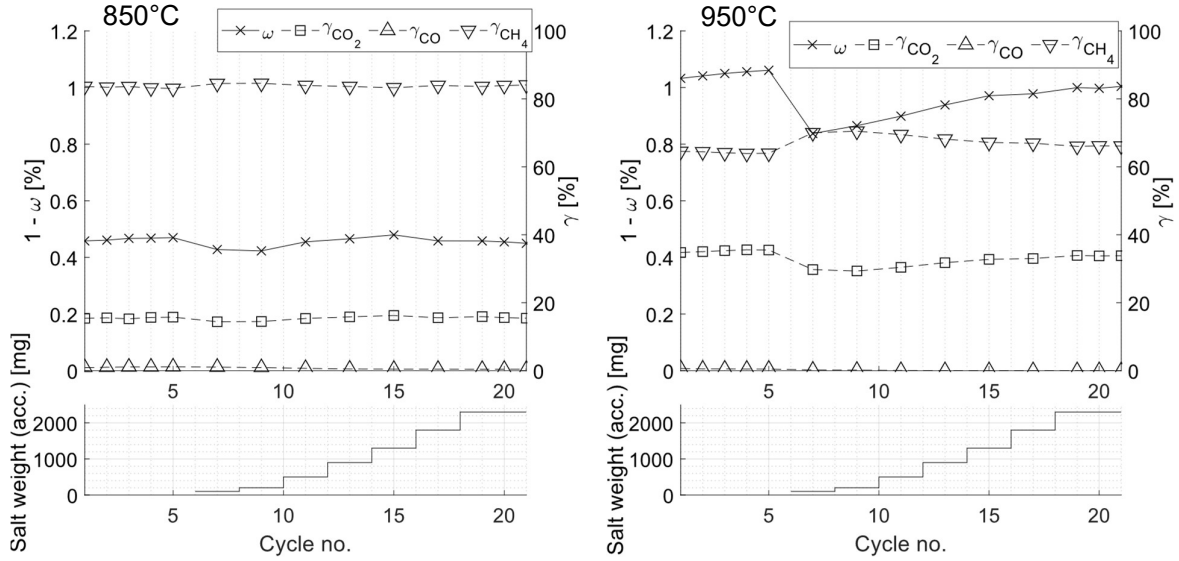


Figure 21: Mass-based conversion ($1-\omega_{final}$), CO₂-yield (γ_{CO_2}), CO-yield (γ_{CO}), and CH₄-yield (γ_{CH_4}), as a function of cycle number for the experiments with K₂CO₃-addition. Left: 850°C, right: 950°C. The lower panels show the accumulated addition of K₂CO₃ (mg).

The fuel conversion during the experiment at 850°C is presented in the left-hand graph. The fuel conversion remained more or less unaffected throughout the experiment. In the experiment at 950°C (displayed on the right-hand side in Figure 21), the fuel conversion decreased after the first addition of salt, as can be seen as a drop in ω and CO₂ yield. However, the conversion increased again after that, and no trend between K-amount and fuel conversion could be identified. The drop in fuel conversion could be due to some decrease in contact between the fuel and the oxygen carrier. This could be the case if the diffusion into the particle is initially slow and the K deposits on the particles and forms some initial, deactivating layer.

The interactions between oxygen carriers and ash model compounds observed in this thesis are summarized in Table 15.

Table 15: Summary of results from experimental studies.

Material	Ash component reaction path	Presence of salt components after interactions (wt.-%)	Structural/visual changes of the sample**	Reactivity with fuel (TGA or CLC cycles with methane)
Fixed bed experiments				
	KCl(s) → KCl(g)	No	Porous. No agglomeration	(Not analyzed)
Iron mill scale	K ₂ CO ₃ → K ₂ O + CO ₂ (g)	No/Low. K(0.6)*	Porous. No agglomeration	Increased
	K ₂ SO ₄ → (decomposition)	No/Low. K(0.6)*	Unaffected***	Unaffected***
	KH ₂ PO ₄ → KPO ₃ + H ₂ O(g)	Agglomeration bridge, together with Fe. K(6.8) P(7)*	Coated. Agglomeration.	Decreased
	→ K-Fe-P-component			
LD-slag	KCl(s) → KCl(g)	No	Unaffected***	(Not analyzed)
	K ₂ CO ₃ → K ₂ O + CO ₂ (g)	Mainly surface, together with V. K(2.3)*	Unaffected***	Decreased
	K ₂ SO ₄ → (decomposition)	Inside the particles, together with V. K(2.6)*	Unaffected***	Unaffected***
	KH ₂ PO ₄ → KPO ₃ + H ₂ O(g)	Agglomeration bridge, together with Ca. K(5.9) P(7.8)*	Some agglomeration.	Unaffected***
	→ K-Ca-P-component			
Fluidized bed experiments				
Ilmenite, 850°C	K ₂ CO ₃ → K ₂ O + CO ₂ (g)	A thin layer on particle surfaces Separated grains in the sample	Some small clumps of material. White grains.	Unaffected***
Ilmenite, 950°C	K ₂ CO ₃ → K ₂ O + CO ₂ (g)	A thin layer on particle surfaces K Diffused into the particles	Large and small lumps of material. Sudden defluidization	Decreased

*Composition: Oxygen-free elemental bulk composition in wt.-%. The analysis is done with SEM/EDS on a cross-section of many particles and the data is normalized. For complete composition, see Paper I.

** "Agglomeration" in the fixed bed interactions means that the particles were glued together in the sample holder.

*** Unaffected means that the property is similar to that of the oxygen carrier without salt added.

Chapter 5: Conclusions

The outlook for utilizing affordable oxygen carriers for OCAC and CLC with biomass and waste derived fuels has been explored in this thesis. Implementing OCAC in existing FBC plants enhances the fuel conversion and has other positive effects on the boiler and on the emissions. Since biomasses and waste are fuels with reactive ash, the regeneration of bed material is expected to be high in these processes. For comparison, the silica sand consumption in FBC boilers is large and could account for approximately 20% of all the silica sand mined in Sweden. This can be considered unsustainable and that is another good reason to look into using alternative materials instead. The current work estimates that there is potentially a good size match between the existing production of by-products in the steel industry and the current bed material consumption. There are uncertainties in how the cost of processing those materials would affect the competitiveness with sand. Thus, further research is needed to determine their behavior and lifetime in the boiler.

Experimental work has been done to better understand the interactions that might take place between some oxygen carriers and K, since K is the most critical ash compound in biomass and waste fuels. In order to make oxygen carriers economically viable, it is important to understand their lifetime and their development over time in operation. LD-slag and iron mill scale were subject to fixed bed interaction experiments with 4 different potassium salts as ash model compounds. Compared to ilmenite, which is known to absorb and stabilize fuel-K, both materials showed only a small uptake of K. This is significant for operation, since it means that utilizing those materials as the only bed material would probably contribute to high concentrations of gas-phase alkali. Silica sand and ilmenite, on the other hand, can capture K from the fuel. Iron mill scale also showed some tendency to agglomerate in the presence of KH_2PO_4 . The interaction resulted in the formation of a K-P-Fe phase with low melting temperature. This phase was not visible for LD-slag, since LD-slag contains Ca and formed a K-P-Ca phase instead with high melting temperature and low risk for agglomeration.

This work has also presented a new experimental method for studying alkali interactions with oxygen carriers in fluidized CLC conditions and with an ash model compound. The advantage of the current setup is that the K interactions can be studied in realistic conditions but at the same time isolated from the other ash compounds. Understanding the K interactions is important for the process but difficult in the presence of other fuel ash species. The Fe-Ti-K system was studied in this work with ilmenite as oxygen carrier and K_2CO_3 as ash model compound.

Chapter 6: Future studies

Some future studies are suggested and planned on the basis of the findings in this thesis.

- Copper slag has been found to be a potentially suitable oxygen carrier in terms of the form and amount in which is it available in the industry, and in preliminary experimental examinations. A semi-industrial scale experimental OCAC campaign with copper slag is planned to take place in early 2023. The infrastructure to be used for this is the 12MWth research boiler at Chalmers, explained by Thunman et al. [6].
 - The OCAC process with copper slag will be evaluated regarding things like increase boiler load and emissions of CO, SO_x and NO_x.
 - The copper slag will be analyzed to evaluate changes in structure and composition.

- The newly constructed lab-scale fluidized bed reactor was found to be suitable for studying the performance of an oxygen carrier during accumulation of a potassium specie.
 - The setup could be used with more combinations of oxygen carriers and potassium species. For example copper slag is an interesting option.
 - Also Ca is known to play a central role in ash layer formation on ilmenite particles and could be included in interaction experiments.

References

- [1] V. Masson-Delmotte *et al.*, "IPCC, 2018: Global Warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of cli," 2018.
- [2] M. Erans, E. S. Sanz-Pérez, D. P. Hanak, Z. Clulow, D. M. Reiner, and G. A. Mutch, "Direct air capture: process technology, techno-economic and socio-political challenges," *Energy Environ. Sci.*, vol. 15, no. 4, pp. 1360–1405, 2022.
- [3] W. K. Lewis and E. R. Gilliland, "Production of Pure Carbon Dioxide," 2665972, 1954.
- [4] M. Ishida, D. Zheng, and T. Akehata, "Evaluation of a chemical-looping-combustion power-generation system by graphic exergy analysis," *Energy*, vol. 12, no. 2, pp. 147–154, 1987.
- [5] T. Mattisson *et al.*, "Chemical-looping technologies using circulating fluidized bed systems: Status of development," *Fuel Process. Technol.*, vol. 172, no. October 2017, pp. 1–12, 2018.
- [6] H. Thunman, F. Lind, C. Breitholtz, N. Berguerand, and M. Seemann, "Using an oxygen-carrier as bed material for combustion of biomass in a 12-MWth circulating fluidized-bed boiler," *Fuel*, vol. 113, no. x, pp. 300–309, 2013.
- [7] A. Lyngfelt, B. Leckner, and T. Mattisson, "A fluidized-bed combustion process with inherent CO₂ separation; Application of chemical-looping combustion," *Chem. Eng. Sci.*, vol. 56, no. 10, pp. 3101–3113, 2001.
- [8] A. Lyngfelt, A. Brink, Ø. Langørgen, T. Mattisson, M. Rydén, and C. Linderholm, "11,000 h of chemical-looping combustion operation—Where are we and where do we want to go?," *Int. J. Greenh. Gas Control*, vol. 88, no. February, pp. 38–56, 2019.
- [9] N. Berguerand and A. Lyngfelt, "Design and operation of a 10 kWth chemical-looping combustor for solid fuels - Testing with South African coal," *Fuel*, vol. 87, no. 12, pp. 2713–2726, 2008.
- [10] A. Coppola and F. Scala, "Chemical Looping for Combustion of Solid Biomass: A Review," *Energy and Fuels*, 2021.
- [11] T. Berdugo Vilches, F. Lind, M. Rydén, and H. Thunman, "Experience of more than 1000 h of operation with oxygen carriers and solid biomass at large scale," *Appl. Energy*, vol. 190, pp. 1174–1183, 2017.
- [12] N. E. L. Haugen *et al.*, "Building the world ' s largest Chemical Looping Combustion (CLC) unit," in *6th International Conference on Chemical Looping*, 2022.
- [13] A. Lyngfelt, D. Pallarès, C. Linderholm, F. Lind, H. Thunman, and B. Leckner, "Achieving Adequate Circulation in Chemical Looping Combustion—Design Proposal for a 200 MWth Chemical Looping Combustion Circulating Fluidized Bed Boiler," *Energy and Fuels*, 2021.
- [14] J. Beiron, F. Normann, and F. Johnsson, "A techno-economic assessment of CO₂ capture in biomass and waste-fired combined heat and power plants – A Swedish case study," *Int. J. Greenh. Gas Control*, vol. 118, no. September 2021, 2022.
- [15] P. Moldenhauer, A. Corcoran, H. Thunman, and F. Lind, "A Scale-Up Project for Operating a 115 MWth Biomass-Fired CFB boiler with Oxygen Carriers as Bed Material," in *5th International Conference on Chemical-Looping*, 2018.

- [16] F. Störner, F. Lind, and M. Rydén, "Oxygen Carrier Aided Combustion in Fluidized Bed Boilers in Sweden — Review and Future Outlook with Respect to Affordable Bed Materials," *Appl. Sci.*, vol. 11, no. 17, 2021.
- [17] J. Adánez, A. Abad, F. Garcia-Labiano, P. Gayan, and L. F. De Diego, "Progress in chemical-looping combustion and reforming technologies," *Prog. Energy Combust. Sci.*, vol. 38, no. 2, pp. 215–282, 2012.
- [18] A. Lyngfelt, "Chemical-looping combustion of solid fuels - Status of development," *Appl. Energy*, vol. 113, pp. 1869–1873, 2014.
- [19] A. Nandy, C. Loha, S. Gu, P. Sarkar, M. K. Karmakar, and P. K. Chatterjee, "Present status and overview of Chemical Looping Combustion technology," *Renew. Sustain. Energy Rev.*, vol. 59, pp. 597–619, 2016.
- [20] T. Mattisson, A. Lyngfelt, and H. Leion, "Chemical-looping with oxygen uncoupling for combustion of solid fuels," *Int. J. Greenh. Gas Control*, vol. 3, no. 1, pp. 11–19, 2009.
- [21] M. Keller, H. Leion, and T. Mattisson, "Mechanisms of Solid Fuel Conversion by Chemical Looping Combustion (CLC) using Manganese Ore: Catalytic Gasification by Potassium Compounds," *Energy Technol.*, no. 1, pp. 273–282, 2013.
- [22] H. Leion *et al.*, "Solid fuels in chemical-looping combustion using oxide scale and unprocessed iron ore as oxygen carriers," *Fuel*, vol. 88, no. 10, pp. 1945–1954, 2009.
- [23] J. Adánez, A. Abad, T. Mendiara, P. Gayán, L. F. de Diego, and F. García-Labiano, "Chemical looping combustion of solid fuels," *Prog. Energy Combust. Sci.*, vol. 65, pp. 6–66, 2018.
- [24] A. Lyngfelt and B. Leckner, "A 1000 MWth boiler for chemical-looping combustion of solid fuels – Discussion of design and costs," *Appl. Energy*, vol. 157, pp. 475–487, 2015.
- [25] B. Leckner and F. Lind, "Combustion of municipal solid waste in fluidized bed or on grate – A comparison," *Waste Manag.*, vol. 109, pp. 94–108, 2020.
- [26] D. Kunii and O. Levenspiel, *Fluidization Engineering*. Stoneham, MA: Butterworth-Heinemann, 2004.
- [27] J. D. Morris, S. S. Daood, S. Chilton, and W. Nimmo, "Mechanisms and mitigation of agglomeration during fluidized bed combustion of biomass: A review," *Fuel*, vol. 230, pp. 452–473, 2018.
- [28] Åbo Akademi, "Åbo Akademi University Chemical Fractionation Database." [Online]. Available: <https://web.abo.fi/fak/tkf/ook/bransle/database.php>. [Accessed: 29-Jun-2022].
- [29] M. Zevenhoven, P. Yrjas, and M. Hupa, *Handbook of Combustion, Chapter 14: Ash-Forming Matter and Ash-Related Problems*, vol. 4. Weinheim: Wiley-VCH, 2010.
- [30] A. A. Khan, W. de Jong, P. J. Jansens, and H. Spliethoff, "Biomass combustion in fluidized bed boilers: Potential problems and remedies," *Fuel Process. Technol.*, vol. 90, no. 1, pp. 21–50, 2009.
- [31] L. J. R. Nunes, J. C. O. Matias, and J. P. S. Catalão, "Biomass combustion systems: A review on the physical and chemical properties of the ashes," *Renew. Sustain. Energy Rev.*, vol. 53, pp. 235–242, 2016.
- [32] D. Boström *et al.*, "Ash transformation chemistry during combustion of biomass," *Energy and Fuels*, vol. 26, no. 1, pp. 85–93, 2012.

- [33] A.-L. Elled, L.-E. Åmand, and B.-M. Steenari, "Composition of agglomerates in fluidized bed reactors for thermochemical conversion of biomass and waste fuels Experimental data in comparison with predictions by a thermodynamic equilibrium model," *Fuel*, vol. 111, no. 1, pp. 696–708, 2013.
- [34] M. Zevenhoven-Onderwater, M. Öhman, B. J. Skrifvars, R. Backman, A. Nordin, and M. Hupa, "Bed agglomeration characteristics of wood-derived fuels in FBC," *Energy and Fuels*, vol. 20, no. 2, pp. 818–824, 2006.
- [35] C. Sevonius, P. Yrjas, and M. Hupa, "Defluidization of a quartz bed - Laboratory experiments with potassium salts," *Fuel*, vol. 127, pp. 161–168, 2014.
- [36] V. Barišić, L. E. Åmand, and E. Coda Zabetta, "The role of limestone in preventing agglomeration and slagging during CFB combustion of high phosphorus fuels," in *World Bioenergy*, 2008, pp. 1–6.
- [37] E. Brus, M. Öhman, and A. Nordin, "Mechanisms of bed agglomeration during fluidized-bed combustion of biomass fuels," *Energy and Fuels*, vol. 19, no. 3, pp. 825–832, 2005.
- [38] H. He, D. Boström, and M. Öhman, "Time dependence of bed particle layer formation in fluidized quartz bed combustion of wood-derived fuels," *Energy and Fuels*, vol. 28, no. 6, pp. 3841–3848, 2014.
- [39] M. Kuba, N. Skoglund, M. Öhman, and H. Hofbauer, "A review on bed material particle layer formation and its positive influence on the performance of thermo-chemical biomass conversion in fluidized beds," *Fuel*, vol. 291, no. September 2020, 2021.
- [40] A. Corcoran, P. Knutsson, F. Lind, and H. Thunman, "Mechanism for Migration and Layer Growth of Biomass Ash on Ilmenite Used for Oxygen Carrier Aided Combustion," *Energy and Fuels*, vol. 32, no. 8, pp. 8845–8856, 2018.
- [41] A. Corcoran, J. Marinkovic, F. Lind, H. Thunman, P. Knutsson, and M. Seemann, "Ash properties of ilmenite used as bed material for combustion of biomass in a circulating fluidized bed boiler," *Energy and Fuels*, vol. 28, no. 12, pp. 7672–7679, 2014.
- [42] I. Staničić, J. Brorsson, A. Hellman, T. Mattisson, and R. Backman, "Thermodynamic Analysis on the Fate of Ash Elements in Chemical Looping Combustion of Solid Fuels—Iron-Based Oxygen Carriers," *Energy and Fuels*, vol. 36, no. 17, pp. 9648–9659, 2022.
- [43] H. Wiinikka, C. Grönberg, O. Öhrman, and D. Boström, "Influence of TiO₂ additive on vaporization of potassium during straw combustion," *Energy and Fuels*, vol. 23, no. 11, pp. 5367–5374, 2009.
- [44] M. Zevenhoven *et al.*, "Defluidization of the oxygen carrier ilmenite – Laboratory experiments with potassium salts," *Energy*, vol. 148, pp. 930–940, 2018.
- [45] F. Hildor, M. Zevenhoven, A. Brink, L. Hupa, and H. Leion, "Understanding the Interaction of Potassium Salts with an Ilmenite Oxygen Carrier Under Dry and Wet Conditions," *ACS Omega*, vol. 5, no. 36, pp. 22966–22977, 2020.
- [46] I. Staničić, M. Hanning, R. Deniz, T. Mattisson, R. Backman, and H. Leion, "Interaction of oxygen carriers with common biomass ash components," *Fuel Processing Technology*, vol. 200, 2020.
- [47] I. Staničić, V. Andersson, M. Hanning, T. Mattisson, R. Backman, and H. Leion, "Combined manganese oxides as oxygen carriers for biomass combustion — Ash interactions," *Chemical Engineering Research and Design*, vol. 149, pp. 104–120, 2019.

- [48] D. Yilmaz and H. Leion, "Interaction of Iron Oxygen Carriers and Alkaline Salts Present in Biomass-Derived Ash," *Energy and Fuels*, vol. 34, no. 9, pp. 11143–11153, 2020.
- [49] V. Andersson *et al.*, "Alkali-wall interactions in a laboratory-scale reactor for chemical looping combustion studies," *Fuel Process. Technol.*, vol. 217, no. December 2020, p. 106828, 2021.
- [50] H. Leion, V. Frick, and F. Hildor, "Experimental method and setup for laboratory fluidized bed reactor testing," *Energies*, vol. 11, no. 10, 2018.
- [51] H. Leion, A. Lyngfelt, M. Johansson, E. Jerndal, and T. Mattisson, "The use of ilmenite as an oxygen carrier in chemical-looping combustion," *Chem. Eng. Res. Des.*, vol. 86, no. 9, pp. 1017–1026, 2008.
- [52] H. Leion, T. Mattisson, and A. Lyngfelt, "Solid fuels in chemical-looping combustion," *Int. J. Greenh. Gas Control*, vol. 2, no. 2, pp. 180–193, 2008.
- [53] P. Wang, H. Leion, and H. Yang, "Oxygen-Carrier-Aided Combustion in a Bench-Scale Fluidized Bed," *Energy and Fuels*, vol. 31, no. 6, pp. 6463–6471, 2017.
- [54] M. Keller, H. Leion, T. Mattisson, and H. Thunman, "Investigation of natural and synthetic bed materials for their utilization in chemical looping reforming for tar elimination in biomass-derived gasification gas," *Energy and Fuels*, vol. 28, no. 6, pp. 3833–3840, 2014.
- [55] M. Rydén, M. Hanning, and F. Lind, "Oxygen Carrier Aided Combustion (OCAC) of Wood Chips in a 12 MW th Circulating Fluidized Bed Boiler Using Steel Converter Slag as Bed Material," *Appl. Sci.*, vol. 8, no. 12, 2018.
- [56] P. Moldenhauer, C. Linderholm, M. Rydén, and A. Lyngfelt, "Avoiding CO₂ capture effort and cost for negative CO₂ emissions using industrial waste in chemical-looping combustion/gasification of biomass," *Mitig. Adapt. Strateg. Glob. Chang.*, 2019.
- [57] H. Leion, T. Mattisson, and A. Lyngfelt, "Use of Ores and Industrial Products As Oxygen Carriers in Chemical-Looping Combustion," *Energy and Fuels*, vol. 23, pp. 2307–2315, 2009.
- [58] P. Moldenhauer, M. Rydén, and A. Lyngfelt, "Testing of minerals and industrial by-products as oxygen carriers for chemical-looping combustion in a circulating fluidized-bed 300 W laboratory reactor," *Fuel*, vol. 93, pp. 351–363, 2012.
- [59] R. L. Lehman, J. S. Gentry, and N. G. Glumac, "Thermal stability of potassium carbonate near its melting point," *Thermochim. Acta*, vol. 316, pp. 1–9, 1998.
- [60] E.ON Sverige AB, "Bio-CCS blir effektivare med Improbed visar storskaliga tester," *TT*, pp. 1–8, 2022.
- [61] F. Lind, A. Corcoran, and H. Thunman, "Validation of the oxygen buffering ability of bed materials used for OCAC in a large scale CFB boiler," *Powder Technol.*, vol. 316, pp. 462–468, 2017.
- [62] F. Lind and P. Knutsson, "Distribution of oxygen and carbon monoxide in the cross section of a circulating fluidized bed furnace during operating with inert and oxygen active bed materials," in *Clearwater clean energy conference*, 2019.
- [63] A. Corcoran, F. Lind, H. Thunman, and P. Knutsson, "Leachability of potassium from ilmenite used as bed material during OCAC," in *23rd International Conference on Fluidized Bed Conversion*, 2018.
- [64] A. Corcoran, P. Knutsson, F. Lind, and H. Thunman, "Comparing the structural development of sand and rock ilmenite during long-term exposure in a biomass fired 12

- MWth CFB-boiler,” *Fuel Process. Technol.*, vol. 171, no. June 2017, pp. 39–44, 2018.
- [65] M. Vigoureux, P. Knutsson, and F. Lind, “Sulfur Uptake during Oxygen-Carrier-Aided Combustion with Ilmenite,” *Energy and Fuels*, vol. 34, pp. 7735–7742, 2020.
 - [66] A. Gyllén, P. Knutsson, F. Lind, and H. Thunman, “Magnetic separation of ilmenite used as oxygen carrier during combustion of biomass and the effect of ash layer buildup on its activity and mechanical strength,” *Fuel*, vol. 269, no. December 2019, p. 117470, 2020.
 - [67] F. Lind, A. Corcoran, B.-Å. Andersson, and H. Thunman, “12,000 hours of operation with oxygen-carriers in industrially relevant scale,” *VGB PowerTach*, vol. 7, pp. 1–6, 2017.
 - [68] F. Lind, M. Israelsson, and H. Thunman, “Magnetic separation for the recirculation of oxygen active bet materials when combusting municipal solid waste in large scale CFB boilers,” in *Clearwater clean energy conference*, 2018.
 - [69] F. Hildor, T. Mattisson, H. Leion, C. Linderholm, and M. Rydén, “Steel converter slag as an oxygen carrier in a 12 MW th CFB boiler – Ash interaction and material evolution,” *Int. J. Greenh. Gas Control*, vol. 88, no. June, pp. 321–331, 2019.
 - [70] F. Hildor *et al.*, “LD slag as an oxygen carrier for combustion processes,” in *5th International Conference on Chemical Looping*, 2018.
 - [71] S. Pissot, T. Berdugo Vilches, J. Maric, and M. Seemann, “Chemical looping gasification in a 2-4 MWth dual fluidized bed gasifier,” in *23rd International Conference on Fluidized Bed Conversion*, 2018.
 - [72] M. Hanning, A. Corcoran, F. Lind, and M. Rydén, “Biomass ash interactions with a manganese ore used as oxygen-carrying bed material in a 12 MWth CFB boiler,” *Biomass and Bioenergy*, vol. 119, pp. 179–190, 2018.
 - [73] M. Rydén, M. Hanning, A. Corcoran, and F. Lind, “Oxygen Carrier Aided Combustion (OCAC) of Wood Chips in a Semi-Commercial Circulating Fluidized Bed Boiler Using Manganese Ore as Bed Material,” *Appl. Sci.*, vol. 6, no. 11, p. 347, 2016.
 - [74] K. Davidsson, “Slutrapport för projekt: Användning av restprodukter från gjuterier som bäddmaterial vid avfallsförbränning,” Borås, 2019.
 - [75] K. Davidsson, B. Andersson, H. Leion, M. Hedberg, and P. Karmhagen, “Foundry slag as bed material in fluidised-bed combustion of waste (Extended abstract),” in *Nordic Flame Days*, 2019.
 - [76] P. Moldenhauer, S. Sundqvist, T. Mattisson, and C. Linderholm, “Chemical-looping combustion of synthetic biomass-volatiles with manganese-ore oxygen carriers,” *Int. J. Greenh. Gas Control*, vol. 71, pp. 239–252, 2018.
 - [77] Geological Survey of Sweden, “Bergverksstatistik 2018: Statistics of the Swedish Mining Industry 2018,” 2019.
 - [78] M. Öhman, A. Nordin, E. Brus, B.-J. Skrifvars, and R. Backman, “Förbrukning av bäddmaterial i bibränsleeldade fluidbäddar p g a bäddagglomereringsrisk – beläggingsbildning och möjligheter till regenerering,” 2001.
 - [79] S. Z. El-Tawil, I. M. Morsi, A. Yehia, and A. A. Francis, “Alkali reductive roasting of ilmenite ore,” *Can. Metall. Q.*, vol. 35, no. 1, pp. 31–37, 1996.

