# The use of waste materials from steel industry for reduction of $CO_2$ emissions

*Bachelor’s Thesis in the Bachelor Degree Programme, Chemical engineering*

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# Sammanfattning

Stål tillverkas genom antingen järnutvinning från järnrik malm eller genom återvinning av tidigare producerad stål. Produktion av stål från järnmalm sker genom två steg; reduktion av järnoxider till råjärn i en masugn (blast furnace) följt av omvandlingen av järn till stål genom raffinering i en annan sorts masugn vid namn basic oxygen furnace. Stålproduktionen beräknas öka på grund av den ekonomiska tillväxten. Detta resulterar i en ökad produktion av dess biprodukter, så som slagg och växthusgasen $CO_2$. Stålproduktion bidrar med fem procent av världens $CO_2$-utsläpp och har därmed en signifikant effekt på den globala uppvärmningen. Befintliga långsiktiga lösningar för minskning av $CO_2$-utsläpp är otillräckliga med tanke på hastigheten med vilken $CO_2$-utsläppen ökar. En kortsiktig lösning vore att förvara $CO_2$ – som annars hade släpps ut i atmosfären - i undermarksdepåer; en process som kallas för Carbon Capture and Storage. För att på ett effektivt sätt ta tillvara de begränsade depåerna måste $CO_2$ uppta så liten volym som möjligt, vilket åstadkoms genom dess separation från andra gaser i atmosfären innan förvaring. Det billigaste sättet att separera $CO_2$ är genom en process som kallas Chemical-Looping Combustion där en syrebärare överför syre från en syrereaktor till en bränslereaktor. På detta vis kan bränsle i bränslereaktorn förbrännas i rent syre och därmed avge nästan ren $CO_2$. I detta arbete har biprodukter från järnmalmsreduktion har undersökts för sina syrebärarförmågor i CLC. Det undersökta materialet är Hyttslam och LD-sten från SSAB. Båda biprodukterna är rika på järn, vilket har visat ha goda syrebäraregenskaper. Hyttslammet består av för små partiklar för att kunna användas som syrebärare i sitt råa tillstånd. Därför har större partiklar producerats av slammet på två olika sätt och med två olika bindningsmaterial – PVA-binder och refractory cement. CLC-experimenten genomfördes i en fludserad-bädd reaktor med en reaktor av kvartsglas, med metan och syngas som bränsle. Hyttslammet och de större partiklar som tillverkades av hyttslam visade hög kolomvandling i syngas, men när metan användes minskade omvandlingen dramatiskt. De PVA-baserade partiklarna kunde inte fluidisera, partiklarna var också för dyra att producera. Däremot visade sig de cementbaserade partiklarna både vara billiga att framställa och ge god kolomvandling i metan, vilket indikerar en god omvandling i syngas också. Det finns potential hos de cementbaserade partiklarna om fortsatta studier genomförs på dem. LD-stenarna visade låg omvandling av kol dels på grund av deras inhomogena innehåll och dels på grund av deras relativt låga järnhalt.

# Abstract

Steel is produced by either iron winning from iron rich ores or by recycling of already produced steel. The iron ore-based production is a two-step process, consisting of reducing iron oxides into metallic iron in a blast furnace, followed by converting iron into steel in a basic oxygen furnace. Due to economic growth, the generation of steel is predicted to increase significantly in the future. This will of course result in a higher generation of its by-products, such as slag and the greenhouse gas $CO_2$. Steel production stands for five percent of the world's total $CO_2$ emissions; thereby having a considerable effect on the increase in global surface temperatures. Long term solutions in reduction of $CO_2$ emissions are insufficient considering the rate in which $CO_2$ emissions are increasing. A short term method of reducing $CO_2$ emissions is by Carbon Capture and Storage, where the idea is to store $CO_2$ in underground deposits instead of releasing it into the atmosphere. In order for efficient use of the limited deposit space, it is necessary to separate $CO_2$ from other gases prior to storage. The most inexpensive method of separation is by a process called Chemical-Looping Combustion; a separation method that requires an oxygen carrier to transfer oxygen from an air-containing reactor to a fuel-containing reactor; by these means, fuel is combusted in a nitrogen-free environment and the gas leaving the fuel reactor will be almost pure $CO_2$. In this work, by-products from iron ore-based steel production were examined for their ability as oxygen carriers in a chemical-looping combustion; flue dust and LD-slag from the blast furnace and the basic oxygen furnace are the by-products investigated in this work. The reason why by-products are considered as oxygen carrier materials is because of their iron content, which has in previous research shown to have good oxygen carrier abilities. The flue dust consists of very fine particles; too fine to be used as oxygen carrier material. Therefore, larger particles were produced from the dust in two ways, using to different binder materials – PVA binder and refractory cement. The experiments were carried out in a tubular quartz glass fluidizing bed reactor, using the fuels syngas and methane. Flue dust and its particle derivates showed high carbon conversion in the case of syngas used as fuel. When methane was used as fuel a very low conversion was observed. The PVA-based particles did not fluidize in the reactor. Further on, the production of that particular particle showed to be too expensive for the process to be profitable. However the second type of particles produced, based on refractory cement, are both cheap and showed acceptable conversion rates, indicating a potential in high carbon conversion in syngas. However, further work is required to verify if these particles work well also with other fuels. The results for the LD-slag showed that it would not be a very good oxygen carrier; partly due to its inhomogeneous composition, but also because of its relatively low iron content.

Key words: steel, flue dust, LD-slag, by-products, $CO_2$-emissions, recycle, chemical-looping combustion, oxygen carrier

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# 1. Introduction

The term “steel” is usually used to describe alloys containing iron as a major constituent and in which the carbon content is normally less than two percent [1]. Steels are known to be very useful materials with metallic properties due to their high versatility, durability, abundance and relatively low price [2]. By modifying the content of alloying elements and the performed heat treatment, a wide range of mechanical and physical properties can be obtained – steel can be modified to be soft when shaping, which is an important property, or very hard when the materials have to withstand high load without deforming or breaking; furthermore, the corrosion properties can be altered to acquire high resistance which additionally increases the durability [1]. The highly versatile material steel is used mainly in the construction industry, but it is also found in domestic appliances, packaging-, transport- and power industries [3]. Figure 1 shows a graph of the annual increase in steel production in 64 countries in the period between year 2000 and 2011. In 2011, over 1.49 billion tons of steel was produced worldwide [4]. The production is estimated to continue increasing annually, due to the development of third world countries, where the availability of steel is vital. [5].

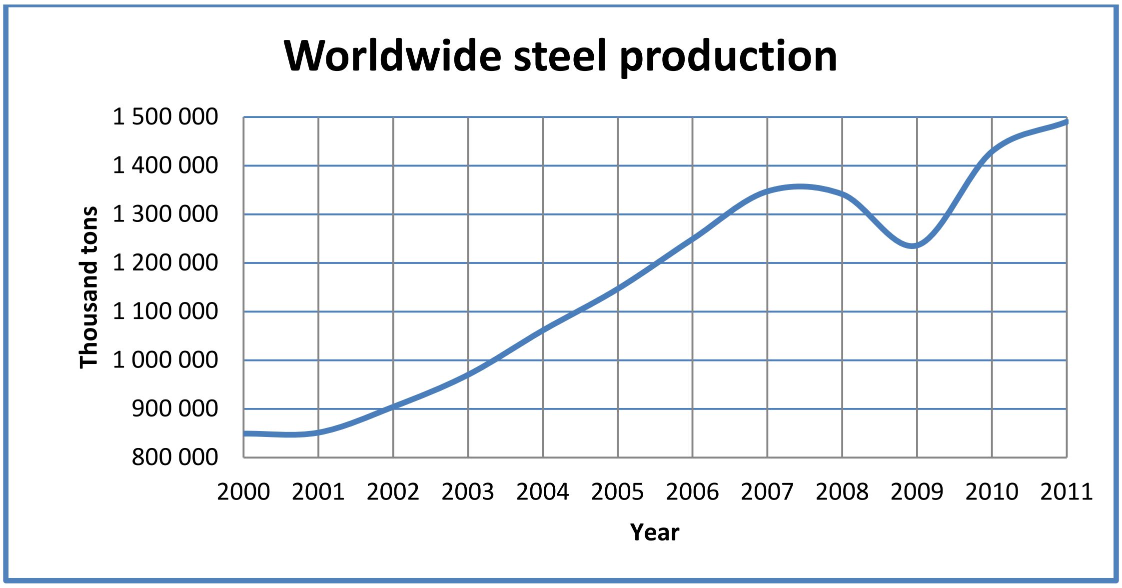


**Figure 1. Annual steel production based on data collected from 64 countries [4].**

Steel is mainly produced in two ways; by iron extraction from iron rich ores and by recycling of already used steel. Production of steel from iron ore is done in a blast furnace (BF) followed by a basic oxygen furnace (BOF). In the blast furnace, iron is extracted by reducing the iron oxides from the ore to elemental iron (hot metal) under high temperatures. The hot metal is in its turn converted to steel in the basic oxygen furnace by oxidizing carbon contained in the hot metal to CO and $CO_2$.This step is done in order to lower the concentration of elemental carbon in the metal to below two percent, which is the content that defines the conversion to steel [1]. When steel is produced through recycling of already used material, it is done by melting it in an Electric arc furnace (EAF). Inside the EAF, the melt is further refined in order to remove any impurities. The steel melt is then tapped from the EAF and remolded to new products.

Apart from being the most widely used material with metallic properties, steel is also the most recycled material in the world [6, 7], with about 500 million metric tons (mmt) of steel scrap being melted each year [6]. However, solely recycling of used material does not meet the increasing demand for new steel, which makes it necessary to include iron ore in the production [5]. This in turn leads to the generation of by-products. The total amount of non-gaseous by-products per ton of produced steel is around 2-4 tons [8]. By-products from steel industry are commonly recycled and used in a number of different productions, but still large amounts of generated wastes have to be disposed in e.g. landfills. Waste disposal is expensive due to the cost of disposal itself and to the loss of possible source material. The disposal is also environmentally damaging, as the waste contains harmful components, such as heavy metals.

One of the unwanted by-products from the steel industry is the emitted $CO_2$. $CO_2$ is a greenhouse gas (GHG), thereby contributing to keep appropriate temperatures in the atmosphere. However, the increase of $CO_2$ concentration in the atmosphere caused by anthropogenic emissions has shown to have a clear effect on global warming [9]. An average of 1.9 tons of $CO_2$ are emitted for every ton of steel produced making the iron and steel industry account for approximately 4-5 percent of total world $CO_2$ emissions [5]. The impact that steel production has on global warming can however be prevented by finding ways of producing steel in a more sustainable manner, either by a production method that produces less $CO_2$ or by preventing the produced gas from being released into the atmosphere.

The aim of this thesis is to investigate the possibility of decreasing the amount of $CO_2$ emissions from steel production with the use of the by-products generated within the steel plant. Iron rich by-products are analyzed in their oxygen carrier abilities in order to be used in chemical-looping combustion - a $CO_2$-isolating combustion process. Reusing by-products in this manner would lead to a more sustainable steel production through the minimizing of landfill waste disposals, reduction of $CO_2$ emissions and preservation of natural resources. Further on, many steel manufacturers share similar methods for steel production and thereby generate similar by-products; the results from this study can therefore be used generally as contribution for reaching an efficient and sustainable steel production. Two waste materials from steel industries have been examined in the present thesis – flue dust from the blast furnace and LD-slag from the basic oxygen furnace. Both materials originate from the Swedish steel manufacturer SSAB.

# 2. Background

Steel can be produced through a number of ways, the most common being from the reduction of iron oxides in iron ore. The generation of by-products during this production is inevitable; the most common being slags, dusts and sludges. The content of the by-product varies depending on its origin; however all of them contain a considerable amount of iron; an element which could be useful as a tool in the fairly new method of reducing $CO_2$ emissions by Carbon capture and storage.

This chapter describes the general methods of steel production, with focus on the most common form of production, iron ore based production. The description of the production methods is followed by a description of by-products generated from the processes. Lastly, the environmental problem of high $CO_2$ emissions and its relation to the steel industry will be introduced followed by the idea of reusing certain by-products in order to reduce the emissions.

## 2.1 Steel production process

There are two main ways in which steel is produced; it is either based on iron ore or on scrap. About 70 percent of the world steel production is through the iron ore based process. Iron ore based steel, as the name indicates, is produced from iron rich ores, containing a high amount of iron oxides, such as magnetite ($Fe_3O_4$) and hematite ($Fe_2O_3$). The process of steel production from iron ore is mainly carried out in two steps; producing iron via the blast furnace (BF) followed by steel production in the basic oxygen furnace (BOF). Another way for producing ore-based steel is through the process of direct reduction (DRI) of iron oxides followed by steel production in the electric arc furnace (EAF). Scrap recycling accounts for the remaining 30 percent of steel production worldwide. Scrap based steel is produced from recycled steel scrap in an Electric arc furnace (EAF) [10]. Scrap based steel production lies outside the focus of this work; therefore its description is left out of the text.

### 2.1.1 Iron ore-based steel production

Iron ore-based steel production is a two-step process including the extraction of iron from iron oxides in a blast furnace (BF), followed by reduction of excessive carbon from the iron in a basic oxygen furnace (BOF). The overall process of steel production from iron ore is shown in figure 2.

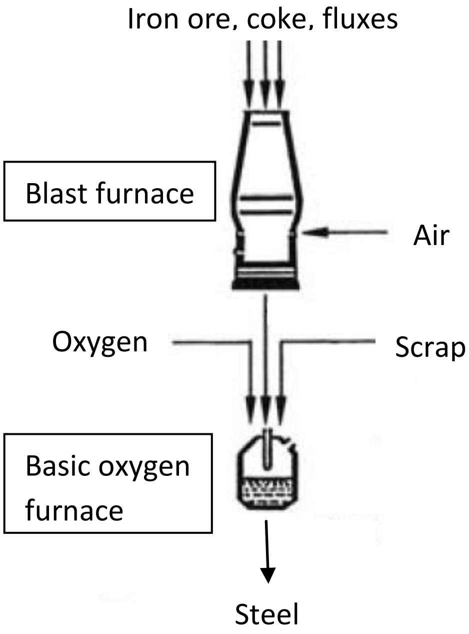


Figure 2. Schematic image of the iron ore-based steel production process [11].

The BF is a large chemical reactor in the form of a vertical shaft [12]. Pelletized iron ore, coke and fluxes, in the form of either limestone or dolomite, are continuously charged on its top. Coke, which is a carbon rich fuel, reacts with the oxygen in the blast furnace to form CO in the following reaction:

$C + \frac{1}{2}O_2 \rightarrow CO$ (1)

The formed CO then reduces the iron oxides from the iron ore to metallic iron; a process which is described further on in the text. The heat generated during the CO-formation is used for melting of the iron and sustaining adequate temperatures for overall reactions [12]. At the same time the introduced coke provides structural support within the furnace by creating stable areas of permeability, through which gases can ascend and molten iron can trickle down through [13, 14]. The BF can be divided up into four zones (see figure 3), based on the reactions occurring inside. The zones are arranged in the order of occurrence from the bottom of the furnace to the top [12];

### Zone 1. Hearth and raceway

Zone 1 is where most of the CO is generated. Air enters this zone through pipes, called tuyeres, and creates an air-rich area known as the raceway. Reaction (1) is the sum of reaction (2) and (3), which occur near and inside the raceway respectively. When the descending coke is getting close to the raceway, it is combusted (reaction 2). The combustion is exothermic, generating heat that raises the temperature to about 1370°C. This temperature is necessary since reaction (3), called carbon gasification, is shifted to the right in temperatures above 1100 °C. When the coke reaches the raceway, reaction (3), also known as the Boudouard reaction, occurs [12, 15].

$C + O_2 \rightarrow CO_2$ (2)

$C + CO_2 \leftrightarrow 2CO$ (3)

### Zone 2. Melting zone and reduction of wustite

The second zone is situated just above zone 1 where temperature ranges between 1000°C and 1300°C. In this zone, wustite (FeO) is reduced to metallic iron. The reduction is shown in reaction (4) and is called indirect reduction. The CO in the reaction has ascended from the raceway where it was generated from reaction (1). As long as the temperature is above 1100°C, CO is continuously regenerated in this zone from the Boudouard reaction, for further reduction with wustite. Metallic iron, having a melting point of between 1200°C and 1500°C, starts to melt in this zone [13, 12].

$CO + FeO \rightarrow Fe + CO_2$ (4)

### Zone 3. Thermal reserve zone

By the time the reduction gas, CO, has reached the third zone, the temperature has decreased to about 900°C. This is partially due to the Boudouard reaction, which is endothermic. Another reason for the lower temperature in this zone is the continuous charging of raw materials into the furnace from the top. These materials have a room temperature when charged into the furnace, thereby cooling their surroundings when mixed with the components inside the furnace. Since the Boudouard reaction produces CO only at temperatures above 1100°C, the predominant reaction in this zone becomes the reduction of wustite (reaction 4). This reaction is only slightly exothermic, keeping the temperature in this zone steady, within the range of 800°C and 1000°C.

### Zone 4. Upper stack

In the fourth zone, the temperature is below 800°C [13, 12]. In this upper stack part, the reduction of magnetite and hematite take place. The more wustite is reduced, the more the amount of surrounding CO decreases. When the concentration of CO is low enough, reduction of magnetite ($Fe_3O_4$) and hematite ($Fe_2O_3$) are favored instead. Hematite is first reduced to magnetite before it can be further reduced to wustite (FeO), see reaction (5) and (6). Together, these reactions have a net uptake of energy that causes a lowering of the surrounding temperature. The relatively low temperature in this zone is partially due to these endothermic reactions.

$$CO + 3Fe_2O_3 \rightarrow 2Fe_3O_4 + CO_2 \qquad (5)$$

$$CO + Fe_3O_4 \rightarrow 3FeO + CO_2 \qquad (6)$$

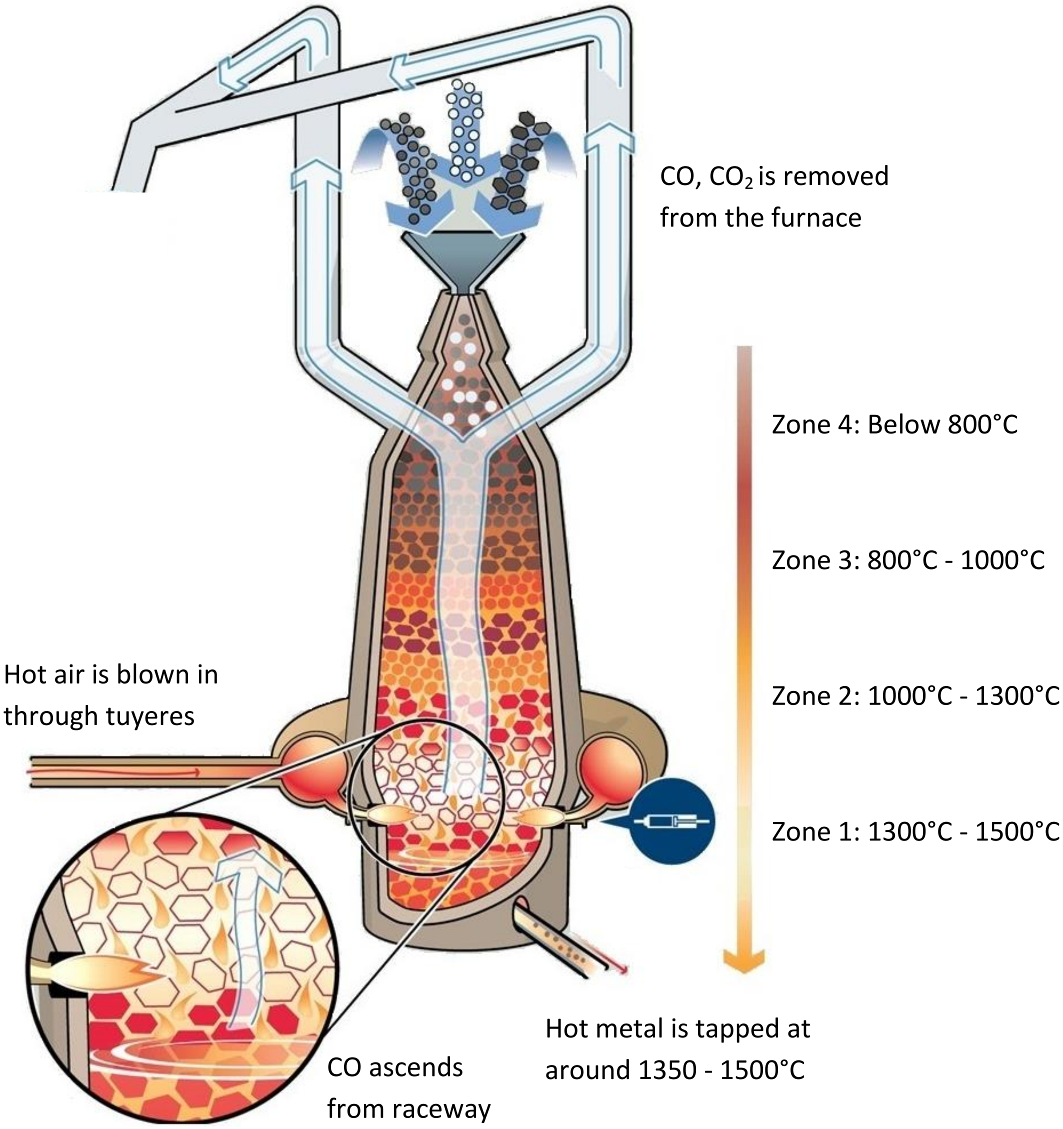


**Figure 3. A overview of the Blast furnace [16]. Zone 1: Hearth and raceway, zone 2: melting zone and reduction of wustite, zone 3: thermal reserve zone, zone 4: upper stack [12].**

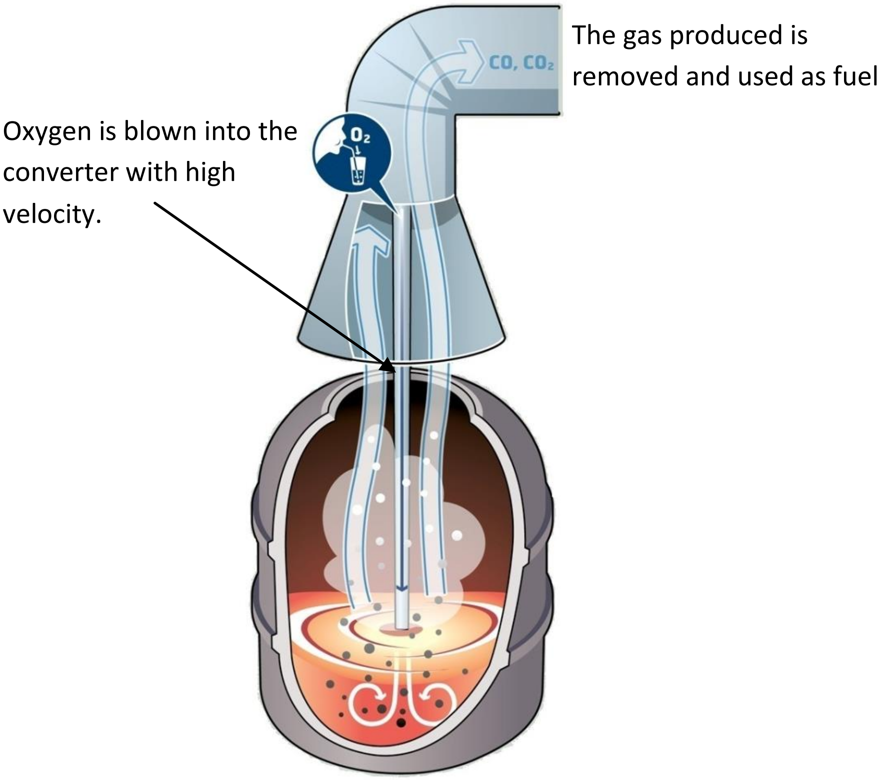
The metallic iron produced inside the BF, called hot metal in melted condition, trickles down the furnace and is collected at the bottom where it is tapped at a temperature of between 1350°C and

1500°C. The remaining $CO_2$ and CO is collected at the top of the furnace and burned to provide energy for the steel plant [11].

In order for the hot metal to convert into steel, its carbon content has to drop below two percent [1]. This carbon level is acquired by the process of decarburization inside a basic oxygen furnace (BOF), which commonly is a Linz-Donawitz converter (LD-converter), shown in figure 4. In an LD-converter, oxygen is injected from above, onto the surface of the melt. The injection is done with high velocity, enabling the oxygen to be mixed thoroughly with the hot metal. When carbon, and other impurities, in the hot metal get in contact with oxygen, they are oxidized. Carbon combusts into CO as shown in reaction (1); this reaction is known as decarburization.

$$C + \tfrac{1}{2}O_2 \rightarrow CO \tag{1}$$

The oxidation raises the temperature of the melt up to 2500°C – 3000°C. Between 10 – 20 percent steel scrap is added to the LD-converter to limit the temperature increase during the oxidation. The gas that is produced is removed and used as fuel for heating of the steel plant. At the end of the oxidizing treatment, the steel produced is tapped onto a ladle by tilting the converter [11].



The gas produced is removed and used as fuel

Oxygen is blown into the converter with high velocity.

**Figure 4. A schematic image of an LD-converter [16].**

An alternative way of producing steel from iron ore is through iron production via direct reduction (DR) followed by steel production in an electric arc furnace (EAF). In DR, iron ore is reduced to solid iron, using a reducing agent e.g. natural gas. Four percent of the world’s steel is produced from DR [17]. In the Electric arc furnace (EAF), the solid iron is melted and refined to produce steel [3]. Since this production method is not the focus of this work, it will not be regarded in detail.

## 2.2 By-products from iron ore-based steel production

Along with the production of iron and steel, by-products are formed at the different steps of the production process. The most common forms of by-products in iron ore-based production are slag flue dust and sludge. Slag is generated from the removal of impurities in the hot metal. These impurities dissolved in the molten metal need to be removed as they either make metallurgical processing more difficult or degrade the iron and steel quality [10]. Dust and sludge, however, are particles entrained in the gas that leaves the reactors. In the following text, the origin, content and current usage of these by-products are described.

### 2.2.1 Slags

Slag consist of a stony matter which is separated from metals during smelting and refining of the iron ore. The by-product, which is a mixture of mostly silica ($SiO_2$), calcium oxide (CaO), magnesium oxide (MgO) and iron oxides, accounts for 90% of the total amount of the produced waste [10].

There are three main types of slag, categorized by how they are cooled after separation – air-cooled, granulated and pelletized. Air-cooled slag is hard and dense and especially suitable for use as construction aggregate. It can also be made into mineral wool which is mainly used for thermal insulation [18]. Granulated slag forms sand-sized particles of glass and is primarily used to make cementious material. Pelletized slag has a vesicular texture and is most commonly used as a lightweight aggregate. If finely ground, it also has cementious properties. In some countries, up to 80 % of the cement contains granulated slag [10].

The content of slag vary slightly depending of the origin of its production, which is mainly divided in iron making slag and steel making slag. Slag produced from steel making contain a high content of free lime (CaO) (30-59%), which causes an expansion of the by-product when in contact with humidity or water [10, 19, 20]. The main use for steel slag is as stone aggregate substitute - however, the expansion properties of the material limits its uses in construction to less than half of the total amount recovered slag [10, 19]. In order to be used as construction material, it needs to be stored in piles for some months to allow for the expansion and leaching out of free lime. Otherwise, the slag may not have the sufficient volume stability as construction material [18, 20].

Some slag is used internally in the steel making furnace or sinter plant [10]. It is used in steel making processes as a substitution for part of the limestone flux. In these processes, the Fe in the steel slag is also recovered. However, significant P and S content of steel slag, which is harmful to iron and steel making, and the substantial content of silica, limits the amount that can be used as limestone substitute. The remaining steel slag is usually subjected to metal recovery from which the residual slag is used as a co-product or stockpiled [19].

### 2.2.2 Dusts and sludges

Dust is the stream of particles that have been entrained in the flue gas exiting the reactor. Sludge is a product of the separation of dust from gas by the addition of water, creating a highly moist and viscous mixture of liquid and dust particles [10, 21].

Chemically, blast furnace sludge is dominated by carbon (19-30%), hematite ($Fe_2O_3$) (45-51%) and significant amounts of Si, Al and Ca. Most modern mills recycle the Fe-rich BF dust/sludge either directly back to the blast furnace or via a sinter plant [19]. Basic oxygen furnace flue dust contains around 2-8% Zn and 0.2-1% Pb while the Fe content is very high, in the range of 50-80%. Although the high Fe content, direct utilization of the dust is however not possible as the dust contains intolerable amounts of Zn and other elements such as Pb, Cu, S, Na and K as well as significant amounts of halides. Zinc causes among other things refractory failure, requiring its content in iron ore to be less than 0.01% for it not to have a negative effect on the steel production process. The recycling of the dust to steelmaking causes the volatile components to recirculate, giving rise to the build-up of impurities in the melt [22].

## 2.3 Steel production from a sustainable perspective

Global warming has come to be of great concern due to its negative effects on the environment; its main cause has shown to be emissions of greenhouse gases such as $CO_2$. Steel production is known to stand for around five percent of the world's total $CO_2$ emissions, thereby having a considerable effect on global warming [5, 9]. Our only short term way of reducing $CO_2$ emissions is by Carbon capture and storage, which is in turn achieved in the cheapest manner through Chemical-looping combustion; a process in need of so called "oxygen carriers". Using iron oxide rich by-products from steel production as oxygen carriers in Chemical-looping combustion could lead to less $CO_2$ emissions as well as making use of by-products which are currently being disposed in landfills. This chapter presents this environmentally sustainable method of producing steel.

### 2.3.1 $CO_2$ emissions and ways to mitigate them

$CO_2$ is a greenhouse gas (GHG), meaning that it is one of the gases that helps to keep the temperature on the earth's surface appropriate. The increase of $CO_2$ levels due to anthropogenic activities has been connected to the observed raise in the average global temperature [9]. During the last hundred years a rise in the earth's temperature of 0.74 ± 0.18°C has been observed. The pre-industrial $CO_2$ level in the atmosphere was 280 ppm; in 2010 the level of $CO_2$ was measured at 390 ppm which represents an increase by 39 % [12, 15]. The anthropogenic emissions of $CO_2$ are mainly from the combustion of fossil fuel; around 30 percent from power production and 20 percent from transportation [9]. In 2004, the combustion of fuel accounted for 56 % of the anthropogenic GHG emissions, expressed in $CO_2$ equivalents [23]; of those 56 %, 77 % were due to $CO_2$. The $CO_2$ emission from steel industry is, as previously stated, around 1.9 tons of $CO_2$ per ton of steel produced, accounting for approximately 4-5 % of the total world $CO_2$ emissions [5, 9].

As the GHG emissions are estimated to increase, particularly due to the economic growth of developing countries [9], finding a way to counteract a possible global warming has become of great importance. Since $CO_2$ represents a significant part of the total GHG, decreasing its concentration in the atmosphere is a key issue worldwide. The existing alternatives for decreasing $CO_2$ emission in the long-term are by increasing the efficiency of energy conversion and usage, and by changing to fuels with lower carbon content. Due to our currently strong dependence on fossil fuels, a method of short-term decreasing of $CO_2$ is needed in order to avoid further accumulations of it in the atmosphere. The only short-term possibility allowing direct decrease in $CO_2$ concentration in the atmosphere is through Carbon Capture and Storage (CCS). In CCS, $CO_2$ from fossil fuel combustion is instead of being released into the atmosphere, gathered, compressed and stored in large underground depots. Combustion of fuel is done in air, which contains around 80 % nitrogen gas. The combustion therefore generates a gas mixture of $CO_2$ and $N_2$, with $N_2$ taking up to 80 % of its volume. The available depots for $CO_2$ storage are limited, and it is therefore important to use them efficiently. Since nitrogen gas has no impact on global warming, it could be separated from $CO_2$ so that the limited deposit space could be used for sole storage of the greenhouse gas. The depots are rarely in connection to a power plant, or other $CO_2$ generating factory, and therefore have to be transported there. The $CO_2$, would then preferably be transported as a liquid which requires that it is compressed after being separated from a combustion process. Compressing the lower volume of the solitary $CO_2$ generates also lower costs compared to compressing the total volume of $CO_2$ and $N_2$. Separation of $CO_2$ after the combustion with air – the post-combustion separation methods - has shown to be very energy consuming and the most costly part of the CCS chain. A way to avoid separation of $CO_2$ from $N_2$ is to change the combustion conditions and separate the $O_2$ from the air prior to its reaction with the fuel, in a so called unmixed combustion. This method of combustion is possible through a process called Chemical looping combustion (CLC) [9].

### 2.3.2 Chemical-looping combustion process

Chemical-looping combustion (CLC) is a method of fuel combustion where a solid oxygen carrying material is used to transport oxygen from the combustion air to the fuel reactor, thereby allowing combustion of fuel in oxygen to take place. Figure 5 shows a schematic image of a CLC combustor. The combustor consists of two fluidized bed reactors; an air reactor and a fuel reactor. The oxygen carrier material transports oxygen to the fuel reactor, where it is used for combustion; afterwards it returns to the air reactor, where it is again enriched in oxygen. The material repeats these steps in a loop motion, hence the name of the process. Reaction 11 describes the process inside the fuel reactor. It can either be exothermic or endothermic depending on the oxygen carrier and the fuel used. Reaction 12 takes place in the air reactor and is always exothermic [9]. The net reaction, reaction 13, is the same as for normal combustion where fuel is combusted in air. The total amount of energy evolved from reactions 11 and 12 is the same as for normal combustion [24]. The temperature range inside the combustor is between 800°C and 1200°C. This relatively low reaction temperature range prevents the production of the environmentally hazardous $NO_x$ from nitrogen that could occur in the fuel [9].

Fuel reactor: $(2n + m)M_yO_x + C_nH_{2m} \rightarrow (2n + m)M_yO_{x-1} + mH_2O + nCO_2$ (11)

Air reactor: $(2n + m)M_yO_{x-1} + (n + \frac{1}{2} m)O_2 \rightarrow (2n + m)M_yO_{x-1}$ (12)

Net reaction: $C_nH_m + (n + \frac{1}{2} m)O_2 \rightarrow mH_2O + nCO_2$ (13)

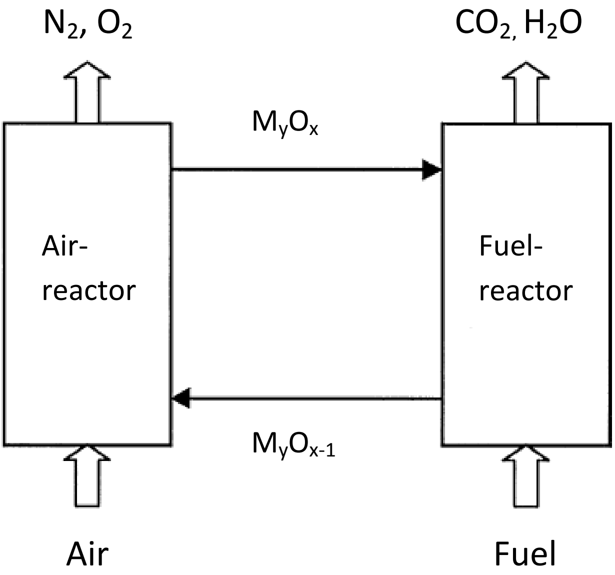


Figure 5. Schematic view of a CLC reactor [9]

As shown in figure 7 and equation 13, the only products in the fuel reactor are $CO_2$ and $H_2O$ (steam). The steam is easily removed by condensation and the $CO_2$ can then be compressed and transported to a depot [9]. The exit gas from the air reactor contains mostly $N_2$ and a small amount of unused $O_2$ [24].

### 2.3.3 The CLC system with two interconnected fluidized bed reactors

In a CLC process, interconnected fluidized bed reactor is the chosen system as the reactor fulfills the important requirements of giving good contact between the solid oxygen carriers and surrounding gas as well as allowing a flow of the solid oxygen carriers between the reactors. A fluidized bed represents a bed of solid particles behaving as a fluid by the help of an upward stream of gas or liquid with a certain volume flow rate (Vmf); the Vm describes the lowest flow rate needed to reach fluidization. The fluidization gives good contact between the particles and gas in the bed and good gas-particle heat and mass transfer [25].

The system, which is shown in figure 6, consists of two interconnected fluidized beds; one is the air reactor and the other is the fuel reactor. The air reactor is a high velocity riser (marked as 1 in figure 6), in which the air passes through in a large and rapid flow. The gas velocity in the riser provides the driving force for the oxygen carrier particles to be circulated between the two beds. The rising particles are caught in a cyclone (marked 2 in figure 6), which makes them lose velocity and fall down to the fuel reactor (marked 3 in figure 6), which is a low velocity bubbling bed. From here, the particles are returned to the air reactor by means of gravity. Non-condensible gas, which is any un-reacted fuel gas, is recirculated to the fuel reactor. A small amount of the non-condensible gas is bled to the air reactor to avoid accumulation of non-combustible gases, such as $N_2$ in the recirculation loop. Flue gas is the exit gas from the air reactor [24].

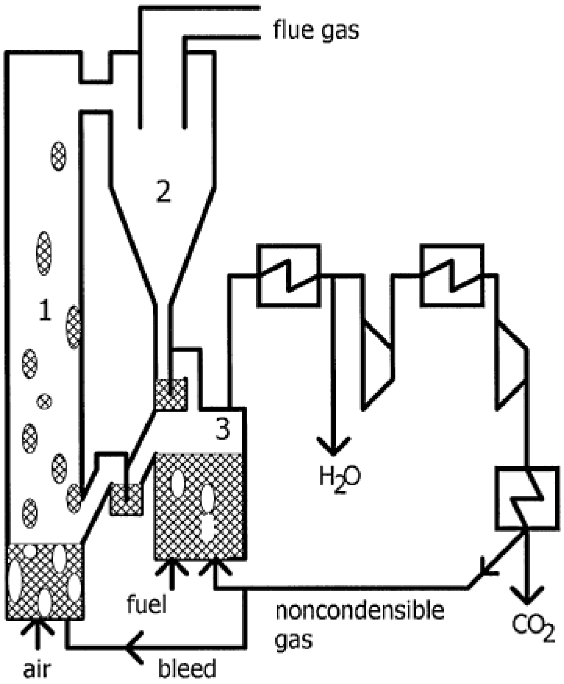


Figure 6. A model of interconnected fluidized bed reactors for CLC [24]

### 2.3.4 Oxygen carriers

To develop this promising technology for $CO_2$ capture, further important research work is needed which includes the development of oxygen carriers. Different metal oxides have been proposed for use as oxygen carriers in CLC. For the feasible metal oxide systems, the thermodynamic equilibrium for the reaction with fuel has to be favorable in order to achieve high fuel conversion to $CO_2$ and $H_2O$.

The oxygen carrier must show high reduction and oxidation reaction rates; otherwise the amount of oxygen carrier needed in the reaction would have to be large, resulting in higher material costs [9]. Since the proposed reactor systems consist of fluidized beds, the particles need to have a low tendency for agglomeration, fragmentation and attrition. Such properties can be found in Fe, Ni, Co, Cu, Mn and Cd [24]. Iron, and its oxides are the cheapest out of these metals as well as not toxic, making it a suitable candidate for oxygen carrier in a CLC process. Different works have shown that iron based oxygen carriers have enough reactivity for efficient usage in CLC. Furthermore, the particles have shown a high enough crushing strength to be used in a CLC system, as well as low tendency for agglomeration [26].

### 2.3.5 Steel by-products as oxygen carriers in chemical-looping combustion

The high amount of iron oxide in flue dust and LD-slag make the wastes an attractive source of oxygen carrier material for Chemical-looping combustion. The by-products were therefore analyzed in this work to get an insight in their oxygen carrying capability for CLC. Experiments were conducted in tubular quarts reactors under fluidized bed conditions (described in chapter 3.3) to create similar conditions as would exist in a CLC-unit; this method of analysis is a cheaper and suitable for experiment. In order for the by-products to be appropriate for use as oxygen carriers they must possess the properties presented in chapter 2.3.4.

The purpose of the experiment is to analyze the by-products behavior in CLC-similar conditions in order to determine if they are applicable as oxygen carriers in chemical-looping combustion. Flue dust in particular has high iron content, making it a suitable candidate for oxygen carrier material; it however consists of small particles that must be fused into larger particles in order to sustain in the reactor with only negligible amounts entrained with gas exiting the reactor.  Part of the aim of the experiment is therefore to find a cheap way of producing the larger particles which are needed in order to use the dust in as oxygen carrier.

If shown to have the right properties for usage in CLC, the by-products can potentially be used as an oxygen carrier for isolation of $CO_2$ in carbon combustion at the mill as well as at any other stationary and high $CO_2$ emitting power producer in the world. This would not only reduce $CO_2$ emissions but also make use of the currently landfill disposed by-product.

# 3. Information Research from internet sources

Many facts and data in this work have been collected from different websites. The relatively large proportion of web-page sources is due to the reliable and useful information they contain for this study. Primarily, three websites have been used as web-page sources; SSAB.com, worldsteel.org and steeluniversity.org.

SSAB.com is the home website of the Swedish steel manufacturing company SSAB, from which the material investigated in this work, derives from. It has been useful in portraying the manufacturing process of the company.

Worldsteel.com is the website of the World Steel Association, which is one of the largest industry associations in the world. It represents approximately 170 steel producers (including 16 of the world's 20 largest steel companies), with its members representing around 85% of world steel production. The website has supplied data on production amounts of steel, iron and their by-products as well as reports on its environmental impacts and recycling options.

Steeluniversity.org is an e-learning page developed by the World Steel Association. It provides information on steel technologies, covering all aspects of iron- and steel production processes through to steel products, their applications and recycling.

# 4. Experimental work

The main focus of the present thesis is to investigate the behavior and sustainability of by-products from steel production in a CLC process. The aim is to determine the by-product´s ability and efficiency as oxygen carrying material i.e. their reactivity in reducing and oxidizing conditions. In order to accomplish this, the by-products were subjected to material characterization to reveal their elemental and crystal structure, the particle size distribution, mechanical stability and density. Material characterizing analyses were done both before and after the experiment, to identify mechanical and chemical changes in the materials as a result of the performed experiments.

## 4.1 Materials used

The materials used for the experiment are by-products from the Swedish steel manufacturing company SSAB. Two by-products are analyzed; flue dust from the Blast furnace and slag from the Basic oxygen furnace.

### 4.1.1 Flue dust

The flue dust, shown in figure 7, comes from the cleaning of the flue gas from the blast furnace. The gas is mixed with water to capture the particles within it. The water-particle mixture is left still for sedimentation of the particles. The sediment particles are then excavated, drained from water and disposed. The dust received has been deposited for at least three months. Despite the draining of water from the particles, they are still highly moist, giving the dust the consistency of sludge. The very small particles contain mostly carbon, coke, calcite ($CaCO_3$) and hematite ($Fe_2O_3$), giving them a black color. A list of the most abundant elements in the dust was given from SSAB and is found in table 1.

Figure 7. Flue dust received from SSAB for analysis

### 4.1.2 Slag

The slag investigated in this present work comes from a type of BOF known as an LD-converter and is therefore called LD-slag. The slag by-product was received as an inhomogeneous mixture of particles with colors ranging from grey to black and sizes ranging between 2 and 10 cm; see figure 8. It has been disposed for an unknown period of time and thereby been exposed to different weather conditions, such as rain and wind. After the slag has been tapped from the LD-converter, it has been cooled by adding of water. The cooled slag is then crushed into a very inhomogeneous mixture of rocks and deposited. Common minerals in the LD-slag prior to deposition are Larnite ($Ca_2SiO_4$), Srebrodolskite ($CaFe_2O_4$), Hatrurite ($Ca_3SiO_5$), Wustite (FeO), Lime (CaO) etc [8]. Once the slag has been exposed to weather conditions the lime in it reacts with water to form Portlandite ($Ca(OH)_2$).

Figure 8. LD-slag received from SSAB for analysis

The minerals that are studied in the present thesis were initially characterized by SSAB. A list of their compositions is shown in table 1. According to SSAB the flue dust contains 35.6 wt% carbon, exceeding the amount of iron in the material. The carbon would amount to 130 wt% $CO_2$ in combustion.

| **Element** | **Fraction (wt%)** | |
|---|---|---|
| | Flue dust | LD-slag |
| **S** | - | 0.070 |
| **Cr** | - | 0.420 |
| **C** | 35.6 | - |
| **Zn** | 0.423 | - |
| **V** | 0.100 | 1.72 |
| **Al** | 1.53 | 0.582 |
| **Ca** | 2.43 | 31.1 |
| **Si** | 3.04 | 5.52 |
| **Mg** | 1.32 | 6.41 |
| **Fe** | 33.5 | 17.4 |
| **Mn** | 0.163 | 2.63 |
| **P** | 0.0349 | 0.179 |
| **Ti** | 0.162 | 0.887 |
| **Na** | 0.200 | 0.0223 |
| **K** | 0.332 | 0.0166 |

Table 1. Most abundant elements in flue dust and LD-slag.

## 4.2 Material characterization

Particle characterization was done to determine the chemical and mechanical properties of the materials used in the experiment. The crystal structure of the material was characterized by X-ray diffraction (XRD). Crushing strength, density and particle size distribution measurements were done in order to determine the mechanical stability of the particles. All but density measurements were done both before and after the experiment to characterize any changes in the samples due to the performed exposures.

By using the analyses methods of Scanning electron microscope (SEM), and Energy dispersive X-ray spectroscopy (EDX), the microstructure and elemental structure of the materials can be determined. Although these analyses were performed on the materials, a proper review of the results was not done due to lack of time.

### 4.2.1 X-ray diffraction

The goal in using X-ray diffraction is to analyze the crystalline phases present in the material samples. Crystal structure creates a characteristic diffraction pattern when interacting with X-rays. This unique pattern helps to recognize the identity of contained minerals in the sample.

In XRD, monochromatic X-rays are produced in an X-ray tube and directed in a determined angle towards a sample which is to be analyzed. When the X-rays hit the sample they will be scattered in a variety of angles. If the incident X-ray beam hits a compound composed of an ordered atomic structure, such as a mineral, constructive interference will occur between the reflected X-rays in certain angles. Constructive interference, which is portrayed in figure 9, occurs when X-rays reflected at the same angle from different planes in the crystal structure have a path distance of an integer number of waves from each other. Constructive interference obeys Bragg's law of diffraction: $n\lambda = 2d_{hkl}\ sin\theta$ [8]. Here, $d_{hkl}$ denotes the distance between the planes in the crystal, θ is the incidence- and diffracted angles, n is an integer number, and λ – the wavelength of the X-rays [27].

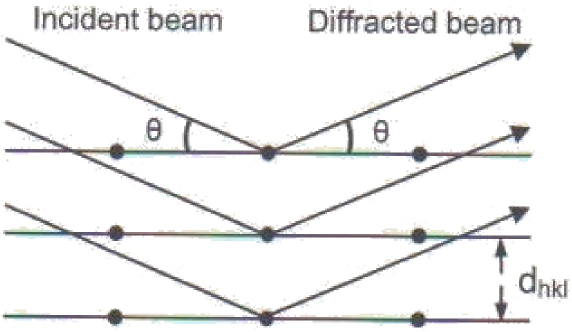


Figure 9. Reflection of incident beams from crystal planes [27]

The setup of an XRD is usually, as shown in figure 10. The X-ray source is fixed at a certain angle and a detector is moving over a determined range of angles in order to detect the scattered waves [27]. A moving detector records wave intensities at different angles. A transducer then converts the intensities into electrical signals that are shown in a diffractogram based on the detected angles and the X-ray intensities [28]. For best result, the sample analyzed should consist of small particles.

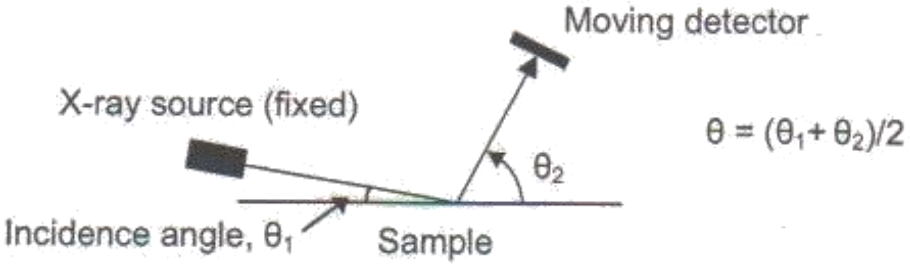


Figure 10. Common set-up of XRD constituents [27]

The recorded diffraction patterns are compared to diffraction patterns from samples with a known content that are summarized in a database. Comparison between them allows determining what crystal structures are present in the analyzed sample. As patterns in the database are in some cases very similar, knowing the elemental composition allows further relating the crystal structure to a chemical substance [28]. XRD is a commonly used non-destructive technique used to characterize crystalline material. It is considered to be a rapid way of analyzing. Still, in order for the obtained results to be reliable, the XRD must be connected to a database with which one can compare the received data in order to attain a result [29].

In the present study the analysis were performed with a Siemens D5000 powder diffractometer equipped with Göebel mirror. A characteristic CuKα radiation with a wavelength of λ=1.54178 Å is used as an X-ray source. The incidence angle is of 8°, and the diffractogram was recorded in the measuring interval of 2θ between 20 and 70° with a step size of 0.005º. Particles sizes below 250 µm were analyzed in XRD after milling in an agate mortar. The peaks were identified based on the chemical composition given by SSAB.

### 4.2.2 Crushing strength and particle size

Measuring the crushing strength of particles is done by applying pressure on particles in a size range between 180 and 250 µm until they break into smaller pieces, and note the amount of force in Newton (N) that was exerted on the particle in the moment it crumbled. To achieve a reliable mean value of a materials crushing strength, at least 30 particles from each tested material had to be crushed. The crushing strength is measured by compressing particles with a pen-shaped device, manually, on a small table that is sensitive to compression. The sensitive table determines the peak force exerted on the particle in order for it to crumble.

In the present study a Shimpo, FGN-5, digital force gauge was used. Particle size distribution was complicated due to the fineness of the particles. Three different approaches were undertaken in order to overcome this – through sieving in ranges of <125 µm, 125-180 µm and 180-250 µm, through size determination by optical microscope pictures and by determining the mean value of the size of the particles from SEM images.

### 4.2.3 Density determination

The density of the particles was measured manually by adding ethanol to the particles in a beaker with a known volume. By knowing the total volume of the mixture, the weight of the particles and the added ethanol as well as the density of ethanol, the density of the particles could be calculated by using the equation $V = m/\rho$ .

## 4.3 Experimental setup and process

All experiments were conducted in a tubular quartz glass reactor under fluidized bed conditions. The reactor has an inner diameter of 22 mm and an overall length of 870 mm. Inside the reactor there is a quartz plate on which the analyzed particles are placed. The quartz plate has a porous structure in order to evenly distribute the gas that is entering the reactor. The temperature in the electrically heated reactor is measured with two CrAl/NiAl thermocouples; one is 50 mm below the quartz plate and the other is 10 mm above the quartz plate inside the bed. Figure 11 shows a schematic picture of the reactor setup, giving an overall view of the gas stream. The gas enters from the bottom of the reactor with composition controlled via magnetic valves and mass flow controllers. The off-gas is measured in a gas analyzer before it is transferred to ventilation. On its way to the analyzer, the gas is cooled to condense any water in it. The pressure inside the reactor is continuously measured and used as an indication of the fluidizing properties of the tested material [30].

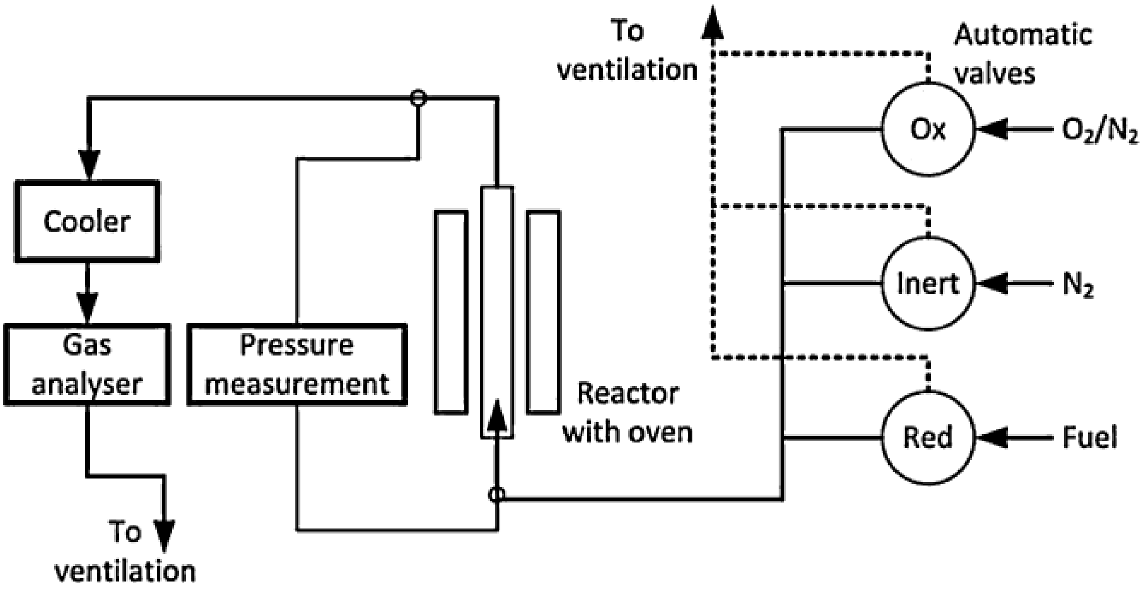


Figure 11. Schematic representation of a batch CLC system

Reducing, inert and oxidizing gas is injected into the reactor in programmed periods, forming an experimental cycle. The introduced gas fluidizes the bed particles and chemically reacts with them. When fuel gas is inserted in the batch reactor, the oxygen carrier is reduced while the fuel itself is oxidized. The reduced oxygen carrier is then put in a contact with an oxidizing gas. In an oxidizing atmosphere the oxygen carrier is re-oxidized to its initial state which completes the experimental cycle for the batch reactor. The reactions resemble the reactions in an interconnected fluidized bed reactor, with the only difference being that the reactions take place in a semi-batch reactor. Since the reduction and oxidation of the iron oxide takes place in the same bed, inert gas has to be injected in between the reduction and oxidation periods to clear the reactor from gases inserted and produced from the previous period in the cycle. A full cycle consists of inert period of 180 seconds (inert phase 1) followed by a reduction period of 18 seconds, which is when the chosen fuel is inserted. An inert period of 180 seconds is then repeated (inert phase 2) and is followed by an oxidation period of 300 seconds. The fuel gases used in these experiments are Methane ($CH_4$) and Syngas, consisting of 50 vol% CO and 50 vol% $H_2$. The oxidation gas is synthetic air consisting of 79 vol% $N_2$ and 21 vol% $O_2$. The inert gas used is $N_2$. The inflow of gases ranged between 500 and 900 ml/min depending on the particles analyzed. An inflow of 1300 ml/min was used in order to make the particles fluidize, when the pressure dropped. The particles were analyzed in a temperature range of 800°C to 900°C.

## 4.4 Procedure of analysis

The following text describes the practical steps taken in preparation and analysis of the by-products inside the batch reactor. The preparation and experiments inside the batch reactor have been described separately for the two materials; whereas the material characterization process is the same for both by-products and is described in chapter 4.2. Quartz sand is added to the materials in the batch reactor to ease fluidization and to increase the area of the particles that is available to the entering gas, which increases the reaction rate.

### 4.4.1 Flue dust preparation and analysis

A sample of the material was put in an oven at 100°C over night in order to measure its moisture content. Finding that there is a considerable amount of water in the sample, all analyzed flue dust was dried prior to analysis.

The initial test of dust in the batch reactor was done only to analyze the behavior of the sample during the heating up process of the reaction; therefore no cycles were run in that attempt. A mass of 15 g of the dust was placed in the reactor and heated up to 800°C and fed with $N_2$ with a flow rate of 500 ml/min. Showing to be usable in a batch reactor, the dust now needed to be applicable to the industry, where larger particles than dust are required for effective use; in actual use as oxygen carrier, high temperatures will result in large amounts of loss of dust due its entrainment into air. The dust was therefore sieved to achieve a particle size range between 125-180 µm and 15 g of it was placed in the reactor. The reactor was heated up in 500 ml/min $N_2$. When the temperature reached 800°C the feed was switched to the reducing gas, syngas, with the same flow rate. After 11 cycles, the reducing gas was changed to methane in which three cycles were run.

From the performed experiments a conclusion was drawn that the majority of the fraction with sieved particles were below 125 µm, which was observed as high dust, was entrained to the filter. In order to increase the particle size the dust was bound together with the help of binding material. Two binding materials were tested on the dust; they are called for simplicity “Binder 1” and “Binder 2”. Binder 1 is based on 5 wt% Polyvinyl Alcohol (PVA-binder), 1 wt% starch, 1 wt% ammonium and 2 wt% ammonium hydroxide. Binder 2 is refractory cement based on aluminium oxide. In the particle production 40 wt% of the cement was mixed with flue dust. The binding-materials were used in separate attempts of particle production. Production was done by mixing the flue dust and binding material, then adding distilled water in small amounts until the knead mixture obtained a clay-like mass. The clay was then extruded into strings onto a steel plate and left to dry.

When using binder 1, the extruded material was put in an oven at 100°C to dry over night. Once the extrudates had dried, they were crushed into smaller particles and put in high temperature in order to fuse them and achieve a particle hardness sufficient to endure the conditions inside the batch reactor. An oven was programmed to steadily rise the temperature to a maximum and then slowly decrease to room temperature again; a heating up process that usually takes over 24 hours. A schedule of the ovens program is shown in figure 12. A sample of the extrudate particles were placed in the oven with a selected maximum programmed temperature of 1000°C. Two other samples from the same extrudates batch were run separately in the oven at temperatures 1100°C and 1200°C. Only the particles run in the maximum temperature of 1200°C showed a sufficient hardness for the purpose and could be used. They were crushed and sieved to particle size ranges of 125-180 µm and 180 -250 µm. The particle size range of 125-180 µm were then used for the experiment. During the heat-up, the binder that is mixed with the particles burns out. The particles produced from this binder are called “Particles type 1”.

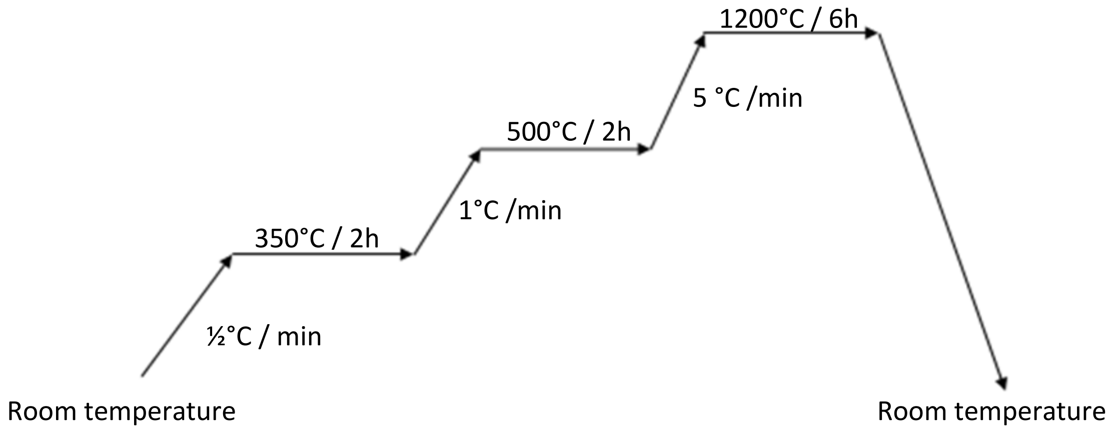


Figure 12. Temperature schedule of the hot oven used for particle fusion when using PVA-binder material

15 grams of the Particles type 1 was placed together with five grams of quartz sand of the same size range inside the reactor.  The reactor was heated up in oxidizing conditions and the inflow of gas was set to 500 ml/min. Once the temperature had reached 800°C, the inflowing gas was switched to the reducing agent, syngas. In the second inert period, the temperature was increased to 850°C and the flow - to 1300 ml/min in order to sustain fluidization. The experiment was repeated, this time with an increased amount of quartz sand; 10 g of extrudates were mixed with 10 g of quartz sand. The gas flow was set to 900 ml/min and the reducing gas - to syngas. The temperature was held at 800°C for all the 11 cycles that were run.

The second type of particles produced – Particles type 2 – are based on the second type of binder (binder 2), refractory cement. When producing Particles type 2, the extrudates were left to dry in only room temperature. After 5-6 days the particles had reached the needed hardness for use in the batch reactor. The extrudates were then crushed and sieved. 15 g of the obtained particles in the size range of 125-180 µm were mixed with 5 g of quartz sand of the same particle size range, and placed in the batch reactor. The reactor was heated up to 900°C under oxidizing conditions and the gas flow was set to 900 ml/min. The reducing gas used in this experiment was methane. The temperature was decreased to 850°C before the reduction period of the 9th cycle. The temperature was further decreased to 800°C before the 12th cycle. The experiment was then run for another two cycles before it was stopped.

### 4.4.2 LD-slag preparation and analysis

Based on the difference in the appearance of the rocks, they were categorized into five different groups that were analyzed separately, namely group 1-5. Once separated into groups, the particles were crushed to powder and placed in separate containers. The samples were placed in an oven at 100°C over night for measuring their moisture content, which showed to be negligible. The particles were investigated by XRD where the main purpose was to connect the difference in their appearance to possible difference in their mineral content. A mixture of all the five groups of the LD-slag material was then sieved to three different particle size fractions: below 125 µm; between 125 – 180 µm and 180 – 250 µm.

The particle size range of 125 -180 µm were used in the batch reactor. Five grams of LD-particles were mixed with five grams of quartz sand of the same particle size range and placed on the quartz placed inside the reactor. The reactor was heated up to 900°C under oxidizing conditions and eight cycles were performed; all with methane as reducing agent. During inert phase 2 in the eighth cycle, the temperature was lowered to 850°C and an additional four cycles were run. As a next step, the temperature was lowered further to 800°C in inert phase 2 during cycle 12 and an additional four cycles were run.

# 5. Results

The results of the batch experiments are presented by plotting the integral $CO_2$ yield, $\gamma_{CO_2,\mathrm{int}}$, of each reducing period in a cycle against the total amount of cycles in the experiment. $\gamma_{CO_2,\mathrm{int}}$, which is derived from equation 7, describes the total amount of converted carbon during a reduction period. The equation is based on the outgoing flow of component *i* at time *t*, $\dot{n}_{i,out}(t)$. $\dot{n}_{i,out}(t)$ is obtained multiplying the molar fraction of $CO_2$ by the total flow (mol/s) and dividing the product by the mean molar volume, $\overline{V}$ ($m^3$/mol), see equation 8. Both the molar fraction as well as the total volume flow has been logged throughout every experiment.

$$\gamma_{CO_2,\mathrm{int}} = \frac{\int_{t0}^{t1} \dot{n}_{CO_2,out}(t)dt}{\int_{t0}^{t1} (\dot{n}_{CO_2,out}(t) + \dot{n}_{CO,out}(t))dt} \tag{7}$$

$$\dot{n}_{i,out}(t) = x_{i,out}(t) \cdot \frac{\dot{V}_{tot,out}(t)}{\overline{V}} \tag{8}$$

## 5.1 Mechanical and chemical properties

Table 2 shows the chemical and mechanical properties of the analysed materials, before and after being subjected to the batch reactor experiments. LD-slag has the highest crushing strength, but it also has a relatively high standard deviation in the strength data. This is due to the inhomogeneous mixture of rocks the LD-slag consists of. The crushing strength of raw flue dust could not be measured due to the very fine particles it consists of. The relatively high crushing strength of Particles type 1 compared to the raw flue dust is due to the high temperature heating that the particles were subjected to a possible fusion of the particles.

The XRD results revealed that the flue dust materials contained iron oxides (FeO, $Fe_2O_3$, $Fe_3O_4$) as expected. The only mineral identified in the LD-slag before the batch reaction was akermanite ($Ca_2Mg[Si_2O_7]$). After exposing the material in the batch reactor, magnetite was identified; indicating either a conversion of a mineral or that an iron oxide phase present in the slag was not detected in the XRD-analysis prior to the reaction. The silicon oxide found in all of the materials after exposures in batch reactor is from the quartz sand added initially to the material in the reactor. Except for Particles type 2, no unexpected changes in the mineral composition of the particles were detected as formed products. It seems as if the separate components of Particles type 2 have agglomerated in the batch reactor.

The measured changes in density of the particles after exposure to the reactor are very large; a decrease of up to 67 % was calculated. These measurements are unreliable partly due to high risk for error in the measurement process. The amounts of material available for measurement were insufficient for a reliable result. A larger sample mass l would have given a more exact value of the density. Unfortunately, the raw flue dust that was exposed in the batch reactor was lost before having a chance to measure its density after the reaction.

| **Material** | **Crushing strength (N)** | **Density – fresh material (kg/m$^3$)** | **Density – used material (kg/m$^3$)** | **Minerals identified by XRD - fresh particles** | **Mineral identified by XRD - used particles** |
|---|---|---|---|---|---|
| **LD-slag** | 6.4 ± 2.0 | 2247 | 1275 (44% decrease) | $Ca_2Mg[Si_2O_7]$ | $SiO_2$, $Fe_3O_4$, CaO |
| **Flue dust raw** | unknown | 2179 | Data lost | FeO , $Fe_3O_4$, $SiO_2$ | $Fe_2O_3$, $SiO_2$, $CaCO_3$ |
| **Flue dust - Particles type 1** | 3.7 ± 0.73 | 4136 | 1385 (67% decrease) | $Fe_2O_3$, $CaCO_3$, $Fe_3O_4$ | $SiO_2$, $Fe_2O_3$ |
| **Flue dust – Particle type 2** | 1.96 ± 0.71 | 2181 | 995 (54% decrease) | $Fe_2O_3$, $Fe_3O_4$, $CaCO_3$ | $SiO_2$, $Ca_2MnFe_2O_5$ |

Table 2. Chemical and mechanical properties of LD-slag, raw flue dust, particles type 1 and 2, before and after batch reactions.

## 5.2 Raw flue dust

When heating up the reactor to reaction temperatures of above 800°C, the reactor is only fed with the inert gas $N_2$. The graph in figure 13 shows the composition on the outgoing flow of gas from the reactor during the heat up process. It clearly shows how the molar fraction of $CO_2$ rises in the reactor with increasing temperature. This is the result of the combustion of carbon within the sample – since the waste materials contain an amount of carbon, indicating that the iron oxides within the sample have released oxygen during the heat up, and that the amount of oxygen released has increased with the increase in temperature. A decrease in $CO_2$ concentration was measured at 800°C since all carbon in the sample had been consumed. Since the high temperature part of the experiments were performed in temperatures of at least 800°C, it can be concluded that the carbon compounds detected in the outgoing flow originate from the fuel inserted into the reactor, and not from any carbon in the material itself. This can be concluded for all the samples run in the batch reactor.

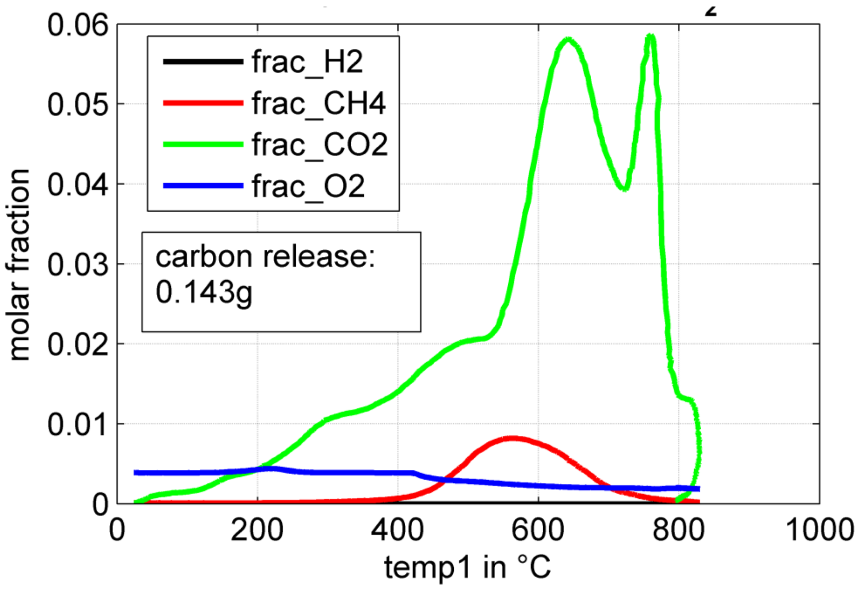


**Figure 13. Composition of the outgoing flow of gases during the heat up of the raw flue dust in the fluidizing bed reactor.**

The results from the experiment with flue dust in a batch reactor are shown in figure 14. During the first 13 cycles, when the inserted fuel was syngas, the carbon conversion was held at above 80 %, and increasing slightly with every cycle, reaching near 100% values at cycles 11-13. The slight increase is a result of so called “oxygen activation”, which is simply that some oxygen carriers start to release oxygen later in the process after initial activation. In the last three cycles, where fuel was switched to $CH_4$, a significant decrease in carbon conversion can be observed. This is not surprising since methane is known to be difficult to convert. The three cycles performed with $CH_4$ as fuel had an integral $CO_2$ yield of 10 %. No further cycles beyond the 16 were run due to the high amount of dust entrained to the quartz filter.

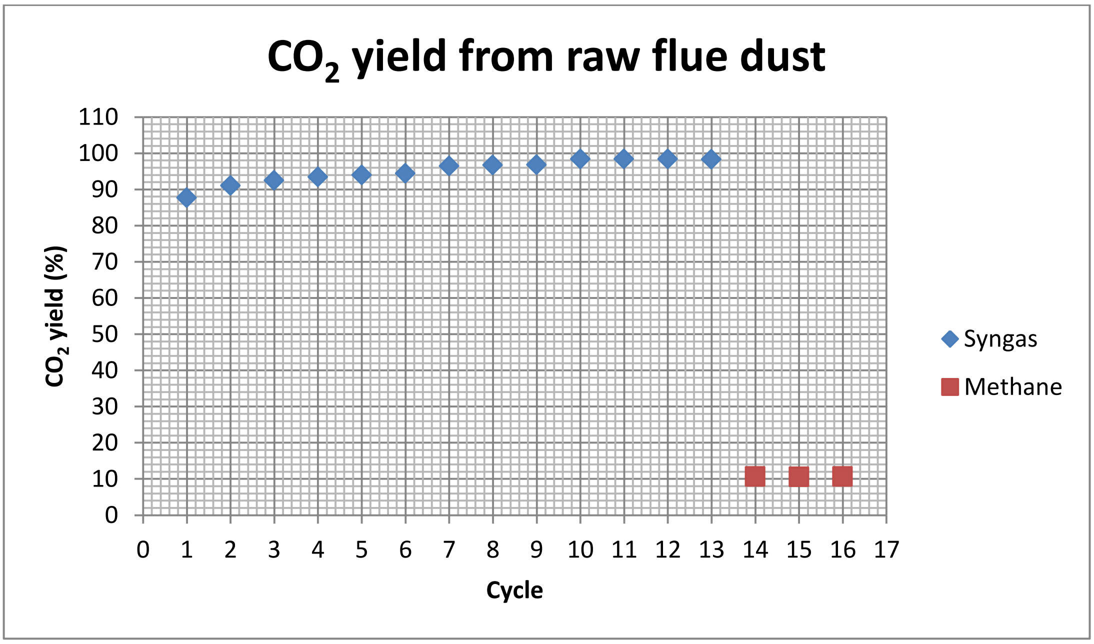


**Figure 14. Integral $CO_2$ yield from flue dust. Switching fuel to methane decreases the carbon conversion dramatically.**

### 5.2.1 PVA-based particles – Particles type 1

Unfortunately, the data from the first experiment with Particles type 1 has been lost during logging, so only the second experiment with Particles type 1, when a 50/50 amount of sand and particles where placed in the reactor, is analyzed. The integral $CO_2$-yields during the reduction of Particles type 1, which was done with syngas, was shown in figure 15. In the first four cycles the carbon conversion increases with every cycle, due to oxygen activation. In cycle five the conversion dropped to 70 %; this is most likely because of a shutdown of the reactor between the cycles four and five, which most probably resulted in decreasing the activity of the carrier particles. In the reductions following the eighth cycle, only a small increase in integral $CO_2$-yield was noted, which is probably because the particles had reached their maximum activation rate. The reactor was shut down after the 11th cycle due to that the particles were not fluidizing, even though the inflow of gas was raised to 1300 ml/min. Fluidization could only be achieved by mechanically induced shaking of the reactor during the experimental set-up fluidization. Figure 16 shows the material after it was taken out from the reactor. The image shows that the particles have agglomerated; which can be one of the reasons for the defluidization of the material. The defluidization can explain the slightly lower integral $CO_2$ yield from Particles type 1 compared to the raw flue dust.

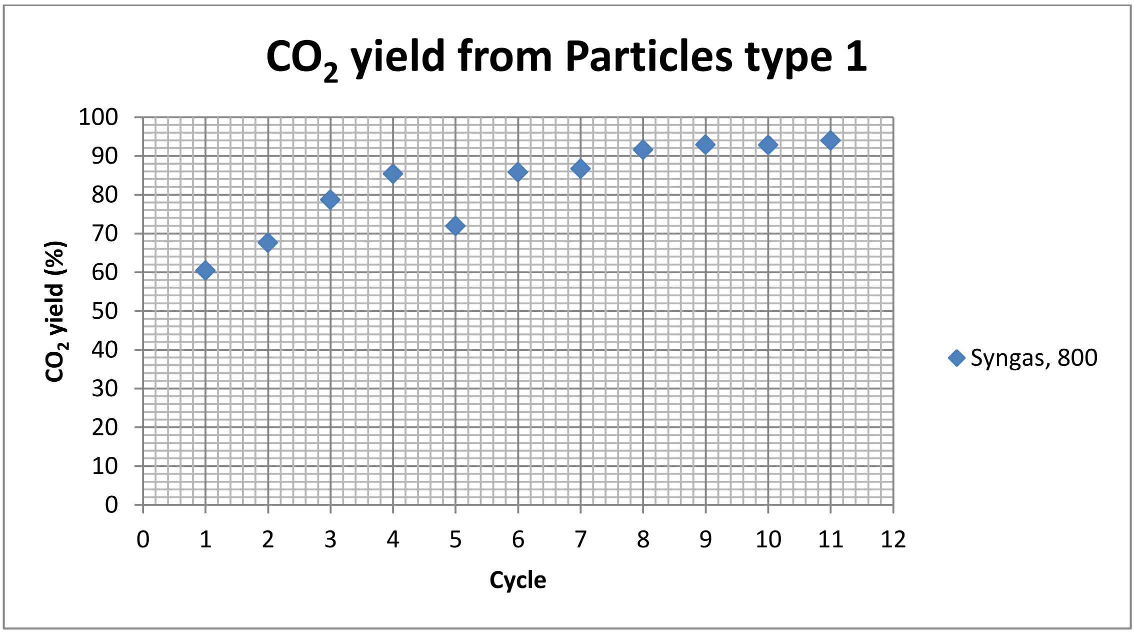


Figure 15 The integral $CO_2$-yields during reduction of Particles type 1 with syngas.

Figure 16 The material, Particles type 1, after the reaction process. Agglomeration of the particles is observed.

### 5.2.2 Refractory cement-based particles – Particles type 2

Figure 17 shows the integral $CO_2$ yield from Particles type 2 in a batch reactor with methane as fuel. The first eight cycles, which were run in 900°C, started with a carbon conversion of just below 10 % and increased with every cycle to nearly 16 %, due to oxygen activation. When the temperature was decreased to 850°C, the conversion decreased as well. Further decrease in conversion was observed when the temperature was lowered further to 800°C. Thus temperature decrease has a significant effect on the reactivity of the oxygen carrier.

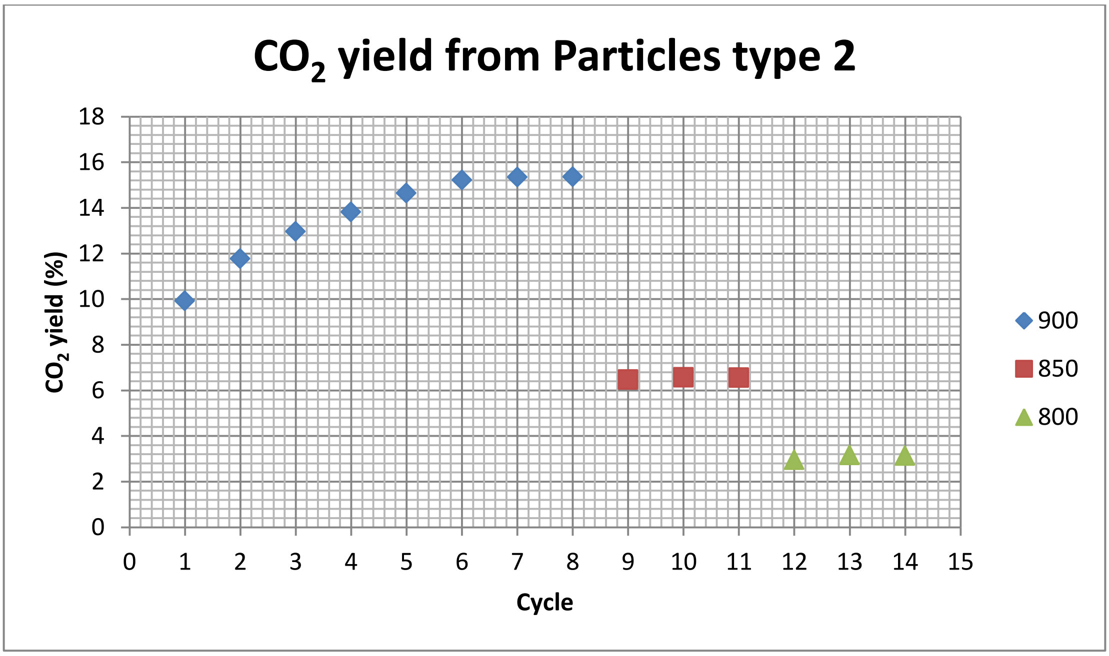


Figure 17. Integral CO2 yield from Particles type 2 with methane as fuel. A temperature decrease leads to the decrease of reactivity of the oxygen carrier.

## 5.3 LD-slag

The integral $CO_2$ yield of each cycle is shown in figure 18. Methane was the fuel used in this reaction. In the first seven cycles, when the temperature was 900°C, the carbon conversion started at 10 % but decreased gradually in the following cycles. Decreasing the temperature to 850°C cuts the carbon conversion in half. An additional decrease to 800°C resulted in a further, yet not as large, decrease in carbon conversion to around 1.5 %. The color used in the figure denotes the temperature in which the cycle has taken place. As mentioned in the discussion of the previous reactions where methane was used, methane is difficult to convert under such conditions; therefore the carbon conversion is very low. The decrease of carbon conversion with every cycle in the temperature of 900°C can be caused by a number of different reasons; the oxygen uptake of the particles can be decreasing for every cycle; this is unlikely since the decrease does not occur at cycles of the lower temperatures. Another reason can be that the pores in the oxygen carriers have been blocked under such high temperatures; the increase in volume of the oxygen carriers during the oxidation periods can block methane from diffusing through the particles, thereby decreasing the reaction rate.

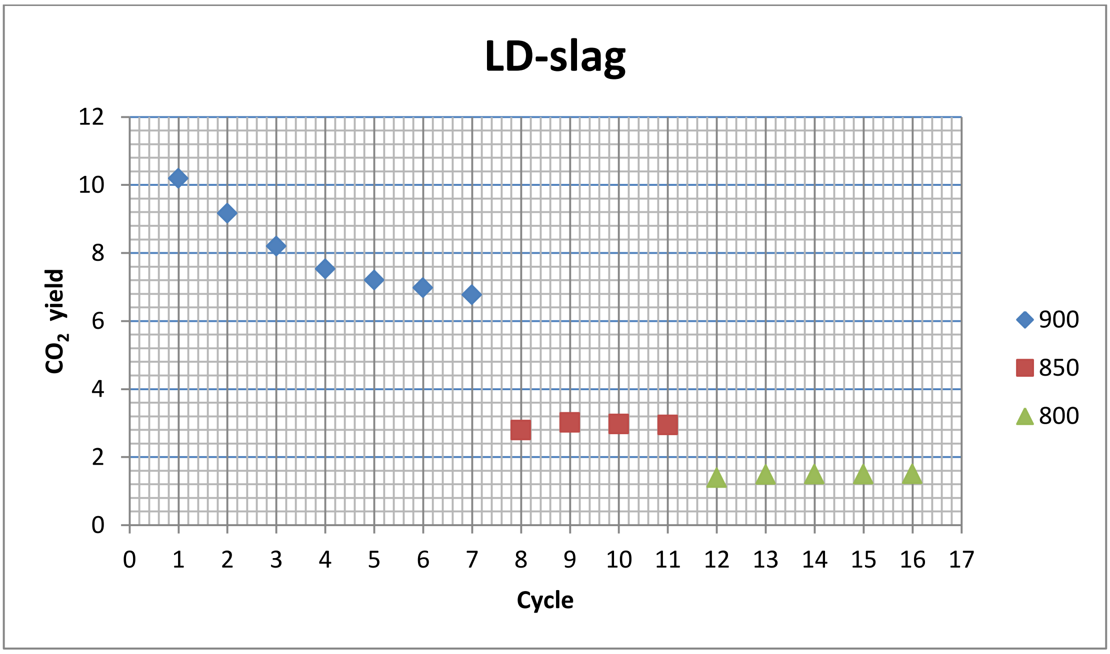


Figure 18. Integral CO2 yield from LD-slag in batch reactor with methane as fuel.

# 6. Discussion

All of the materials tested contained iron oxides and showed ability to transfer oxygen in a batch reactor, although displaying different reduction behaviors. Methane is known to have a low reaction rate in fluidizing bed conditions; therefore it was not a surprise that its use as fuel in these experiments gave such a low integral $CO_2$ yield. Unfortunately, after the first two experiments, I was forced to use methane since no syngas was available for experiments. In the case of the raw flue dust, the fuel change to methane resulted in a decrease in conversion from almost 100 % to 10 %. From this result it can be concluded that Particles type 2 and LD-slag, which were both run with methane, would have given much higher conversion rates if used with syngas. Therefore, for the purpose of comparing the results, it would have been practical to have used the same fuel throughout all of the batch reactions. Such experiments should be done if further work on the flue dust is carried out.

When comparing the materials used in syngas, which were flue dust and Particles type 1, both materials show a high carbon conversion and a similar steady increase in conversion during the first few cycles. Comparison of the materials run in methane, Particles type 2 and LD-slag, show that a higher carbon conversion is obtained with Particles type 2; Particles type 2 reaches a carbon conversion of 15 % in 900°C, while LD-slag started with 10 % at the same temperature, but that decreased with every cycle down to just below 7 %. The higher reaction rate obtained with Particles type 2 could be due to its flue dust basis, which contains double the amount of iron oxide than that found in the LD-slag. The reaction rate of both materials is halved for every temperature decrease of 50°C, showing that the reaction rate is highly temperature dependent.

Based on the low conversion results from LD-slag in methane, the slag should be excluded as a possible oxygen carrier used for $CH_4$ conversion; it would however be interesting to see its carbon conversion ability in syngas and it also needs further analyses to determine the effect of the large amount of “non-oxygen carrying” components in the slag. The slag would probably not get up to as high conversions in syngas as flue dust due to its relatively low iron oxide content; therefore it could be a suggestion to put the focus on the possibilities in flue dust particles..

Even though Particles type 1 shows sufficient ability to be used as oxygen carrier, its production involves heating it up in 1200°C, which is energy inefficient and expensive. Since the idea is the reuse of waste materials, the costs connected to its use should be low so that its use is beneficial and sustainable in time. Particles type 2 only needs room temperature for production and it did not have any problems fluidizing in the reactor in contrary to Particles type 1; however, analyses of the carbon conversion in syngas of such particles would be needed to assure its conversion rate is high enough for usage. It is unlikely to observe low conversion rates , based on the experience with the great decrease in conversion rates connected to the use of methane. Based on experience of earlier work in the CLC group, the relatively low density of Particles type 1 compared to Particles type 2 can mean that it has higher porosity and thereby higher reactivity than Particles type 2; however its lower density makes it more vulnerable to attrition, and thereby less durable as an oxygen carrier. If proved to be durable, Particles type 2 has good potential for use as oxygen carrier.

# 7. Conclusions

The oxygen carrying ability of flue dust and LD slag from steel industry has been investigated in the present work. Flue dust showed to have high integral $CO_2$ yield in syngas. Larger particles were produced from the flue dust in two separate ways, using two different binding materials – refractory cement and PVA-based binding material. The second type of particles produced, Particles type 2, showed ability to fluidize as well as relatively high carbon conversion rates in methane. Particles type 2 is also both easier and cheaper to produce than Particles type 1. If further analyses are done on Particles type 2, it can have good potential in use as oxygen carrier material. LD-slag was analyzed in much smaller extent and showed to have low carbon conversion in methane. The slag's much smaller amount of iron oxide compared to flue dust as well as its inhomogeneous composition is considered to be one of the reasons. The low conversion rates observed, makes its use as oxygen carrier more difficult. Still further research is needed on its composition and oxygen carrying ability to make a proper conclusion of its usefulness as an oxygen carrier.

# 8. Future work

Further work on these materials would firstly be by running batch experiment using the same fuel during all the exposures, preferably syngas, in order for better comparison and more straightforward conclusions from the materials. More cycles should be run to see the behavior of the different materials over longer periods of time; to analyze their durability and activity. Scanning electron microscopy can be further used to find chemical and structural changes in the materials after the reaction that could affect their performance during experiments.

It is recommended to put focus on Particles type 2, by trying to find the best ratio between flue dust and refractory cement to obtain the strongest particles. If the particles showed good results in the batch reactor, the next step would be to gain more adequate understanding of the particle behavior by testing them in a small prototype of a real Chemical-looping combustion system, where particles are continuously circulated between an air and fuel reactor.

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# 10. Appendix

The figure below shows the diffractogram of the LD-samples 1 to 5. Samples 1-4 have almost identical diffractograms, while the one of sample 5 differs from the rest.