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Testing of Mn-ores impregnated with Fe, Cu and K as oxygen carriers in chemical-looping combustion

Report for Master's Thesis in Sustainable Energy Systems Engineering
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ABSTRACT

The amount of greenhouse gases in our atmosphere has been increasing during the latest centuries and this is the main reason for the global warming that our earth is experiencing, with the most contributing gas being CO_2. An option which can mitigate the CO_2-problem and allow continued use of fossil fuels is Carbon Capture and Storage (CCS).A promising emerging technology for CCS is Chemical Looping Combustion (CLC) which uses oxygen carriers that can transport oxygen from air to the fuel.

In this study it was investigated whether the performance of manganese ore as an oxygen carrier could be enhanced by impregnating it with Fe, Cu or K. Three different manganese ores were used and experiments were performed to test both CLOU-performance as well as standard CLC-performance. Thermogravimetric Analysis (TGA) was used for testing CLOU and a single fluidized bed at 800 °C with CO as fuel was used for testing standard CLC. Some tests at lower temperatures were also performed.

Impregnation with copper showed improved CLOU and CLC behaviour, although high copper content led to agglomeration. It was also found that the CLOU-behaviour of one of the manganese ores could be enhanced by adding either iron or potassium. Iron-impregnated ore showed a decrease in CLC-performance while impregnation with potassium showed improved CLC-performance but also led to severe agglomeration. Further investigation of copper impregnation for CLC was performed and it was found that adding very small amounts of copper could greatly enhance the manganese ores ability to convert CO to CO_2 at 800 °C. This effect was also seen at 700 °C and 600 °C.

Table of Contents

1. Introduction

1.1 Background

Over the last couple of decades our earth has seen an increase in average global temperature, more melting of ice sheets and an accelerating rise of sea level[1]. The main reason for this, according to the Intergovernmental Panel of Climate Change (IPCC), is the amount of greenhouse gases in our atmosphere which has been increasing since 1750[1][2]. The greenhouse gas that has been contributing the most is CO_2 and the main source of its increase is from burning fossil fuels in the energy sector [3].

An ideal solution would be to simply stop using fossil fuels and switch to renewable energy sources. However, due to economic aspects, the wide use of fossil fuels and the fact that many societies rely on fossil fuels make it problematic to quickly change to a complete renewable energy society. An option which can mitigate the CO_2-problem and allow continued use of fossil fuels is Carbon Capture and Storage (CCS). It is also a technology that could be used with biomass in order to directly reduce the CO_2-levels in the atmosphere[4][5].

1.2 Carbon capture and storage

The idea of CCS is simple: burn the fuel and store the carbon dioxide produced in a safe place instead of releasing it to the atmosphere. Since flue gases from burning fossil fuels typically only contain around 3-15% CO_2[6] it is needed to increase this concentration in order to use as much space as possible for pure CO_2. Pure CO_2 is also easier to handle than a mixture of different gases. To obtain this it is possible to apply CO_2-capture technologies, discussed further in the next section. Once this is done and a stream of almost pure CO_2 is obtained, it can be transported (mainly by pipelines or ships[6][7]) to a suitable storing location. These locations may be depleted oil reservoirs, deep saline aquifers or depleted gas fields[6][7][8]. Storing CO_2 in the ocean is also an alternative although the techniques required for this are less developed[6]

1.2.1 Conventional capture technologies

The three most common techniques for capturing CO_2 from combustion processes today are known as:

- Pre-combustion, where the carbon in the fuel is removed before the combustion. This is done by gasifying the fuel to syngas consisting of CO and H_2 and then using steam and the water-gas shift reaction to get a mixture of CO_2 and H_2[8]. The CO_2 can then be removed from the process by scrubbing, leaving H_2 to be used in a gas turbine. Issues with pre-combustion are that there are problems with using pure hydrogen as fuel in turbines and that the plant efficiency decreases[9].
- Oxyfuel combustion, which uses the simple concept of combusting fuel with pure oxygen instead of air (which is only 21% oxygen) yielding an exhaust gas consisting of mainly CO_2 and H_2O[8]. By condensing the water it is possible to get a stream of pure CO_2. It's however very expensive to separate oxygen from air which is the main drawback of using oxyfuel combustion[10].
- Post-combustion, which is a mature technology and relies on using amine solutions (usually monoethanolamine, MEA) or some other substance that can absorb CO_2 from the flue

gases[8]. It has the advantage of being able to be built on an already existing plant but requires a lot of heating and cooling of the solution in order to separate the CO_2 which leads to an efficiency penalty. A lot of research about using membranes to improve the efficiency of post-combustion is currently being made[11].
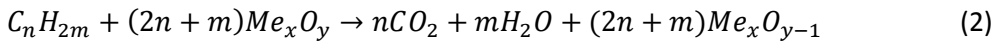
1.2.2 Chemical Looping Combustion

Chemical Looping Combustion is a promising emerging technology which uses oxygen carriers that can transport oxygen from air to the fuel. The system is set up as a circulating fluidized bed process, which means that it is divided into two fluidized bed reactors, one air reactor where the carriers get oxidized and one fuel reactor where they get reduced by oxidizing the fuel[12]. By using this method an exhaust gas consisting of almost only CO_2 and water vapour can be obtained[13]. The latter can easily be condensed and removed.

The reaction in the air reactor can be written as:

$$2Me_xO_{y-1} + O_2 \rightarrow 2Me_xO_y \tag{1}$$

And the reaction in the fuel reactor can be written as:

$$C_nH_{2m} + (2n+m)Me_xO_y \rightarrow nCO_2 + mH_2O + (2n+m)Me_xO_{y-1} \tag{2}$$

where Me_xO_y is the oxygen carrier in its oxidized state and Me_xO_{y-1} is the reduced state. C_nH_{2m} represents the fuel.
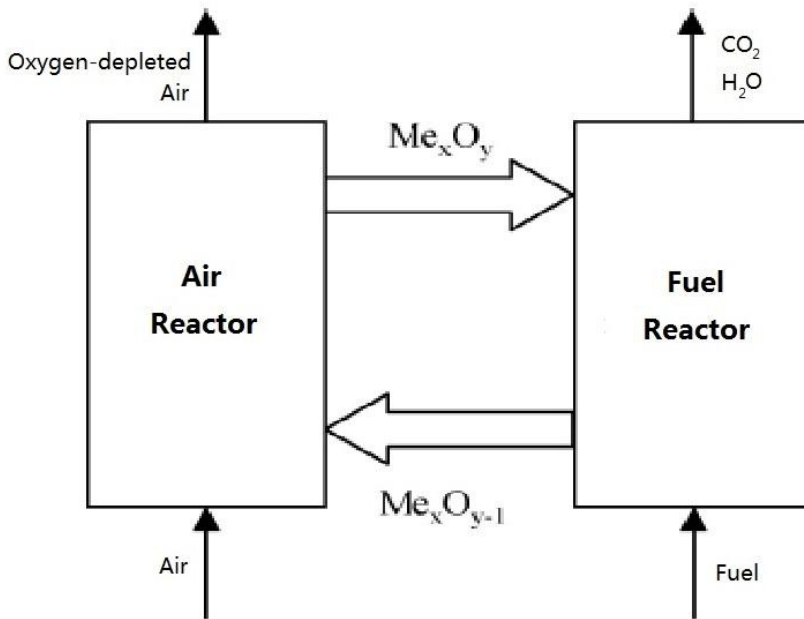
Figure 1. A rough overview of how a CLC-system operates

The reduction in the fuel reactor can be either exothermic or endothermic, while the oxidation of oxygen carriers in the air reactor is always exothermic. The combined heat release from the air and fuel reactor is equal to the heat released from regular combustion[12]. Therefore, using CLC to separate CO_2 will not cause any energy losses for the CO_2 separation. This is a great advantage compared to other CO_2 capture technologies which have energy penalties related to gas separation

steps. Also, the formation of NOx is avoided since the fuel conversion is being achieved without the presence of nitrogen.

Seeing that solid fuels are the most common type of fuel in the world it would be beneficial if they worked well in a CLC process. However, reaction rates between two solids (oxygen carriers and fuel particles in this case) are generally very low due to the small contact area and it is therefore common to gasify the fuel[14][15]. This is usually done by fluidizing the mixture of fuel and particles with H_2O or CO_2 leading to the formation of H_2 or CO so a gas-solid reaction can occur. The kinetics of such a reaction is much more desirable.

Although CLC is not yet used in the industry there exist many pilot plants around the world. For example, at Chalmers in Gothenburg there is a 100 kW_{th} pilot plant and at Vienna University of Technology there is one of 140 kW_{th}[16]. The largest CLC plant using metal oxides today is built in Darmstadt and has a capacity of 1 MW_{th}[17].

China is a very big consumer of energy and some attention has lately been drawn to CLC. In the Southeast University of Nanjing there is a 10 kW_{th} plant where they have tested fuel conversion with biomass[18]. Tsinghua University in Beijing has built a 1 kW_{th} plant and performed several experiments successfully.

1.3 Oxygen Carriers

Oxygen carriers are typically oxides of metals and they are a very important part of the CLC process. There exist many different oxygen carriers with different characteristics. When trying to find a suitable carrier it is important to look at properties such as reactivity, melting temperature, sensitivity to physical and chemical interactions as well as the production price[12]. The most tested metal oxides today are oxides of iron, manganese, copper and nickel[19]. The cheaper oxygen carriers, such as iron oxides, generally perform poorer than the more expensive ones, e.g. copper oxides. Some oxygen carriers such as nickel and cobalt oxides have the drawback of also being toxic or having a negative impact on the environment[20][21].

An oxygen carrier does not need to be an oxide of only one element and can thus consist of a mixture of oxides. This can be advantageous since by making oxygen carriers by mixing two metals it is possible to benefit from both metals properties[19]. It also makes metal, ores with somewhat more complex compositions, interesting as carriers due to the lower prices. Examples are natural ilmenite (an iron titanium mineral), iron ore and manganese ore[13][22].

There exist oxygen carriers with thermodynamic properties that allow them to release their oxygen in gas-phase when exposed to an atmosphere with a lower partial pressure of oxygen . This is known as Chemical Looping with Oxygen Uncoupling (CLOU) and it releases the same amount of heat as a standard CLC-process, with the advantage that the solid fuel does not need to be gasified[23]. The problem boils down to finding oxygen carriers with these properties while still maintaining acceptable chemical and physical characteristics. They still have to be able to be oxidized in the air reactor and release the oxygen in the fuel reactor with good reaction rates at suitable temperatures, as well as not wearing down too fast or interacting too much with ashes etc. Three oxygen carriers with redox system capable of CLOU are shown in Figure2 below.
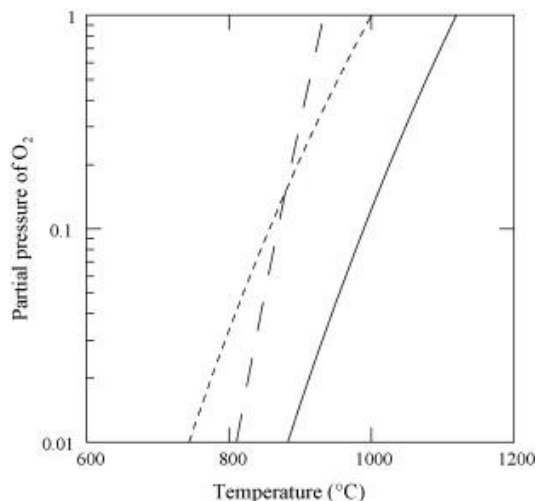
Figure 2. A graph showing the CLOU phase change of Mn₂O₃/Mn₃O₄(- - - - -), Co₃O₄/CoO(— —) and CuO/Cu₂O(—) depending on the partial pressure of oxygen as well as the temperature[23]

Some carriers are rather brittle and would get destroyed rapidly under the conditions in a CLC-system. In order to prevent this, inert support materials can be added to the oxygen carrier to make it more durable[24]. This can also avoid agglomeration issues[25]. It has further been shown in experiments that impregnating oxygen carriers with a foreign element can improve the performance as well[26][27]. This will be discussed further in chapter 1.7.

1.4 Mn-based Oxygen Carriers

Manganese oxides have received some attention and investigation, although not to the same extent as e.g. nickel[28].There exist several forms of manganese oxides of which Mn_2O_3, Mn_3O_4 and MnO are of interest for CLOU and CLC application. Manganese oxides are attractive oxygen carriers due to their relatively cheap price and decent reactivity as well as being non-toxic[19][29]. The most oxidized stable form of manganese oxides, MnO_2, decomposes into Mn_2O_3 at around 500 °C in air, and Mn_2O_3 decomposes further into Mn_3O_4 at 900 °C[19][30].The most suitable redox system for CLC has proven to be MnO/Mn₃O₄ [19].

The following reactions show the different phase changes of manganese oxides. These can occur either because of reduction or thermal decomposition.

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2 \tag{3}$$

$$6Mn_2O_3 \rightarrow 4Mn_3O_4 + O_2 \tag{4}$$

$$2Mn_3O_4 \rightarrow 6MnO + O_2 \tag{5}$$

Figure 3 shows the temperature at which the thermal decompositions occur in air:
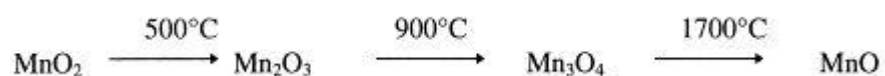

Figure 3. An overview on the decomposition temperatures of manganese oxides in air[31]

For CLOU purposes it has been shown that Mn_3O_4/Mn_2O_3 possesses the necessary properties[23], where Mn_2O_3 releases gaseous oxygen in the fuel reactor (see reaction 4), and Mn_3O_4 absorbs oxygen in the air reactor (reverse reaction 4). The temperature in the air reactor should be below 820 °C for Mn_2O_3 to absorb oxygen if the oxygen partial pressure is 5%[23] (compare with Figure 2). This means that Mn_2O_3/Mn_3O_4 could be a suitable oxygen carrier in processes where the temperature is somewhat lower, e.g. biomass combustion. The oxidation rate of this oxygen carrier seems however to be very low. A study managed to improve this rate by just adding 5% CuO in the manufacturing process which could be a solution to this problem[32]. Another study also managed to enhance the CLOU properties of manganese oxide but by adding 25% Fe_2O_3 instead[33].

Most of the research on oxygen carriers with manganese has been conducted on synthetic manganese oxides. The use of natural manganese ore has however started to receive more interest due to lower costs and decent performance[34].

1.5 Cu-based Oxygen Carriers

Oxygen carriers with copper oxides are more expensive than e.g. manganese oxide but are among the best for CLC when it comes to reactivity and oxygen transfer[35]. The phase change in standard CLC combustion is between Cu and CuO. The physical properties have however shown to be less desirable since the carriers have a tendency to agglomerate, leading to fluidization problems[25]. This agglomeration is due to the fact that upon reduction elemental copper will be present which has a relatively low melting point (1085 °C). Thus, the particles soften and start sticking to each other at high temperatures. To avoid this it is common to combine copper oxide with a stable support material, such as Al_2O_3[25]. In addition to the already good CLC-performance of Cu/CuO, the redox system Cu_2O/CuO has shown very good CLOU reactivity[36].

1.6 Fe-based Oxygen Carriers

Iron oxides do typically not perform as well as other oxygen carriers when it comes to reactivity and oxygen transfer capacity[37][19][38] . However, the low price of iron and the good physical properties make them attractive as oxygen carriers and it is also possible to use natural iron ores ore oxide scales from steel production as carriers instead of producing them synthetically[38][39]. The redox system suitable for CLC is limited to Fe_2O_3/Fe_3O_4 due to thermodynamic reasons[19].

1.7 Impregnations

Impregnation is usually done with an active redox system on an inert support material in order to have durable oxygen carriers with decent reactivity. Studies have however been made on how to improve the performance of an already active compound. One study managed to improve the CLC-performance of ilmenite by eight times by impregnating it with potassium[26]. In a later study potassium-impregnated ilmenite was successfully tested in a dual fluidized bed[27]. Another study tested different ratios between manganese and copper for CLOU purposes and concluded that having very small or very high amounts of copper compared to manganese could be better than having an average amount[32]. As mentioned in 1.4, a study also managed to improve the CLOU-performance of manganese oxide by adding 25% iron.

This type of impregnation is however an area where not many studies have been made. Further research is needed and can open possibilities of finding new and better oxygen carriers.

1.8 Thesis Frame

The purpose of this thesis is to give an insight into the performance and the thermodynamic properties of manganese ores impregnated with copper, iron and potassium as oxygen carriers.

The thesis is divided into two different parts: The first part covers the impregnation procedure and investigates changes in CLOU behaviour, while the second larger part investigates standard CLC performance and looks into the Mn-Cu interaction.

2. Preparation and TGA

This section contains information on how the oxygen carriers were impregnated, which materials were used as well as the TGA results.

2.1 Materials used

Three manganese ores, called Mn1, Mn2 and Mn3 were used as oxygen carriers to be impregnated. The ores were provided by Mugui Manganese Ore Company from Guangxi province in China.

XRF gave the following compositions:

Table 1. Composition of Mn1, Mn2 and Mn3 as received from XRF. Note: "MnO" represents any manganese oxide

	MnO (%)	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	BaO (%)	SO_3 (%)
Mn1	40.5	44.1	7.4	1.7	4.7	0
Mn2	79.6	8.4	5.4	1.5	0.3	2.3
Mn3	42.3	24.8	21.7	6.7	1.7	0.1

As can be seen from Table 1, Mn1 and Mn3 contained about 40% manganese oxide while Mn2 contained about 80% manganese oxide. Mn1 and Mn3 were in particle format while Mn2 was a very fine powder. The materials used for impregnation were potassium carbonate (K_2CO_3), copper nitrate ($Cu(NO_3)_2*3H_2O$) and iron nitrate ($Fe(NO_3)_3*9H_2O$) which were later solved in deionized water.

2.2 Impregnation procedures

Only Mn1 and Mn2 were tested in the TGA since Mn3 was not available at this time.

First, calcination of the raw manganese oxides was performed in a muffle oven for 4 hours at 950 °C. Afterwards, three samples of Mn1 and Mn2 each were impregnated with iron, copper and potassium respectively by immerging them in solutions of iron nitrate, copper nitrate and potassium carbonate. The mass ratio between manganese ore and foreign element was set to 5:1 (20%). This meant that to impregnate 50g of manganese ore with e.g. copper nitrate, an amount of $Cu(NO_3)_2*3H_2O$ corresponding to 10g of Cu was chosen (=38g copper nitrate). The impregnations with iron, copper and potassium for Mn1 were called Mn1-Fe, Mn1-Cu and Mn1-K and for Mn2 they were called Mn2-Fe, Mn2-Cu and Mn2-K.

The impregnation procedure changed slightly during the course of the project due to improvements, and in total three different methods ended up being tested where the last one was decided to be the optimal one:

Method 1:   In the first method the ore and the impregnation solution were simply mixed and after a few hours put into a muffle oven at 500 °C so the nitrate/carbonate could decompose into oxides. The drawback was that the impregnation solution was in excess and the nitrate/carbonate that did not impregnate the ore decomposed outside of the particles.

Method 2:   In the second method all excess impregnation solution was filtered away using filter paper and a funnel before being put into the muffle oven at 500 °C. The drawback

ended up being that it was impossible to determine beforehand how much of the foreign elements actually stuck to the ore.

Method 3: In the third and final impregnation method the ratio between impregnation solution and manganese ore was set to 15ml solution for 50g ore. This meant that all the impregnation solution got soaked up by the ore without leaving any dry spots or excess solution. After this the sample was left for some hours and then put into the muffle oven at 500 °C.

Method 3 is recommended for future work since it is fairly easy to control how much impregnation actually takes place.

For the TGA experiments, Method 1 was used for Mn1 and Method 2 was used for Mn2. Method 2 was also used for the first part of the fluidized bed experiments (Chapter 3.1-3.4). Method 3 was not introduced until later in the study (Chapter 3.5 and onwards).

2.3 TGA

TGA stands for thermogravimetric analysis and is used to measure mass changes and temperature changes of small samples. The procedure and the results are described below.

2.3.1 Procedure

Samples of 5-15mg oxygen carriers were heated up in a thermogravimetric analyser in an atmosphere consisting of pure nitrogen to 850 °C at a rate of 50 °C/min. Pure nitrogen was also used for testing the oxygen release of the carrier, and standard air was used for testing the regeneration to oxidized state. While testing the oxygen uptake the temperature was set to 750 °C due to thermodynamic reasons, which can be seen in Figure 4 where the CLOU phase change depends on the partial pressure and temperature. Once the oxidation cycle was finished nitrogen was introduced at isothermal conditions for 5 minutes in order to get rid of oxygen in the chamber. Both the oxidation and reduction periods lasted 20 minutes each and were repeated 6-8 times.

2.3.1 TGA results

This section shows the results from the TGA experiments. TGA results display curves of mass and temperature change over time. If the mass of a sample increases it means that the oxygen carrier has oxidized, and a reduction in mass means that the carrier has released oxygen. At the start of each TGA experiment moisture leaves the samples and it is not until after that that the behaviour is of interest. An oxygen carrier with good CLOU properties shows a clear cyclic behaviour, such as the following graph which can be used for comparison:
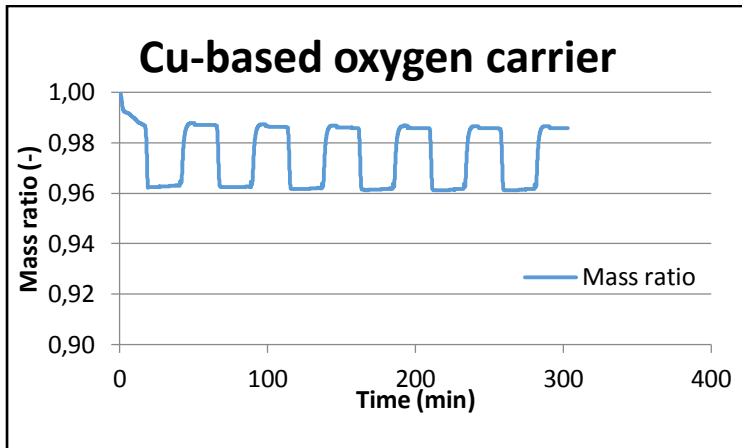
Figure 4. TGA results from an oxygen carrier containing copper oxide, showing a clear cyclic behavior.

2.3.1.1 Mn1

The TGA results for Mn1 and the three impregnations are shown below. The results of the mass ratio from the impregnations will be compared to the behaviour of the mass ratio of Mn1 to see if there is any significant change. These carriers were impregnated with Method 1.
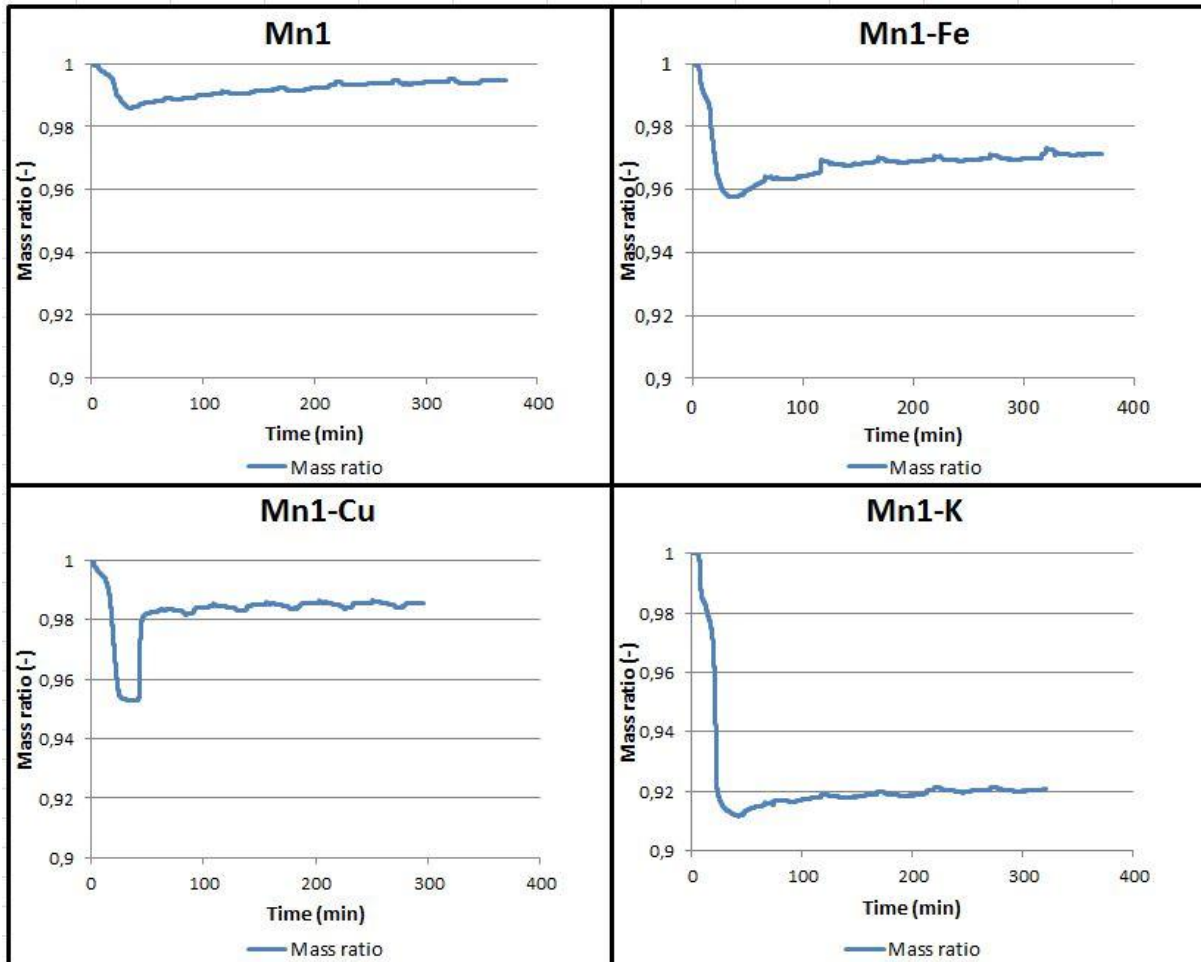

Figure 5. TGA results for Mn1 and the impregnations. Each oxidation and reduction cycle is 20min. After the oxidation period, 5min of pure nitrogen is used to purge the chamber from remaining oxygen.

Figure 5 shows that Mn1 itself does not possess impressive CLOU properties. There is however a slight increase in mass over time which suggests that the sample oxidizes more during the oxidation periods than it reduces during the reduction periods. This could be due to a faster oxidation rate than reduction rate, but it could also suggest that there is leftover oxygen when the reduction period starts. This would mean that the actual reduction period is shorter than 20 minutes.

Impregnation with Fe or K (Mn1-Fe and Mn1-K) does not seem to improve the CLOU properties of Mn1 since the behaviour of the mass ratio is more or less the same as for Mn1. Cu-impregnated Mn1 shows greatly increased oxygen uptake which is to be expected since Cu is known to be a good CLOU carrier. Whether this increase is solely from the Cu_2O/CuO couple or if copper activates CLOU-properties of manganese oxide is unclear. This increase in mass can only be seen in the first cycle since the oxides never reach a reduced phase afterwards. A further experiment was performed where the reduction period was increased to 50min and this led to Mn1-Cu reaching its reduced state again (See Appendix A, Figure A1)

10

2.3.1.2 Mn2

The TGA results from Mn2 and the impregnations are shown below in Figure 6. These oxygen carriers were impregnated with Method 2 which should be kept in mind when comparing them to the results from Mn1 above in Figure 5.
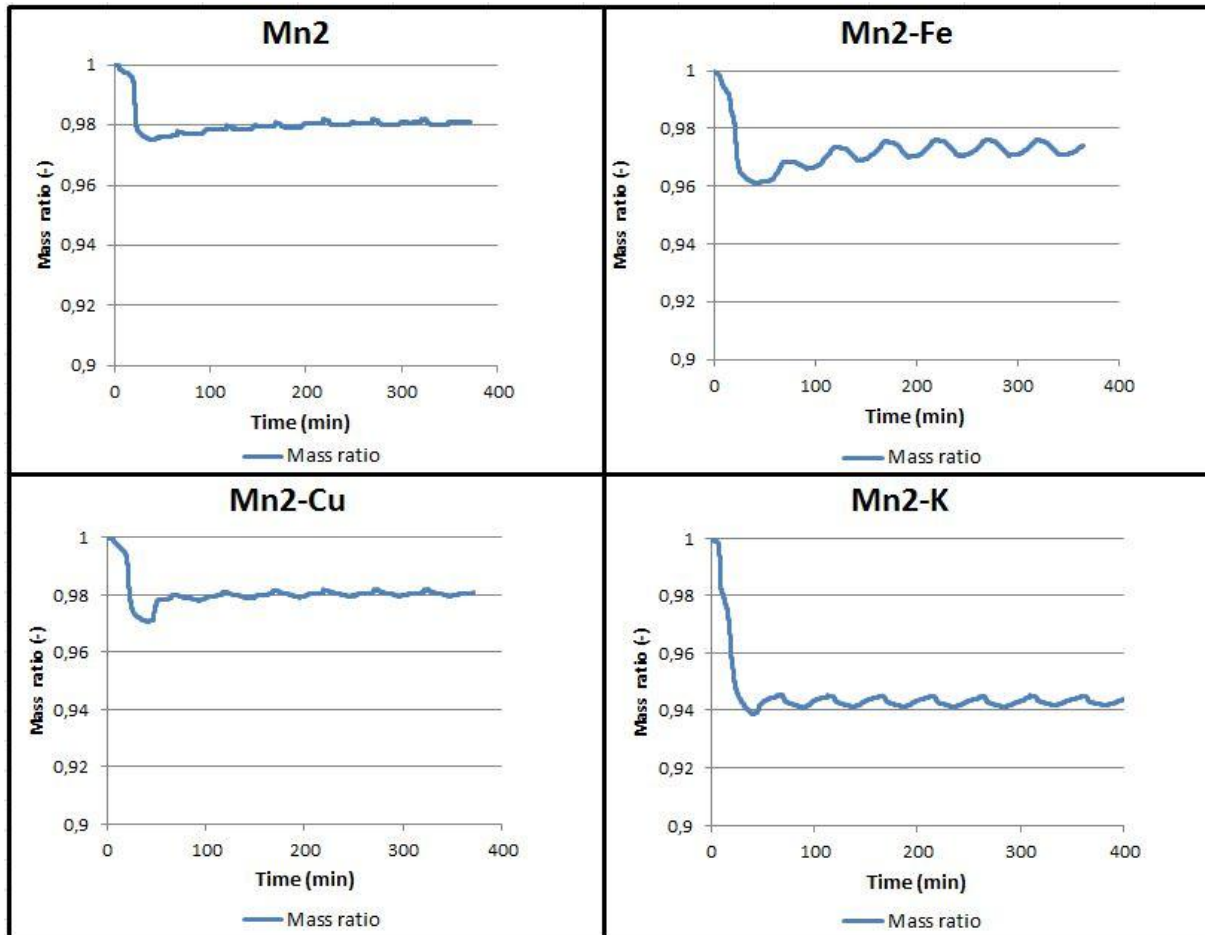

Figure 6. TGA results for Mn2 and the impregnations. Each oxidation and reduction cycle is 20min. After the oxidation period, 5min of pure nitrogen is used to purge the chamber from remaining oxygen.

Looking at Figure 6, it can be stated that Mn2 itself shows the same poor CLOU-behaviour as Mn1 even though Mn2 has much higher manganese content. This strengthens the idea that manganese oxide in itself is very slow when it comes to oxygen uptake and release, i.e. going between Mn_2O_3 and Mn_3O_4.

Impregnation with iron and potassium show a clear improvement compared with Mn2. Both Mn2-Fe and Mn2-K show noticeable oxygen uptake and release in each cycle. This could be interesting since neither potassium nor iron oxide is expected to have CLOU properties, but they seem to enhance the otherwise quite poor CLOU property of Mn_2O_3/Mn_3O_4.

Impregnation with Cu is less remarkable for Mn2 than for Mn1, although a clear initial oxygen uptake can be seen once again. The fact that Mn2-Cu would show less CLOU than Mn1-Cu is surprising and is probably due to the fact that during the impregnation procedure of Mn2-Cu (Method 2) some copper ions were filtered away.

3. CLC Performance of Impregnated Mn1

Experiments were carried out in a single fluidized bed for evaluating the carriers CLC-performance. Only Mn1 and the impregnations of Mn1 were used for the single fluidized bed tests. This is because this ore was already in particle format and easy to sieve to particles of 125-300 μm, compared to the fine powder of Mn2.

3.1 Single Fluidized Bed Set-up and Procedure

A tube reactor with a diameter of 30mm was used for the single fluidized bed experiments. A sample of 30g oxygen carrier was put on a porous plate where it could be exposed and fluidized by different gases. Air and nitrogen was mixed to simulate an oxidizing environment consisting of 10 % oxygen. 10 % CO was used to simulate the reducing environment, and 100 % nitrogen was used between the oxidation phase and reduction phase in order to purge. The temperature for the experiments was set to 800 °C and 10 % oxygen was used during heat up of the reactor. The oxidation period was terminated once the outgoing oxygen level had stabilized at 10 % for three minutes. The reduction period was terminated once the outgoing concentration of CO reached 2 %. The volume flow rate during oxidation and reduction was 2 L/min.

Ten cycles were performed for each oxygen carrier as long as no signs of agglomeration occurred. After these cycles, the temperature was decreased to 700 °C for one cycle and then 600 °C for another cycle in order to get data for lower temperatures too.

3.2 Preparation and XRF

The impregnation procedure used was Method 2, i.e. removing excess liquid from the oxygen carriers before calcination at 500 °C.

The mass ratio between Mn1 and the added elements was kept at 5:1 ratio (20%) except for Mn1-K which was lowered to 20:1 (5%). The reason for lowering Mn1:K to 20:1 is because some preliminary tests with Mn1-K with a ratio of 5:1 caused agglomeration which was very severe. Efforts to mechanically crush the agglomeration with a metal rod were performed as well as using boiling acid but neither could solve the problem, and a new reactor had to be ordered. A picture of the clogged reactor can be seen in Appendix B, Figure B5.

To get an idea of how much impregnation actually occurred, some sample of the particles were sent for and XRF analysis:

Table 2. XRF results of Mn1, Mn1-Fe, Mn1-Cu and Mn1-K

	Mn1 (%)	Mn1-Cu (%)	Mn1-Fe (%)	Mn1-K (%)
MnO	40.5	39.4	41.4	43.8
SiO2	44.1	35.8	36.8	31.6
Fe2O3	7.4	7.7	13.7	8.7
CuO	0.1	9.0	0.1	0.1
K2O	0.2	0.2	0.2	7.3
BaO	4.7	4.2	4.9	4.9
Al2O3	1.7	2.0	1.7	2.0
P2O5	0.4	0.6	0.3	0.6

It can be seen from the XRF that not everything could stick to the particles. The intention was to impregnate with 20% but in fact only 9% CuO stuck for Mn1-Cu and for Mn1-Fe an increase of only 6% Fe_2O_3 could be seen, while Mn1-K showed an increase of 7% K_2O. This leads to the conclusion that the added metal oxides are not evenly distributed over the manganese ore and that there seems to be a maximum amount that can be added to the ore (probably depending on the concentrations used). It should be noted that the percentages shown are the percentages of metal oxides and not of the metals themselves.

3.3 Data evaluation

There are different aspects that are useful to look at when evaluating the results. The main variable that will be looked at in this thesis is the time of complete CO conversion because this is a simple and good indicator of how well the oxygen carrier work can convert the fuel.

Another useful indicator when measuring performance is ω which is the mass-based conversion of the oxygen carrier. It is a measurement of how oxidized the carrier is, where the value "1" means completely oxidized carrier. It is calculated as the mass of the bed at any given point divided by the mass of the bed when it is fully oxidized (maximal mass): $\omega = \dfrac{m}{m_{ox}}$

Where m is the actual mass and m_{ox} is the total mass of the bed when its fully oxidized.

To calculate ω the following equation is used:

$$\omega_i = \omega_{i-1} - \int_{t_i}^{t_i + \Delta t} \frac{M_O}{m_{ox}} (\dot{n}_{CO}) dt$$

Where M_O is the molar mass of oxygen and $\dot{n}_{CO}$ is the molar flow of CO.

Another indicator which is common to use is the gas yield, γ, which is the CO_2 going out of the reactor divided by the sum of CO_2 and CO:

$$\gamma_{CO_2} = \frac{\dot{n}_{CO_2}}{\dot{n}_{CO_2} + \dot{n}_{CO}}$$

The reason why these two variables are common to use is that when used together they create graphs that are very useful for comparing different oxygen carriers since the results are independent of the amount of oxygen carriers used.

3.4 CLC Performance Results

The following graphs show the CO_2 and CO concentrations during the 10 reduction periods for Mn1, Mn1-Fe, Mn1-Cu and Mn1-K, as well as the results obtained for lower temperatures. No agglomeration was observed in any case, unless stated. Carbon deposition was however observed in all cases.

3.4.1 Mn1

The results from Mn1 are shown below and will be used as the baseline for comparing the different impregnations later on. The variable that was evaluated was the time of complete fuel conversion, i.e. the duration of the time while the CO-level is zero.
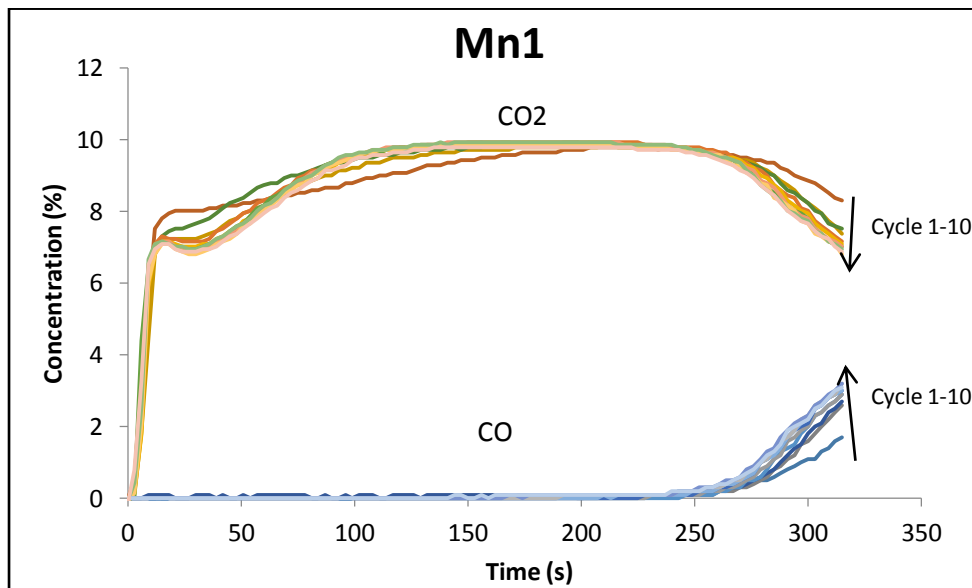
Figure 7. CO_2 and CO concentrations for Mn1 at 800°C.

As can be seen from Figure 7, Mn1 has good CLC-reactivity by itself, completely converting CO for about 250s. The CO_2 comes out very fast at first and then the concentration slowly increases. This behaviour could be explained by the carbon deposition which was observed during the following oxidation phase.
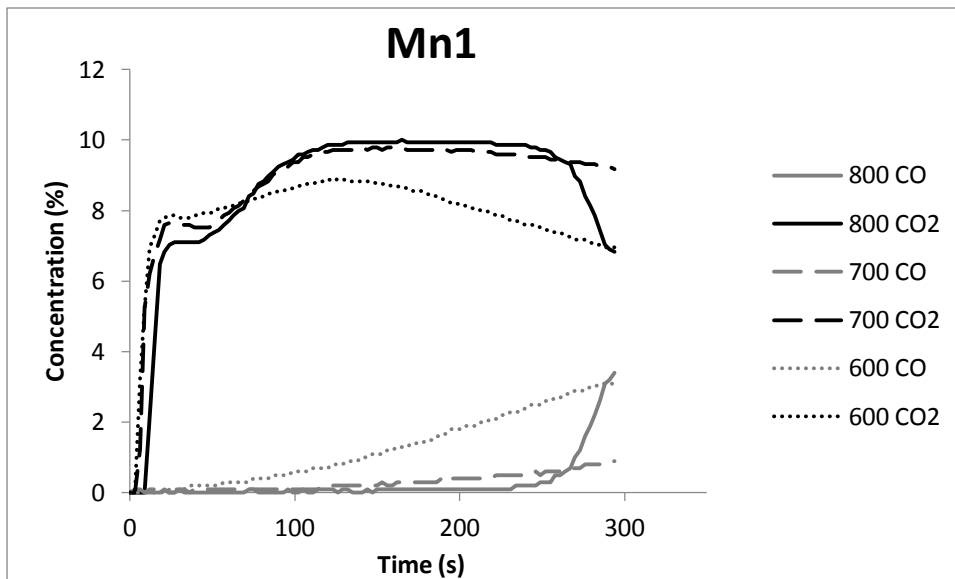
Figure 8. CO₂ and CO concentrations for Mn1 at 800°C (last cycle), 700°C and 600°C

As expected, Figure 8 shows that the CLC-performance of Mn1 is poorer when the temperature decreases. At 700 °C the outgoing CO concentration starts to increase around 1-2min, although very slowly. At 600 °C CO starts coming out almost instantaneously.

3.4.2 Mn1-Fe
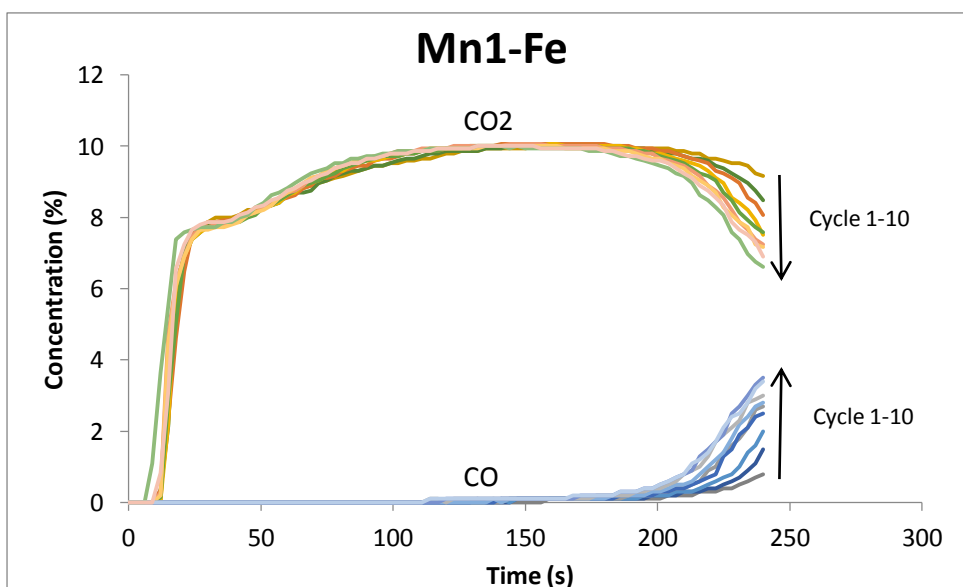The results from Mn1-Fe are shown in Figure 9 below.

Figure 9. CO₂ and CO concentrations for Mn1-Fe at 800°C.

Compared to normal Mn1, iron impregnation does not show any improvement in CLC-performance. In fact the duration with 100% conversion is shortened to about 200s, which is about 50s shorter than for regular Mn1, and for each cycle the performance gets worse.

An interesting observation that could be noted during the experiment was that significant CLOU behaviour was observed during heat up of the reactor. The outgoing O_2 concentration reached an

impressive 15% at one point before going back to 10%, see Appendix B, Figure B2. This is in accordance with the TGA results as well as previous studies[33].
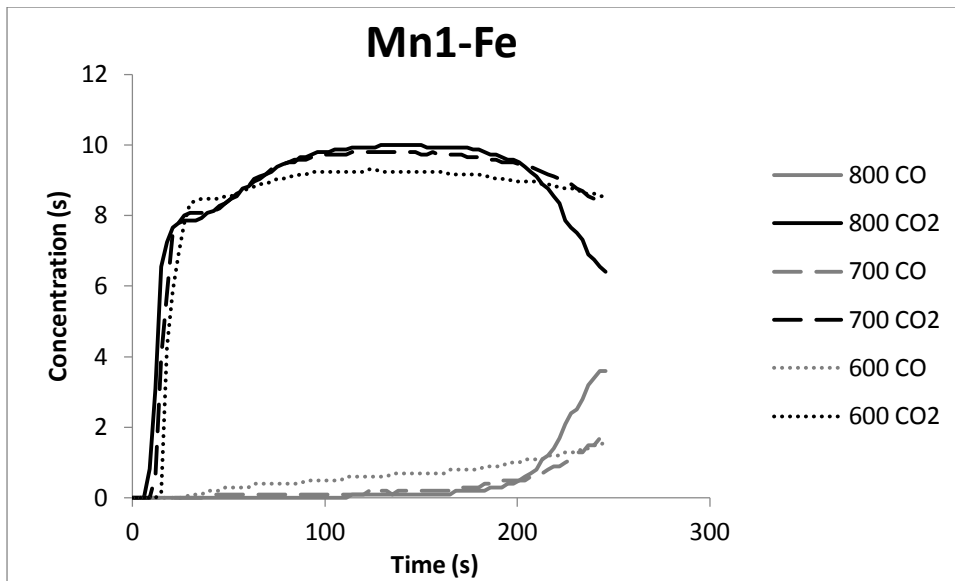

Figure 10. CO_2 and CO concentrations for Mn1-Fe at 800°C, 700°C and 600°C

As with Mn1, Mn1-Fe shows slightly poorer performance at 700 °C compared to 800 °C and even poorer performance at 600 °C. CO can be observed after 50s at 700 °C and almost directly at 600 °C.
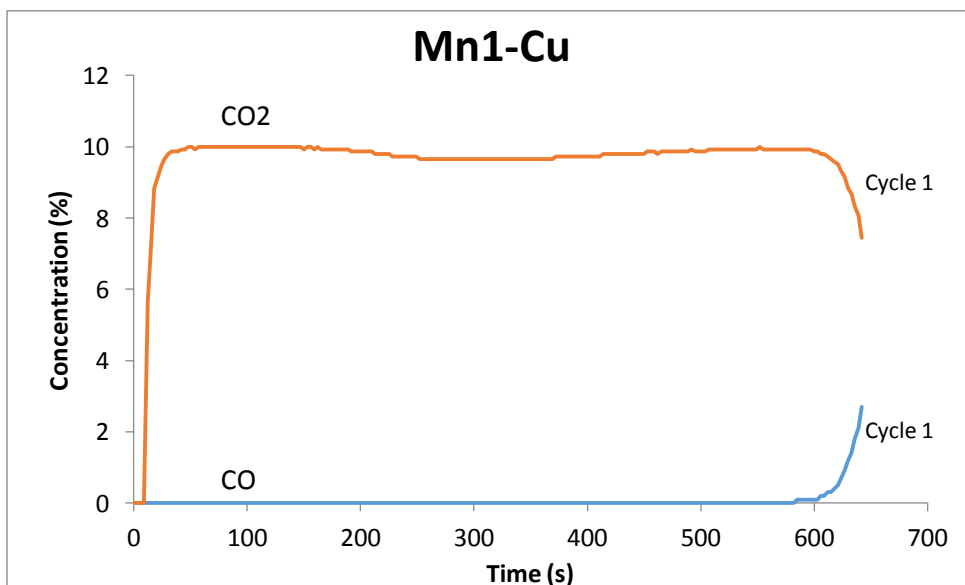
3.4.3 Mn1-Cu
The results from Mn1-Cu are shown below in Figure 11.

Figure 11. CO_2 and CO concentrations for Mn1-Fe at 800°C.

Only one cycle was carried out for Mn1-Cu due to signs of agglomeration. Once the reactor cooled down the agglomeration was investigated and it could be concluded that it was not severe, although clearly noticeable. The performance of Mn1-Cu showed however great promise with complete fuel conversion for almost 600s which is more than double the time of Mn1. This duration is however not

completely reliable since only one cycle was carried out. New Mn1-Cu particles were used for testing at 700 °C and 600 °C.
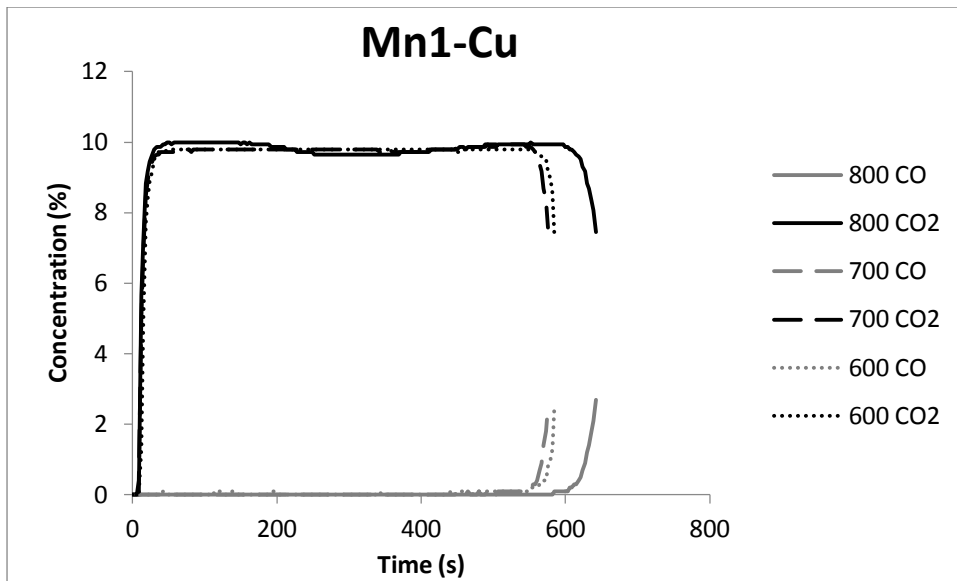

Figure 12. CO_2 and CO concentrations for Mn1-Cu at 800°C, 700°C and 600°C.

According to the results, displayed in Figure 12, Mn1-Cu shows excellent reactivity at lower temperatures too. The oxygen carrier fully converts CO for about 550s both at 700 °C and 600 °C. Agglomeration behavior was observed at 700 °C but not at 600 °C.

3.4.4 Mn1-K
Figure 13 below shows the results from Mn1-K.
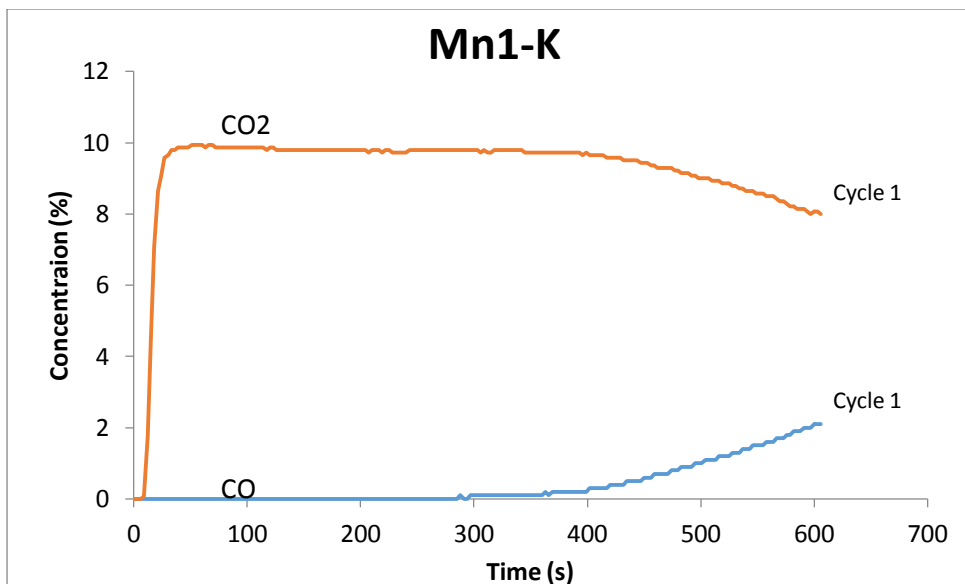
Figure 13. CO_2 and CO concentrations for Mn1-K at 800°C.

As for Mn1-Cu, only one cycle was performed for Mn1-K due to agglomeration. In this case the agglomeration was severe and totally clogged the reactor even though the amount of potassium during the impregnation had already been reduced from 20% to 5% (see 3.2). A metal rod was used to try and destroy the agglomerated particles but this only got rid of part of the clogging and boiling

acid had to be used in order to get rid of the rest. The time of complete CO conversion showed however an improvement compared to the normal Mn1. A decision was made to not investigate Mn1-K further due to the possibility of more agglomeration.

3.4.5 Gamma/Omega Graphs

The gas yield was plotted against the oxygen carrier conversion for the four oxygen carriers tested and is shown below.
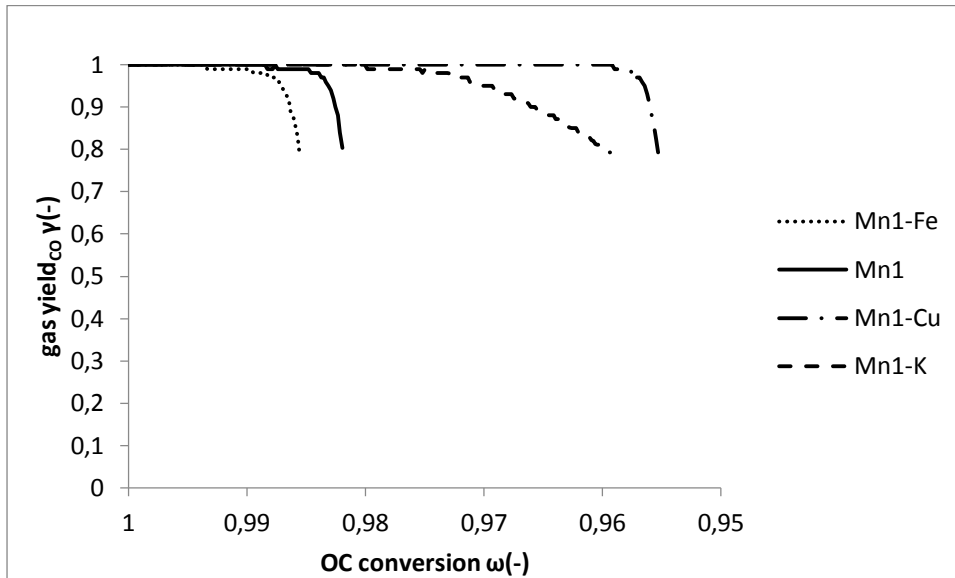

Figure 14. The gas yield is plotted against the carrier conversion for Mn1, Mn1-Fe, Mn1-Cu and Mn1-K at 800°C. The data used for each oxygen carrier is taken from the last cycle of each experiment.

Figure 14 can be used as a comparison between the different impregnations. Although it is not completely reliable since Mn1-K and Mn1-Cu agglomerated and only one cycle was completed for them, it still shows that Mn1-Fe performs the worst and Mn1-Cu performs the best.

3.5 Further Investigation of Mn1-Cu with Lower Copper Content

Since Mn1-Cu showed very high reactivity, Mn1 was impregnated with copper once again but with mass ratios of 2% and 0.5% (instead of 20%) in order to avoid agglomeration. These were labelled Mn1-Cu2% and Mn1-Cu0.5% respectively. The impregnation procedure used was Method 3 which was more accurate than Method 2 and also made sure that all impregnation solution got soaked up by the manganese ore. No agglomeration was observed in any of the cases that follow below.

3.5.1 Mn1-Cu0.5 %

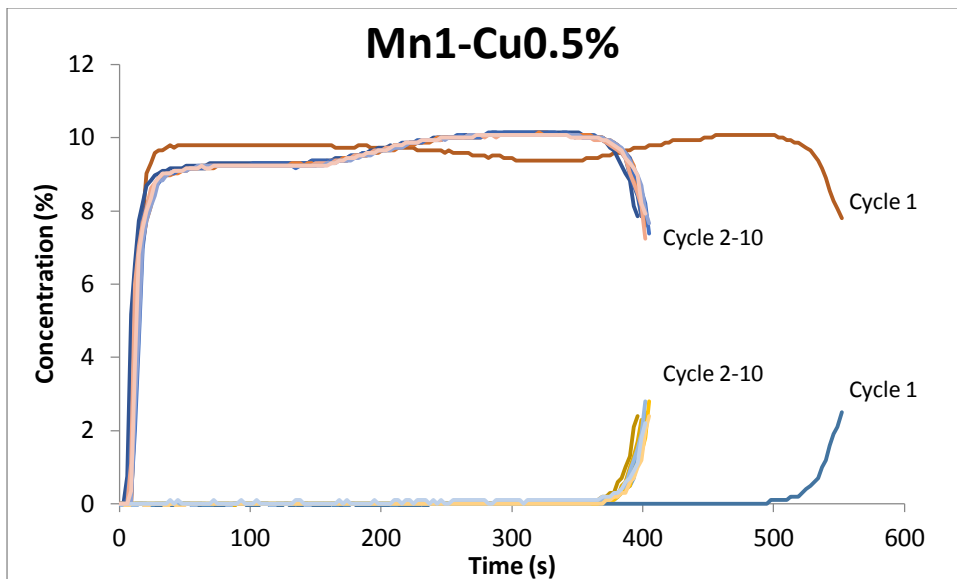Figure 15 below shows the results from the 10 cycles with Mn1-Cu0.5%.

Figure 15. CO$_2$ and CO concentrations for Mn1-Cu0.5% at 800°C.

Mn1-Cu0.5% converts CO completely for almost 400s which is a clear improvement compared to Mn1 (250s). Carbon deposition is most likely the reason for the fluctuating CO$_2$-levels. The first cycle shows a very long reduction time due to being oxidized for a longer period.
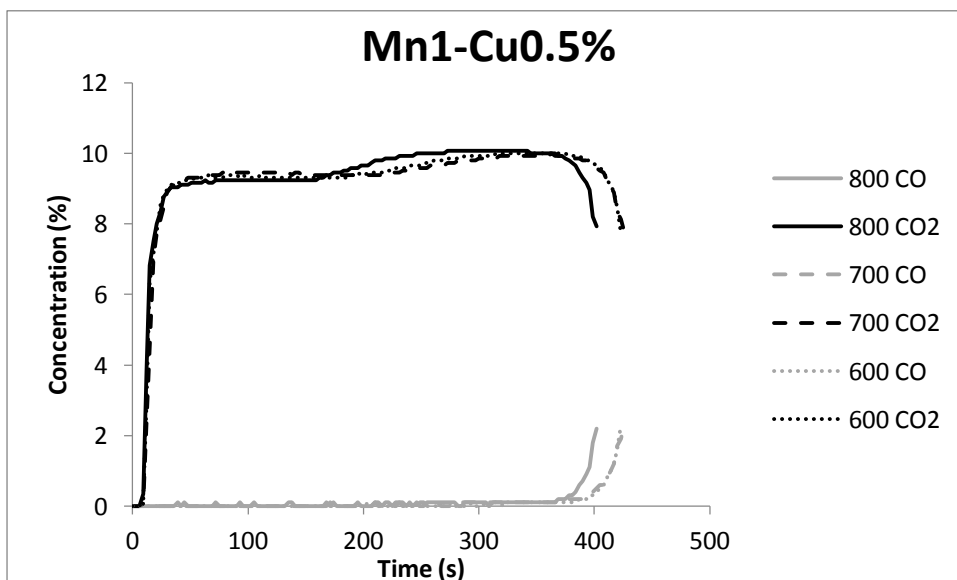

Figure 16. CO$_2$ and CO concentrations for Mn1-Cu0.5% at 800°C, 700°C and 600°C.

In Figure 16 it can be seen that at temperatures down to 600 °C Mn1-Cu0.5% shows very good performance compared to Mn1. The result shows that the performance seems to be better at 700 °C and 600 °C than at 800 °C. This is most likely due to the fact that at 700 °C and 600 °C only one cycle was performed, and the first cycle is always slightly better and less reliable than following cycles. The data for 800 °C is taken from the last cycle. So although the results are not completely comparable,

this graph shows that fuel conversion is possible down to lower temperatures, which was not possible for normal Mn1.

3.5.2 Mn1-Cu2%
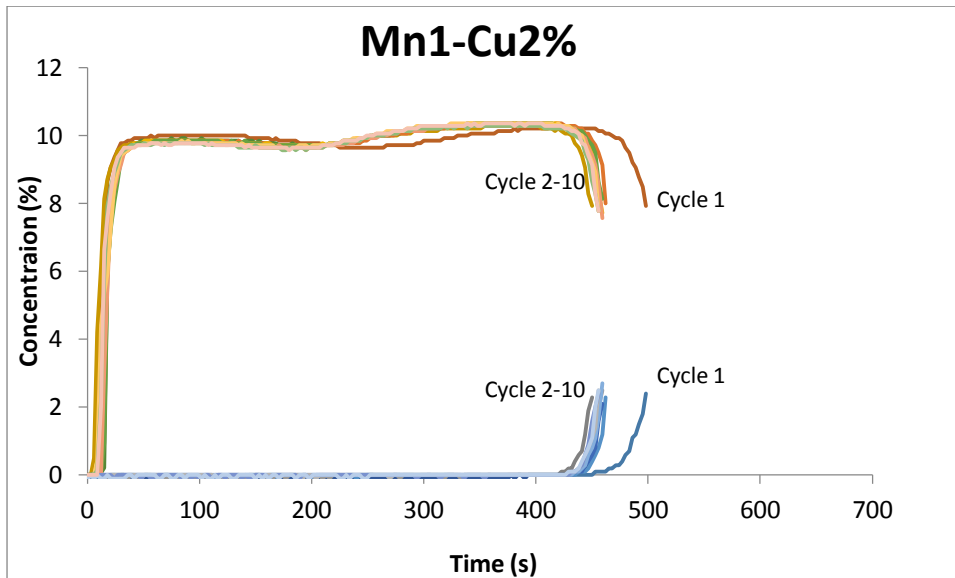
The results for Mn1-Cu2% are shown below in Figure 17.

Figure 17. CO$_2$ and CO concentrations for Mn1-Cu2% at 800°C

Adding 2% copper to Mn1 greatly improved the performance. More than 400s of complete conversion of CO for 10 cycles was observed which slightly longer than for Mn1-Cu0.5%. The first cycle showed somewhat longer reduction time than subsequent cycles.

Compared to the original Mn1-Cu which had a copper content of about 10% and a reduction time around 600s, Mn1-Cu2% still seems to be very good. Although Mn1-Cu2% cannot convert the fuel for as long as Mn1-Cu, agglomeration is avoided and the particle production is cheaper since less copper nitrate is needed.
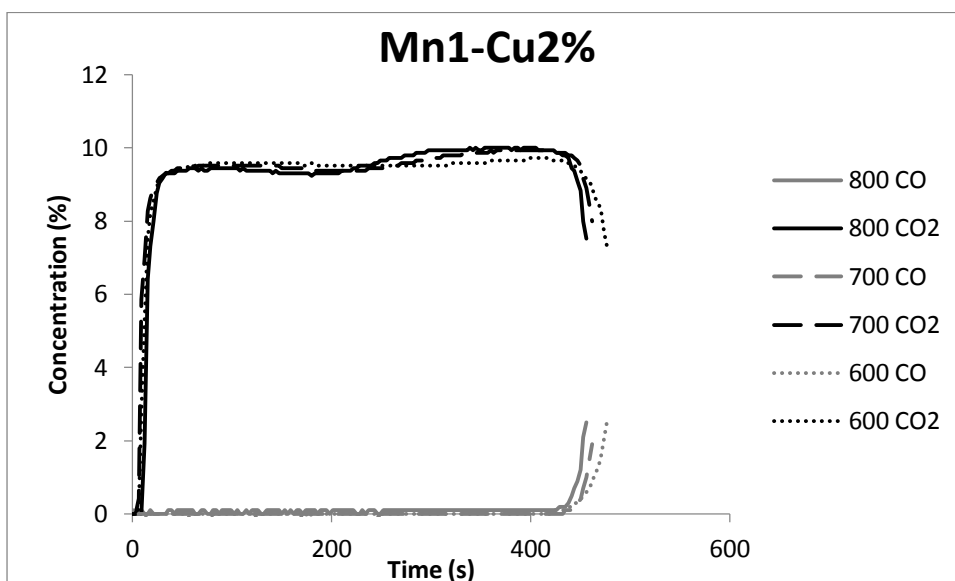

Figure 18. CO$_2$ and CO concentrations for Mn1-Cu2% at 800°C, 700°C and 600°C

Mn1-Cu2% shows great reactivity at 700 °C and 600 °C. In fact, no substantial difference from 800 °C can be seen. This is likely due to the same reason as for Mn1-Cu0.5%, i.e. the data for 700 °C and 600 °C is taken from the first and only cycle which is always somewhat better than the other.

3.5.3 Gamma/omega graphs

The gas yield plotted against the oxygen carrier conversion is plotted below for the three copper impregnations together with the normal Mn1.
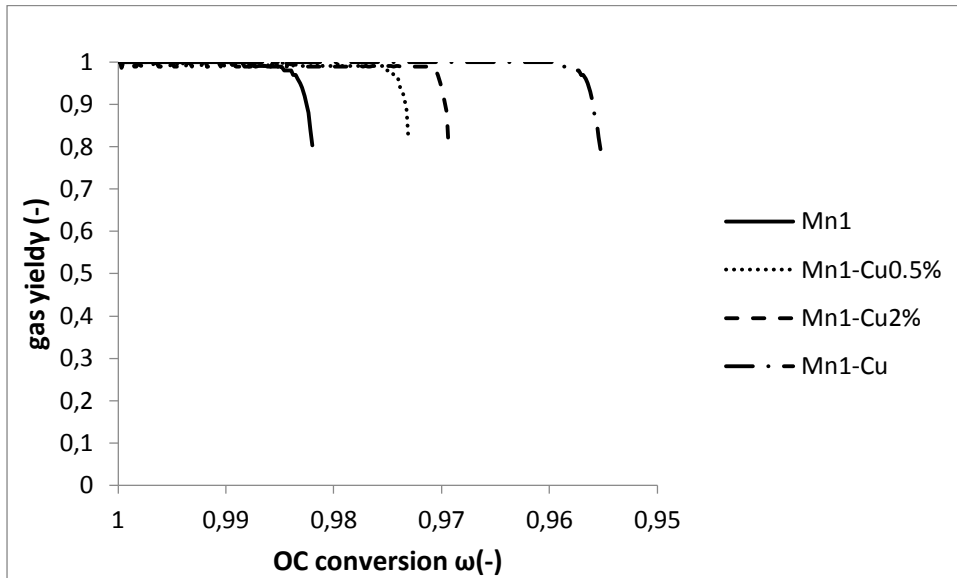

Figure 19. The gas yield is plotted against the OC conversion for Mn1, Mn1-Cu0.5%, Mn1-Cu2% and Mn1-Cu at 800°C.

Figure 19. shows the gas yield plotted against the oxygen carrier conversion for Mn1 together with the different copper impregnations. As can be seen it is very beneficial to add copper to manganese ore. Adding 0.5% Cu increases the performance significantly and adding 2% Cu improves the performance further. The improvement in performance does however not seem to be linear with the amount of copper added. Mn1-Cu is also shown for comparison, although it should be remembered that this carrier agglomerated.

4. Cu-impregnation of low-performing Mn ore (Mn3)

Since copper impregnation apparently improves manganese ore significantly, a decision was made to investigate this further and test it on ore with poorer reactivity than Mn1. This new ore showed much less tendency towards carbon deposition so if the reactivity would be enhanced it could be more attractive as an oxygen carrier than Mn1. The amount of copper impregnation was kept to 2% and 0.5%. The ore was labeled Mn3 and the impregnated ores were labelled Mn3-Cu2% and Mn3-Cu0.5%.

Even lower temperatures were tested this time. After 10 cycles at 800 °C, one reduction cycle at 700 °C, 600 °C, 500 °C, 400 °C and 300 °C each was performed. The oxidation was always performed at 700 °C, except for the 10 cycles at 800 °C.

4.1 Preparation and XRF

Mn3 was sieved to 125-300 µm and then impregnated by using Method 3. As can be seen from Table 2 in chapter 2.1, Mn3 contains more or less the same amount of manganese oxide as Mn1. The main differences between Mn3 and Mn1 lie in the amount of SiO_2, Fe_2O_3 and Al_2O_3. No XRF analyses of Mn3-Cu2% or Mn3-Cu0.5% were made.

4.2 Results

The data received from the fluidized bed experiments is shown in this section. Only the CO levels are shown for the experiments at lower temperatures in order to make the graphs clearer. No agglomeration was observed in any case.

4.2.1 Mn3

The results from all tested temperatures for Mn3 are shown below in Figures 20-22. The results from Mn3-Cu0.5% and Mn3-Cu2% later on will be compared to these figures.
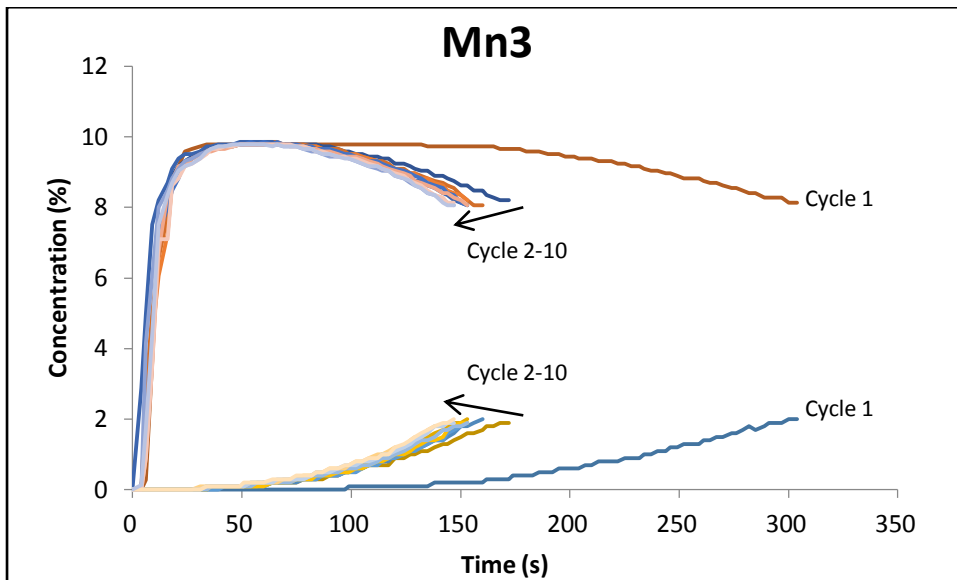

Figure 20. CO_2 and CO concentrations for 10 cycles of Mn3 at 800°C.
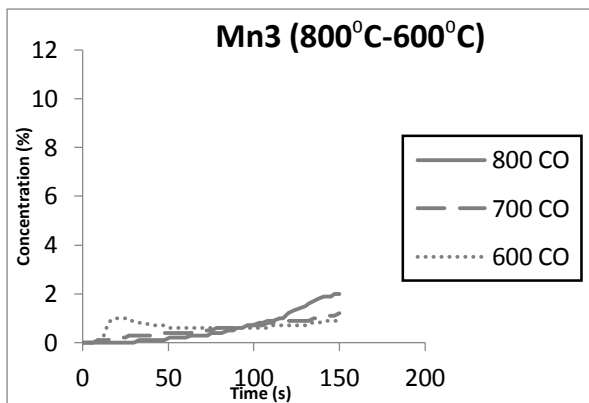

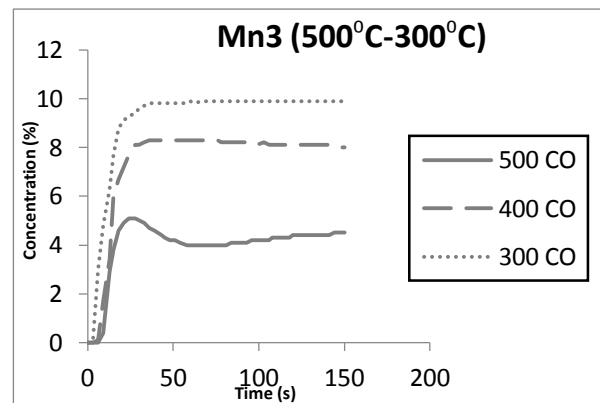**Figure 21. CO concentrations for Mn3 at 800°C, 700°C and 600°C**

Figure 22. CO concentrations for Mn3 at 500°C, 400°C and 300°C

From Figure 20 it can be concluded that Mn3 has much poorer CLC-qualities compared to Mn1, with a complete fuel conversion period of about 50s (except for the first cycle).

Figure 21 and Figure 22 show that the outgoing CO concentration starts increasing already after a couple of seconds at all temperatures below 800 °C.

4.2.2 Mn3-Cu0.5%

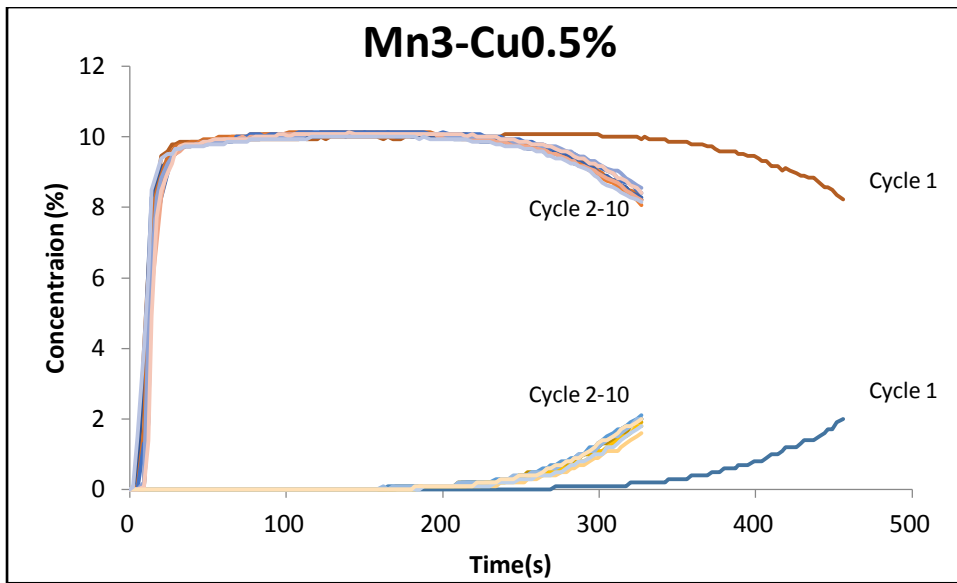The graphs below show the performance for Mn3-Cu0.5% at all tested temperatures.

Figure 21. CO_2 and CO concentrations for Mn3-Cu0.5% at 800°C
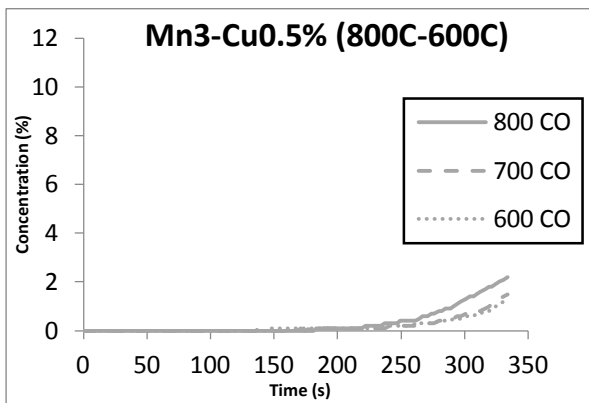

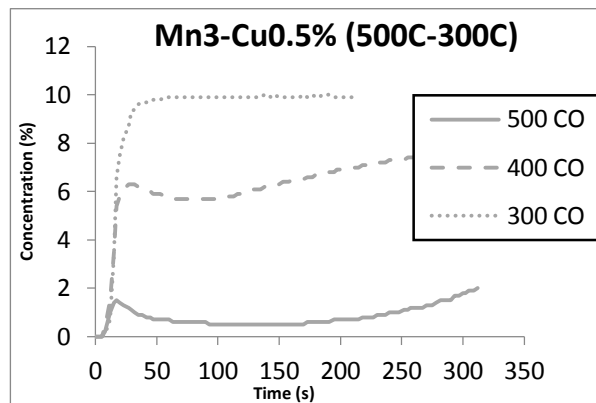**Figure 22. CO concentrations for Mn3-Cu0.5% at 800°C, 700°C and 600°C**

Figure 23. CO concentrations for Mn3-Cu0.5% at 500°C, 400°C and 300°C

From Figure 21 it is clear that Mn3-Cu0.5% can convert the fuel for much longer than normal Mn3 at 800 °C. The time of complete fuel conversion is about 250s which is five times better than the original ore. From Figure 24 and Figure 25 it can be seen that Mn3-Cu0.5% can convert CO very well at temperatures down to 600 °C which is a clear improvement as well.

4.2.3 Mn3-Cu2%

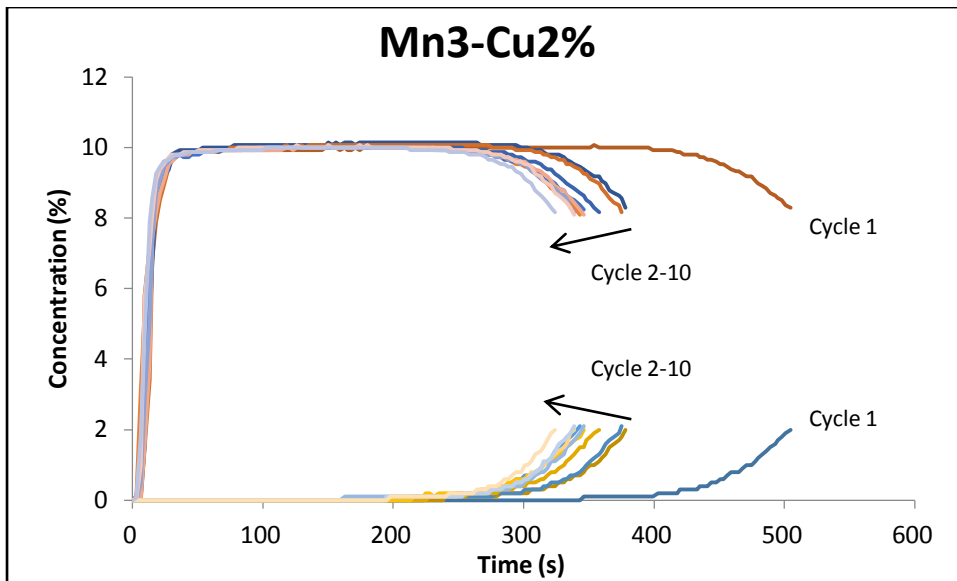The graphs below show the performance for Mn3-Cu2% at all tested temperatures.

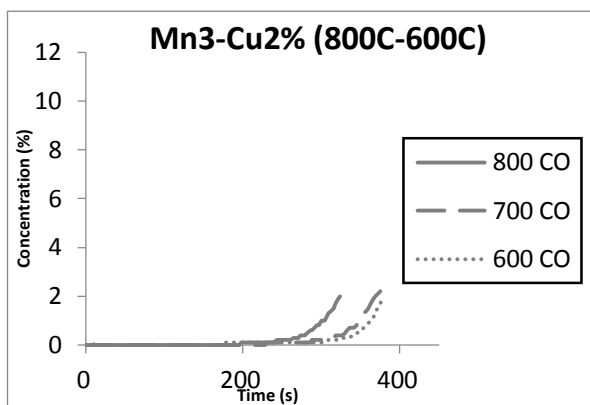**Figure 24. CO2 and CO concentrations for Mn3-Cu2% at 800°C**

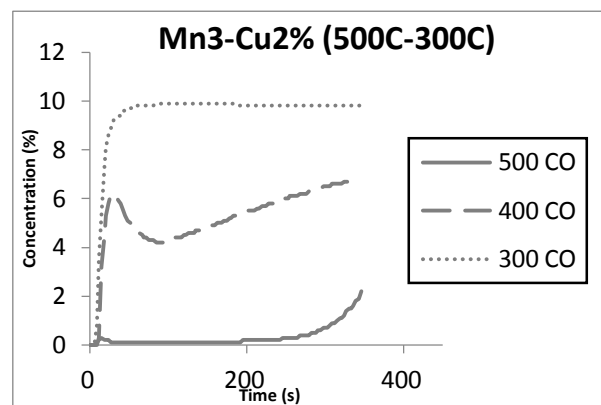**Figure 267. CO concentrations for Mn3-Cu2% at 800°C, 700°C and 600°C**

Figure 258. CO concentrations for Mn3-Cu2% at 500°C, 400°C and 300°C

Mn3-Cu2% fully converts CO for almost 300s at 800 °C which can be seen from Figure 26. This is somewhat longer than for Mn3-Cu0.5%. The results also suggest that the performance decreases with each cycle. It is unclear why this happens.

Mn3-Cu2% continues to perform well at lower temperatures even down to 500 °C (see Figure 27&28) which is something that Mn3-Cu0.5% was not capable of. In Figure 27 it looks like the performance is slightly better at 700 °C and 600 °C than at 800°C but this is most likely due to the oxygen carriers were left to oxidize for a longer time before cycles at lower temperatures (they received additional oxidation during heat up and cool down of the reactor). The data for 800 °C is taken from the tenth cycle.

4.2.4 Gamma/omega graphs

The gas yield for Mn3, Mn3-Cu0.5% and Mn3-Cu2% is plotted below against the oxygen carrier conversion. The data is taken from the tenth cycle for each oxygen carrier at 800 °C
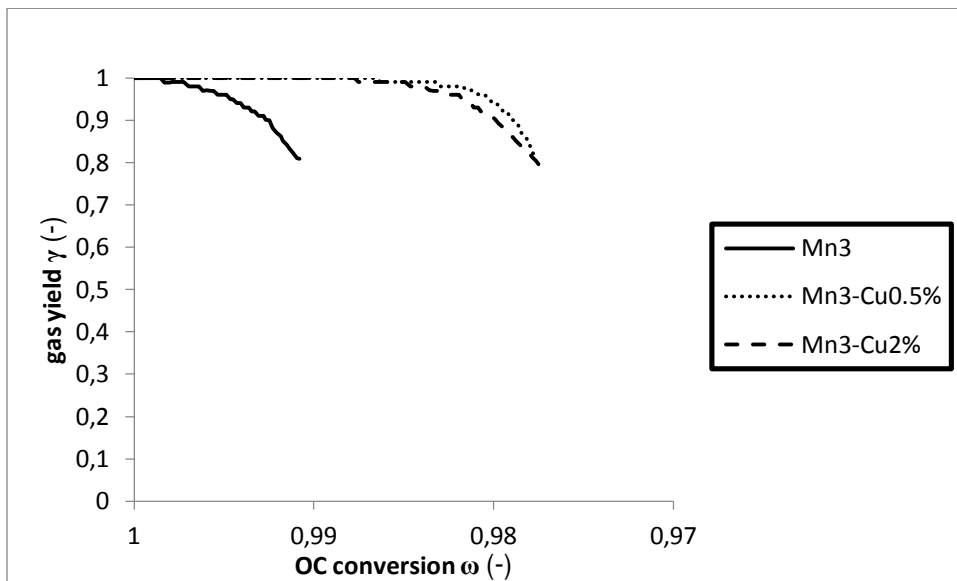
Figure 27. Gas yield plotted against the OC conversion for Mn3, Mn3-Cu0.5% and Mn3-Cu2%

In Figure 29 it can be seen that adding copper to Mn3 enhances the reactivity greatly which is the most important conclusion from these experiments. Something else that can be seen is that the performance of Mn3-Cu0.5% and Mn3-Cu2% seems to be the same. The reason for this can be seen in Figure 26 where the last cycle of Mn3-Cu2% has about the same time of complete fuel conversion as the cycles for Mn3-Cu0.5%, and the data is taken from the last cycle.

4. Discussion

4.1 Impregnation

Some improvements of the impregnation procedure were made during the course of the project which means that it was not constant. The first improvement was to filter away all of the solution that had not been absorbed by the ore, and the second improvement was to control the ratio between solution/ore. The base method, i.e. simply mixing the ore with a dissolved salt, was however the same over the duration of the project.

This very simple method of impregnating manganese ore seems to work very well. This is positive since the procedure is very cheap compared to other methods, such as freeze-granulation, and it is easy to perform without the need of any special equipment. It would also be very easy to use this method on a bigger scale for batches larger than 50g.

A drawback with using ore is that they are heterogeneous and many different elements are present. Together with the fact that the impregnation procedure was very simple, the distributions of elements in the particles were most likely not very even. One consequence of this is that one particle can be much more active than the next, and when performing tests such as TGA very small samples are used (5-20mg) which might not be representative for the entirety of the original batch. Therefore the data received from such experiments could be inconsistent.

4.2 TGA

From the TGA results it can be seen that neither Mn1 nor Mn2 possess significant CLOU properties by themselves when exposed to pure nitrogen and air. The reduction process seems to be slower than the oxidation process. Taking the quite low gas flow rate (100ml/min) into account it probably takes several minutes for the oxygen from the oxidation cycle to leave the chamber and therefore the 5min of purging might not have been enough. In this case the duration of actual reduction was less than the intended reduction duration (20min). However, since the conditions were the same for all carriers, any changes in behavior are still of interest and can lead to conclusions.

Copper is known to have very good CLOU properties so seeing an improvement in Mn1-Cu and Mn2-Cu does not come as a surprise. It is however unclear whether all the extra mass change comes from Cu_2O /CuO alone or if there is some synergy between manganese and copper. The conclusion that can be drawn is that if CLOU is wanted for a manganese ore, it is a good idea to impregnate it with copper. As was seen in the experiments in single fluidized bed the amount of copper should not be very high due to agglomeration issues.

Impregnating Mn1 with iron did not seem to have much effect but impregnating led to an improvement in CLOU behavior, which is interesting and in accordance with previous research. This behavior was also seen with impregnation with potassium. The difference between the experiments with Mn1 and Mn2 is that Mn2 has higher manganese content, has a higher contact area (powder format) and the impregnation procedure was slightly different.

This work only shows that impregnating manganese ore with iron, copper and potassium has the potential of improving the CLOU potential. More experiments are needed to confirm and get more insight into how the interaction actually works.

4.3 Single Fluidized Bed Reactor

Only manganese ores that were in particle form (Mn1 and Mn3) were tested as oxygen carriers in the single fluidized bed test. Mn1 showed promising results for combustion of CO on its own, oxidizing the fuel completely for about 3 minutes.

Impregnation with iron did not improve the manganese ore. In fact it decreased the time of complete fuel conversion, and for each cycle this duration became shorter and shorter. A reason for this is that the temperature of 800 °C might not be high enough for the iron oxide to act as a good oxygen carrier. Another reason is that there is more iron oxide than manganese oxide present in the bed, and since manganese oxide typically performs somewhat better than iron oxide this could lead to a decrease in performance. Therefore it can be concluded that impregnating manganese ore with iron is not desirable for CLC purposes at 800 °C. The interesting fact about Mn/Fe is the enhanced CLOU properties observed during the TGA experiments. Signs of this were also seen during heat up of the reactor (in 10% oxygen) where there was a significant oxygen release.

Impregnating with copper enhanced the oxygen carrier greatly. The drawback was a negative effect on agglomeration. Since the copper content was fairly high it was decided to lower this level to 2% and 0.5%. The results showed that these oxygen carriers with lower copper content avoided all agglomeration problems while still maintaining greatly increased reactivity. This is perhaps one of the most interesting parts of the project since only a very tiny amount of copper affects the performance a lot. In fact, adding only 0.95g of copper nitrate into 50g of Mn3 (Mn3-Cu0.5%) showed a fuel conversion time which was about five times longer than for normal Mn3.

Another important result from the copper-impregnated manganese ore is that it can convert CO at very low temperatures while still maintaining good performance. All copper impregnations led to good CO conversions at 800 °C, 700 °C and 600 °C. Mn3-Cu2% even showed decent CO conversion at 500 °C.

The increase in fuel conversion time is not linear to the amount of copper added and therefore the results suggest that copper activates manganese oxide or acts as a catalyst for CO conversion. This is interesting for the CLC technology and the fact that it works very well with cheap manganese ore can be very important. The reasons why and how this happens were however not investigated in this project.

Adding potassium to manganese ore cannot be recommended due to agglomeration problems, even with quite low potassium content. The added potassium did however increase the reactivity and could be interesting for further research and with other carriers.

An aspect that was not investigated in this thesis is attrition. Many manganese ores perform relatively poorly in attrition tests which is a big drawback for their use as oxygen carriers in CLC-processes. If however a manganese ore that is resistant to attrition is found but rejected due to poor reaction rates for CLC, this thesis shows that the impregnation of copper could make such oxygen carriers much more interesting.

Further research could include adding even lower amounts of copper to manganese in order to find the lowest amount of added copper nitrate that is needed to activate the manganese. Testing Mn-Cu carriers with syngas, methane or other fuels are also of great interests.

For CLOU purposes it would be interesting to look deeper into the Fe-impregnated manganese ore since the oxygen uncoupling was improved and no agglomeration was observed

5. Conclusions

Different manganese ores were impregnated with iron, copper and potassium in order to see whether their performances could be improved. CLOU performance was tested by using TGA and the CLC performance by using a single fluidized bed reactor at 800 °C with CO as fuel.

It was found that:

- Adding copper to manganese ore is good if CLOU properties are wanted
- Adding iron or potassium can improve the CLOU performance under the right circumstances
- Adding copper appears to greatly activate the CLC performance of manganese ore, even at lower temperatures.
- Caution should be taken when adding potassium to manganese ore

Apart from the conclusions mentioned above, this thesis also tested some different impregnation methods and decided on the best one. The main discovery of this thesis is however that it was found that adding copper in very small amounts greatly enhances the reactivity of manganese ore for CLC-purposes. Not only does the overall performance at 800 °C increase significantly, the ore also works very well at lower temperatures. Adding 2% copper even made it possible to have good CO conversion at 500 °C.

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APPENDIX

A) TGA

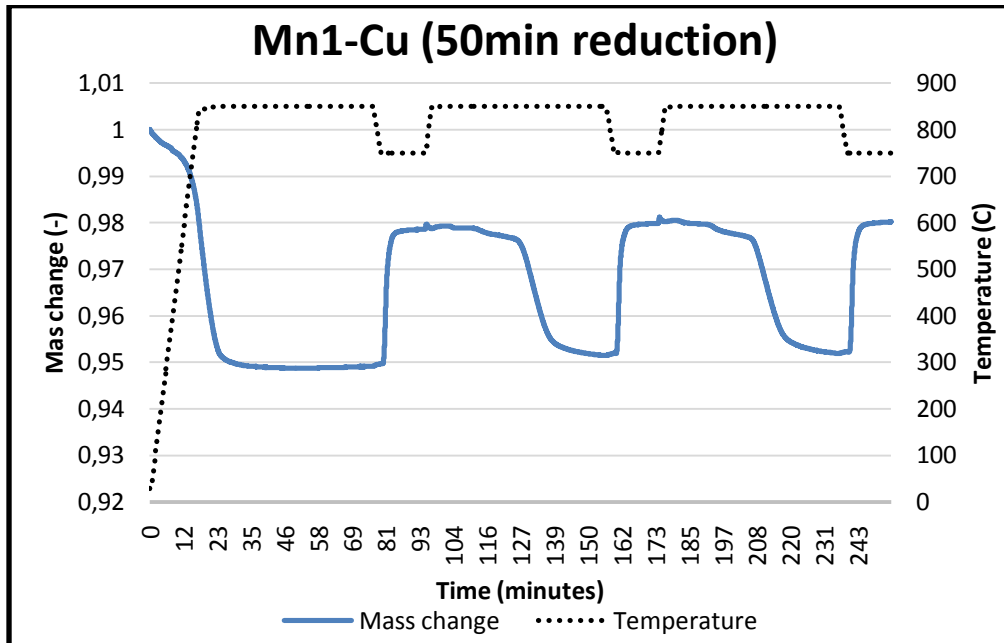### A1. Mn1-Cu with longer reduction time

Figure A1. Mn1-Cu with longer reduction time

In Figure A1 it can be seen that increasing the reduction time makes Mn1-Cu reduce again.
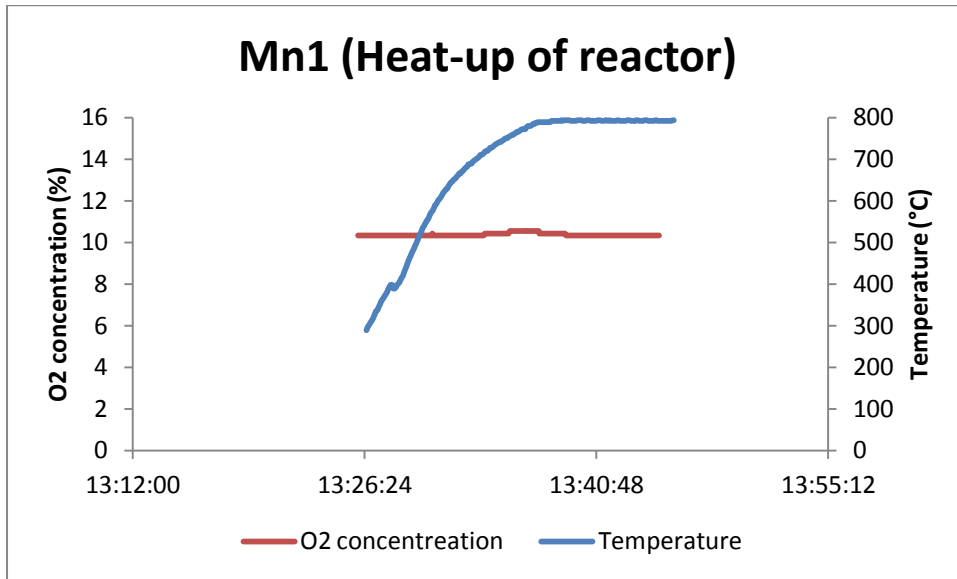
B) SINGLE FLUIDIZED BED

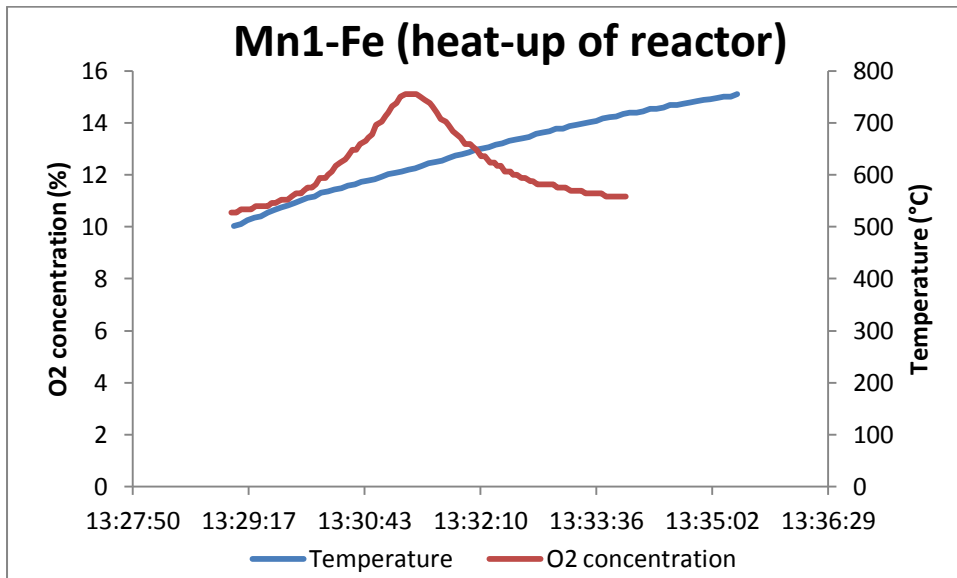Figure B1. O_2 and temperature profile during heat up to 800 °C of the reactor for Mn1

Figure B2. O_2 and temperature profile during heat up to 800 °C of the reactor for Mn1-Fe

A comparison between Figure B1 and Figure B2 was made and it can be stated that Mn1-Fe releases considerably more oxygen during the heat-up than Mn1 does.
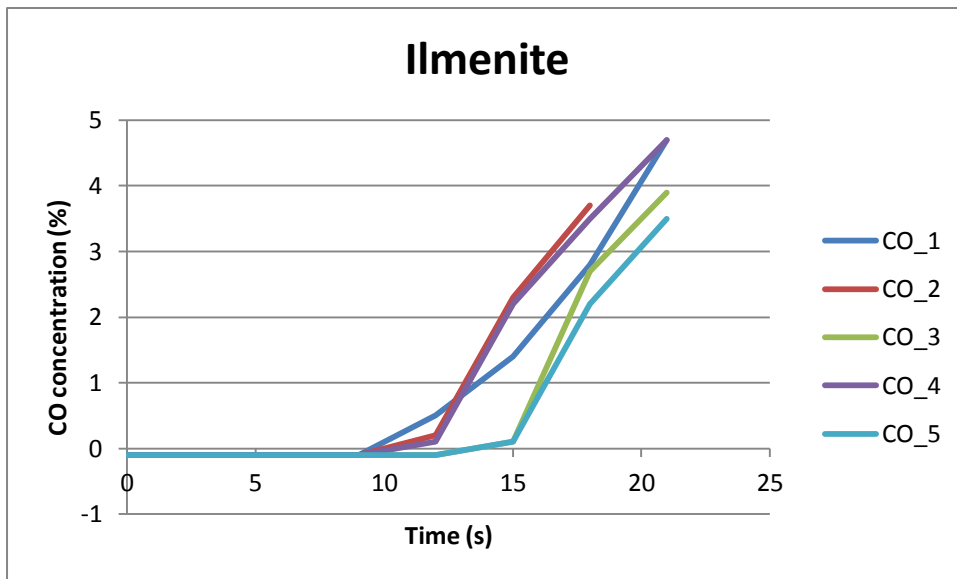
Figure B3. CO-concentration for ilmenite at 800 °C.

Ilmenite was also tested under the same circumstances as the rest of the oxygen carriers and the results can be seen in Figure B3. The performance turned out to be much worse than Mn1 or Mn3.
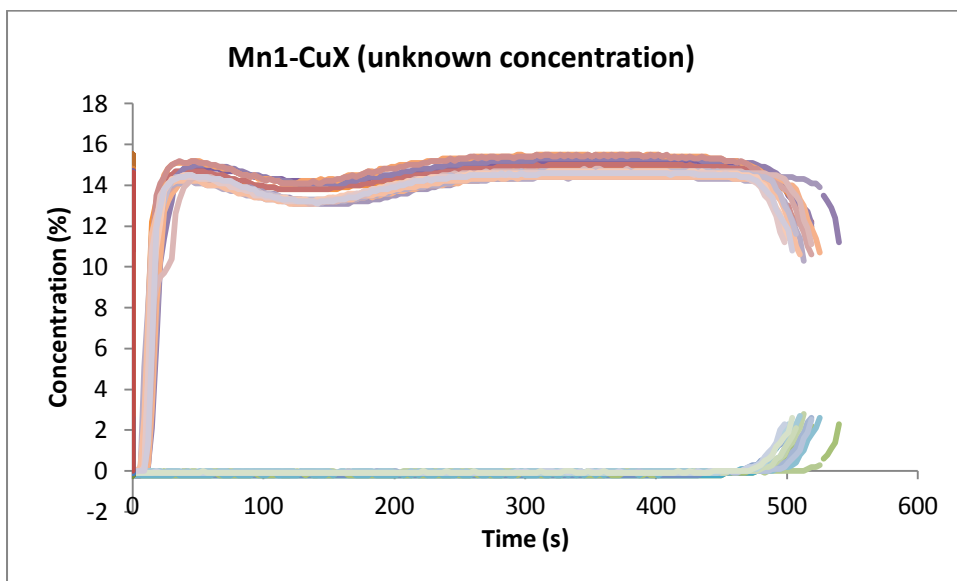

Figure B4. 16 cycles for Mn1-CuX at 800 °C

Fgure B4 shows the CO and CO_2 profiles of a Mn1-sample with unknown copper content, called Mn1-CuX. The concentration was supposed to be 20% but no agglomeration occurred, thus it was probably much lower. The impregnation method used was Method 2. The numbers on the y-axis are the raw uncalibrated values and are therefore not correct.
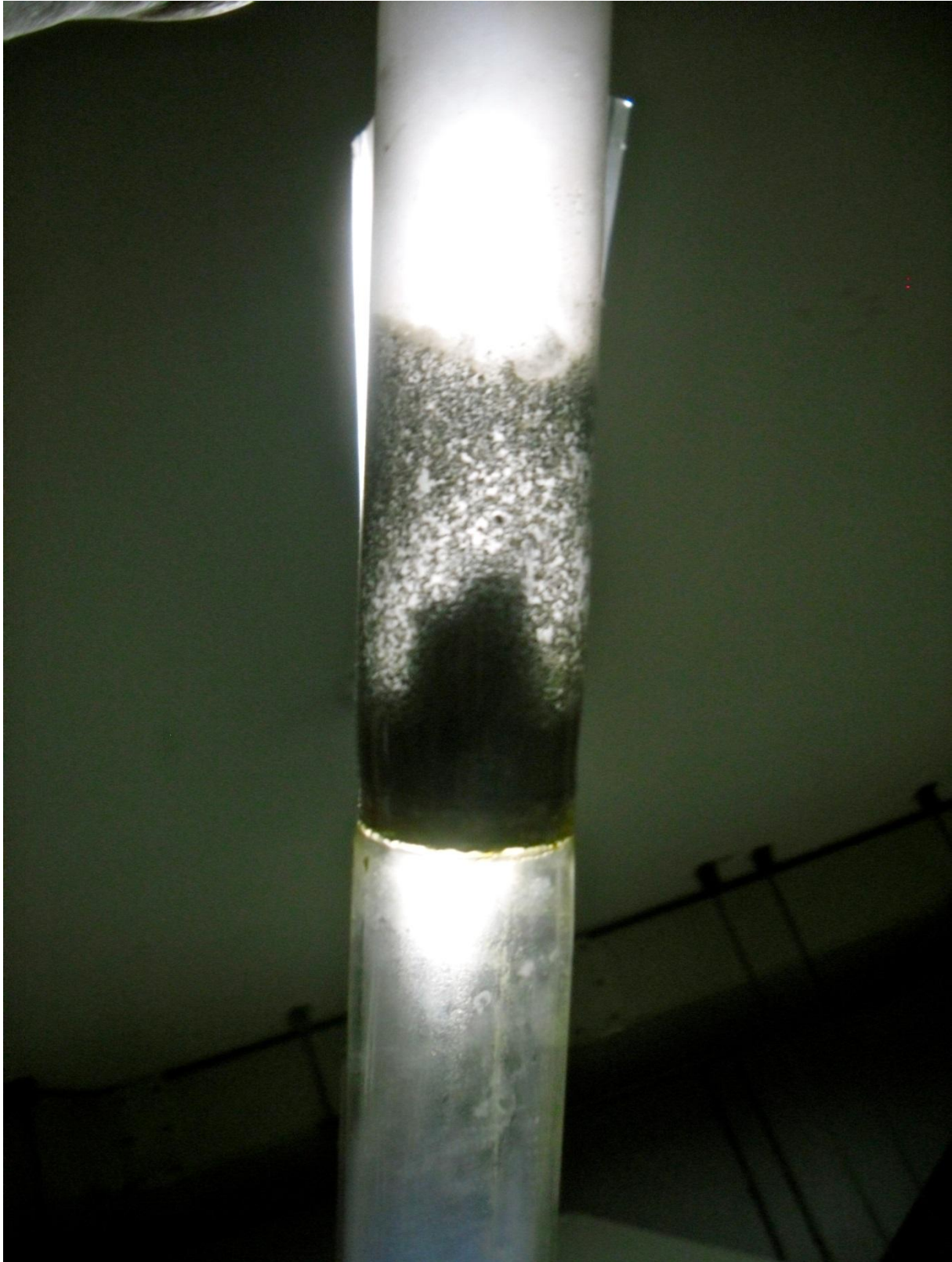
Figure B5. Picture of the reactor after use of Mn1-K (20%).

Figure B5 shows the fluidized bed reactor after the experiment with Mn1-K (20%). Something solid can clearly be seen inside the reactor. This was not possible to get rid of using boiling acid or any other means.