Experimental and Computational Study of Oxygen Carriers in Chemical Looping Combustion

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Abstract

In this paper, the fluidization properties of possible oxygen carriers for Chemical Looping Combustion (CLC) have been studied. Experiments were performed in a cold fluidized bed to study fluidization properties of particles having similar properties as the oxygen carriers. The particles used were Zirconium oxides (ZrO), glass beads and sand. Minimum fluidization velocity, bed expansion and bubble behaviors of the particles have been studied. The Electrical Capacitance Tomography (ECT) was used to analyze bubbles in different planes in the bed of particles. The oxidation properties of ilmenite particles have been studied using Thermal Gravimetric Analysis (TGA). Computational Fluid Dynamic (CFD) numerical method was chosen to model the particle fluidization and simulations were carried out using the commercial CFD software ANSYS Fluent. 2D models were solved for most of the particles and a 3D model was solved for white ZrO. The simulation results are compared with experimental data. The bubble behavior and bed expansion are similar in the experiments and the simulations. However, the simulated results of other fluidization properties are higher than in the experiments due to a wide size distribution in experimental particles that was not possible to consider in the simulations.

Keywords: CLC, fluidized bed, CO_2 capture, combustion, CFD, TGA, ECT,

1 Introduction

Chemical Looping combustion (CLC) is an energy effective CO_2 capturing technology. The technology is based on fuel combustion using two separate reactors: oxidation and reduction reactors. This allows separating CO_2 from other flue gases already during the combustion process. Therefore, the separation does not require additional energy input making the technology more cost effective. The principle of the CLC process is shown in Figure 1. The two reactors presented in the figure are interconnected fluidized bed reactors. One of them is an air reactor. Metal particles (oxygen carriers) are oxidized in this reactor in the presence of air. The particles are then recirculated to the fuel reactor through fast fluidization regime. In fuel reactor, the metal oxide particles provide required oxygen for fuel combustion in the bubbling fluidization regime.

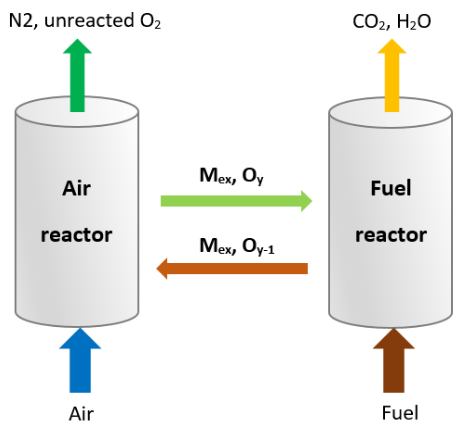

Figure 1: Principles of chemical looping combustion.

In this way, the flue gas coming out of the fuel reactor is only CO_2. The particles coming out of the bubbling fluidized bed fuel reactor are recirculated back to air reactor for further oxidation. The flue gas from both of the reactors are cooled for heat recovery, and almost pure CO_2 is captured. The two fluidized bed reactors maintain a good contact between the gas and solid phases. In addition, CLC does not provide favourable conditions for the formation of *NOx*. Thermal *NOx* is generated at high temperatures. The quantity is significant above 1400°C. In CLC, the air reactor has temperatures in the range of 800°C -1200°C and the temperature in the fuel reactor is in the range of 400°C - 1000°C (Lyngfelt et al, 2001).

The CLC process has been successfully demonstrated both in bench scale fixed-bed reactors and in continuously operated prototype reactors based on interconnected fluidized-bed system in the size range of 0.3–140kW(He Fang, 2009).

2 Oxygen Carriers

The oxygen carrier (metal particles) is oxidized in the air reactor and reduced back to its original state in the fuel reactor. Respective reaction equations for the oxidation and reduction processes are given by Equation 1 and 2.

$$(2n + m)Me_xO_{y-1} + \left(n + \frac{1}{2}m\right) O_2 = (2n + m)Me_xO_y \qquad (1)$$

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

where, Me_xO_{y-1}, Me_xO_y and C_nH_{2m} are metal oxide in its reduced form, metal oxide in its oxidized form and hydrocarbon fuel respectively. The chemical reaction given by Equation 2 shows non-diluted CO_2 as one of the products. The net chemical reaction obtained by adding Equation 1 and 2 give the normal combustion reaction between the oxidizer and fuel.

There has been extensive research on CLC during the last decade with respect to oxygen carrier development, reaction kinetics, reactor design, system efficiencies and prototype testing(He Fang, 2009). Development of a suitable oxygen carrier is one of the challenging task, which determines the commercial success of the technology.

Many researchers have focused on metal oxides in the forms of industrial waste, synthetic materials and naturally occurring materials. A good oxygen carrier should exhibit characteristics such as high reaction rate, high conversion, sufficient oxygen capacity, resistance for attrition, fragmentation, carbon deposition and durability. It should have low cost and should be environmentally friendly. Most of the metal oxides are combined with an inert material (not taking part in the chemical reactions) which acts as a porous support providing a higher surface area for the reaction, and as a binder for increasing mechanical strength and attrition resistance (Labiano et al, 2005). Therefore, the average bulk density of the oxygen carriers are usually lower than that of metals and metal oxides. For example, some metal oxides such as $NiO, CuO, Mn_3O_4, Fe_2O_3$ have been identified as promising candidates, and when they are supported by an inert binder, the carrier particles have shown increased reactivity (Fossdala, 2010; Johansson, 2007).

$AL_2O_3, TiO_2, SiO_2, ZrO$ are recognized as possible inert binders (Naqvi, 2006). Synthetic oxygen carriers are expensive. The naturally occurring oxides such as ilmenite, iron ore and manganese are more suitable because of their low cost. In this paper, we focus on the investigation of the fluidization properties of the possible oxygen carriers in order to minimize gas and solid circulation. For this purpose, we investigated different particles that resemble the approximate properties of oxygen carriers. The experiments were carried out using pressure sensors, ECT and TGA. The simulations were run using the CFD software ANSYS Fluent. One of the promising candidates for oxygen carriers is ilmenite particles. The reactivity of the particles were investigated using TGA analysis and the fluidization properties of the particles were investigated using a validated CFD model.

3 Experimental work

In the CLC plant, air and fuel reactors are fluidized bed reactors for circulating oxygen carrier from one reactor to another. Performance of the reactors is effected by fluidization behaviors of the oxygen carrier used in the reactors. The apparent density of most of the possible oxygen carriers are in between 2000 – 9000 kg/m^3. Therefore, particles with varying density and particle size were used in the experiments to study the fluidization behaviors of the possible oxygen carriers. The particles used in the experimental work are presented in Table 1.

Table 1: Particles used in experimental work.

Particle	Mean particle size[μm]	Density [kg/m^3]
Brown ZrO	709	5850
White ZrO	508	3800
Glass beads	153	2485
Sand	83	2500
Ilmenite	115.83	4580

3.1 Experimental setup and procedure

Experiments were performed in a cold model of a fluidized bed reactor located in the University College of Southeast Norway. The cold model consists of a plastic cylindrical column of 1400 mm height and 84mm inner diameter.

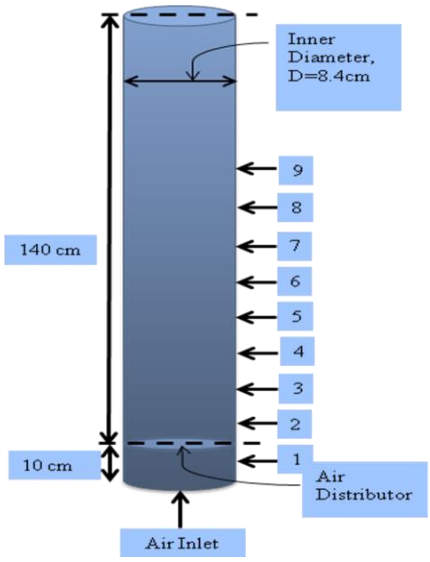

Figure 2: Location of the pressure nodes.

The cylinder has porous metal plate as air distributor at the bottom. A series of pressure nodes are mounted along the height of the cylinder for pressure measurement as shown in Figure 2. The nodes are connected to pressure sensors as well as to a computer with LabVIEW program for pressure reading and airflow measurement. The distance between two pressure nodes is 10mm.

Thermo-Gravimetric Analyzer (TGA) was used to determine the oxidation characteristics of the ilmenite particles when exposed to air at 950°C. The experimental set up is shown in Figure 3. The set up consist of Perkin Elmer TGA7, Perkin Elmer Thermal Analysis Controller TAC7/DX, Thermal Analysis Gas Station MT-0029 and Pyris software.

Figure 3: Experimental set up of TGA.

The TGA analyzer consists of an oven that can reach a temperature of 1000°C, a thermometer, an accurate balance and a platinum pan where the sample is placed. The sample can be purged with nitrogen to prevent it from reacting with oxygen when drying the sample in the oven. When the temperature is high enough, oxygen can be switched on to oxidize the sample.

The water content, organic and inorganic materials, volatile and non-volatile matters in the particle samples can also be analyzed. Approximately 5g ilmenite particles were used for the sample.

According to several investigations, (Ana Cuadrat; Henrik Leion, 2008; Juan Adnez, 2010) ilmenite has shown good results as an oxygen carrier for solid fuels and it has become attractive due to its low cost and abound availability compared to other oxygen carrier particles.

4 Electric Capacitance Tomography

Electrical capacitance tomography (ECT) is used to study bubble behavior of possible oxygen carrier particles. ECT is a novel technique that determines the concentration distribution of a two-phase mixture within a closed cylinder. Using this data the number of bubbles inside a plane of the cylinder can be determined. The ECT sensor consists of two planes and there are 12 electrodes per plane. The electrodes are mounted on the outside of the cylindrical rig as shown in Figure 4.

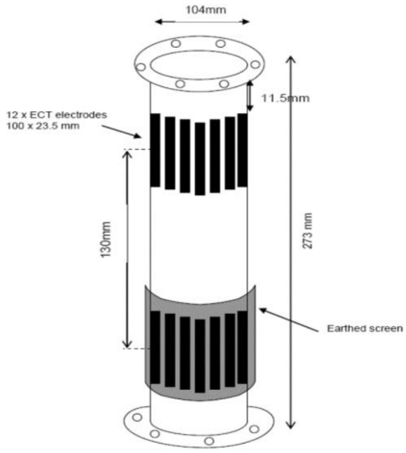

Figure 4: Rig with electrodes for ECT sensors.

5 Computational study

A Computational Fluid Dynamic (CFD) model for the experimental cylinder was prepared for 2D and 3D simulations. The grids for the 2D and 3D simulations are shown in Figure 5. The model was simulated using the CFD simulation software ANSYS Fluent. Simulations were carried out to investigate the minimum fluidization velocities, void fraction variation and bubble behavior. Simulations were run for both a single particle phase and for more than one particle phase. The particle phases were determined by different particle sizes.

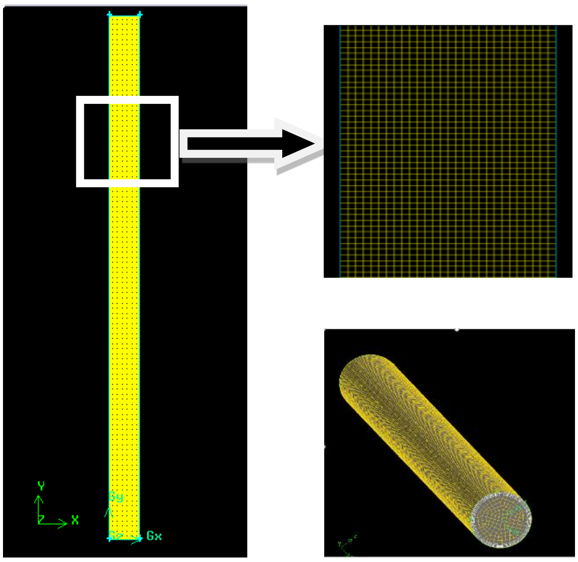

Figure 5: Mesh of experimental rig.

The model parameters used in simulations of the solid phase are shown in Table 2. The drag force between solid and gas phase was modeled using Syamlal & O'Brien's drag model. Five monitors were set in the simulations to record the pressure data. The locations of the monitors in the simulations are similar to the

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location of the pressure nodes in the experimental cylinder. The simulations were performed for maximum 8 seconds.

Table 2: Models used to describe the properties of solid.

Property	Model
Granular viscosity	Syamlal-O'Brien
Granular bulk viscosity	Constant
Frictional viscosity	Schaeffer
Frictional pressure	Based-ktgf
Solid pressure	Ma-ahmadi
Radial distribution	Ma-ahmadi

Simulations were run for all the particles used in experiments (see Table 1). For glass beads, simulations with two particle phases were performed using particle size 120µm as phase 1 and 120µm as phase 2 with corresponding static solid volume fraction of 0.321 and 0.299. For white ZrO, 3D simulations were performed to investigate the bubble formation in different planes along the height of the bed.

6 Results and discussion

6.1 Experimental

A series of experiments were carried out to determine the minimum fluidization velocities for the particles. Figure 6 shows the average pressure drop as a function of superficial air velocity for the four types of particles under consideration. The air velocities are plotted using logarithmic scale in order to cover the wide range of air velocities for these different types of particles.

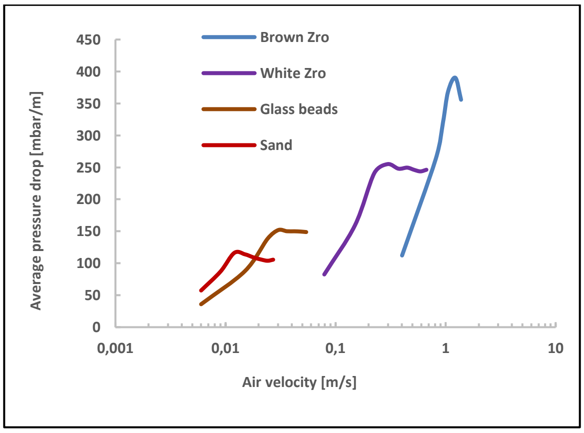

Figure 6: Minimum fluidization velocities.

The fuel reactor in CLC is operated in the bubbling fluidized bed regime while the air reactor operates in fast fluidized regime and should handle about 10 times more air on volume basis (Lyngfelt et al., 2001). Lower minimum fluidization velocity indicates low-pressure drop along the bed height and lower consumption of air in the bed. This makes lower amount of air handling during the CLC process. Particles such as sand, glass beads having lower densities are more suitable for CLC then the particles with higher bulk densities. The experimental observation also shows that the brown ZrO particles has slugging behavior at higher air velocities which is not a desired phenomenon for gas solid mixing.

During the experiment in TGA analyzer, a particle sample of 5g ilmenite was heated in the oven. Figure 7 shows an enlarged view of the oxidation period of the sample.

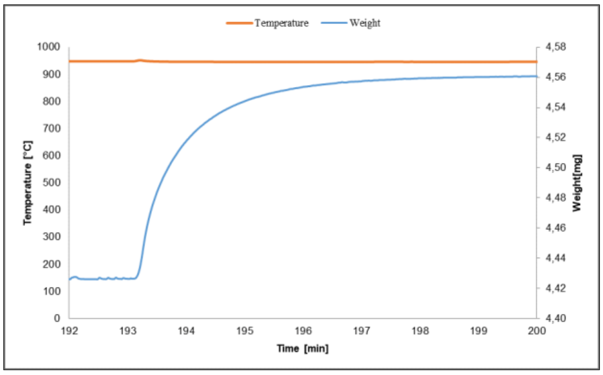

Figure 7: Temperature and weight variation with time in oxidation period for ilmenite.

The sample particles were heated for 30 minutes at the temperature of 25°C and then the temperature was increased from 25°C to 110°C. During the time interval, there was a small weight loss. This is due to volatilization of the moisture. Then the temperature was increased from 110°C to 950°C as shown in Figure 7 and the air flow was turned on. A sharp increase in the weight of ilmenite can be observed due to the oxidation of ilmenite particles in air.

The oxygen transfer capacity of an oxygen carrier determines the number of minimum circulation cycles and the mass of carrier required in the reactor.

$$R_0 = \frac{m_{ox} - m_{red}}{m_{ox}} \qquad (3)$$

where R_0 is mass fraction of oxygen in the carrier, m_{red} is the mass in the reduced form and m_{ox} is the mass in the oxidized form. In the calculation, it is assumed that the weight prior the oxidation period is equal to the weight of the sample in reduced form and weight after the oxidation period is equal to the weight of the sample in oxidized form. The experimental data (see Figure 7) is used to calculate the transfer capacity.

$$R_0 = \frac{4.56 - 4.43}{4.56} = 0.029$$

The experimental results show that the ilmenite entering the fuel reactor contains 2.3% of its mass in the form of oxygen. Reduced ilmenite is in the form $FeTiO_3$ and the oxidized carrier is in the form $Fe_2TiO_5 + TiO_2$ (Henrik Leion, 2008).

Glass beads with size distribution from 100 to 200 µm were used in the experiment with ECT to measure bubble distribution at the two different planes of the cylindrical rig and to determine minimum fluidization velocity. The number of bubbles increases with the increasing air velocity as shown in Figure 8.

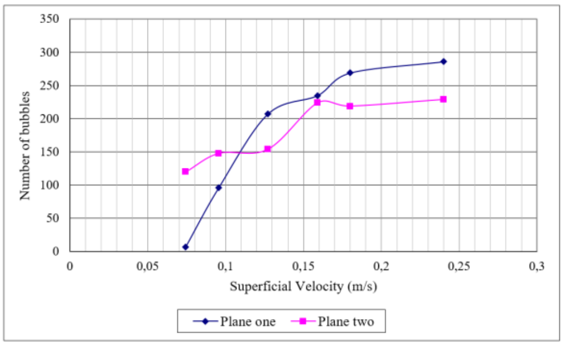

Figure 8: Number of bubbles variation with superficial air velocity.

The number of bubbles are higher in plane one than plane two. The plane one is in the lower part of the bed and the plane two is the upper part of the bed. The results show that the number of bubbles are greater in the lower part of the bed than the upper part.

6.2 Simulations

A series of simulations were carried out to compare and validate the CFD model prediction with experimental results. The simulations are used to study minimum fluidization velocities, void fractions and bubble behaviors in the bed of the particles. There was some difficulties to use ilmenite particles in the experimental fluidized bed rig due to excess moisture content in the sample. Therefore, the validated CFD model has been helpful to determine fluidization properties for ilmenite particles computationally.

The simulation results for average pressure drops as a function of air velocities are compared against experimental results for white ZrO in Figure 9. The packing limit in this case is 0.6.

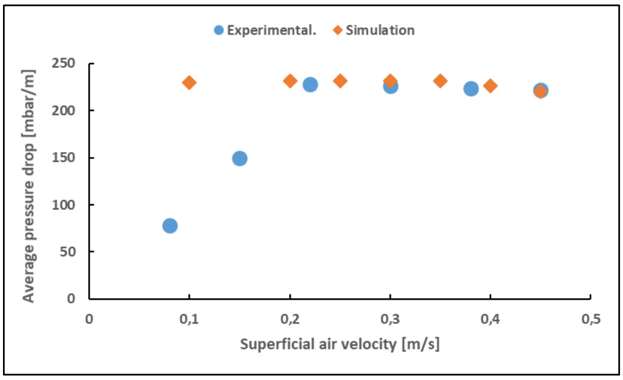

Figure 9: Pressure drop vs. air velocity for white ZrO. Static solid volume fraction 0.6.

The comparison of results show that the experimental and computational minimum fluidization velocities are near to each other, but the computational value is slightly higher than experimental. The results for the other particles show good agreement with experimental results.

3D simulations were carried out to investigate the bubble behavior of the ZrO particles further. Figure 10 shows the bubble in two different planes, located at a distance of 0.2m from each other along the height of the bed. The solid volume fraction at the upper plane (p5) shows that the bed is fluidized with formation of some bubbles at the upper part of the bed. The bubble size is increased with increasing simulation time.

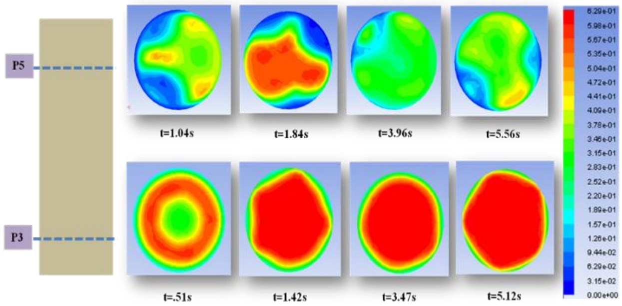

Figure 10: Bubble behavior of white ZrO in 3D simulation at air velocity of 0.4 m/s.

The similarity of minimum fluidization velocity and the bubble behavior between the experimental and the simulation results allows to move further only with simulations to study the fluidization behavior of some oxygen carriers, which could be the good candidates.

The CFD model was used to simulate the fluidization behavior of the ilmenite particles. The computational results of the bubble behavior of the ilmenite particles are shown in Figure 11.

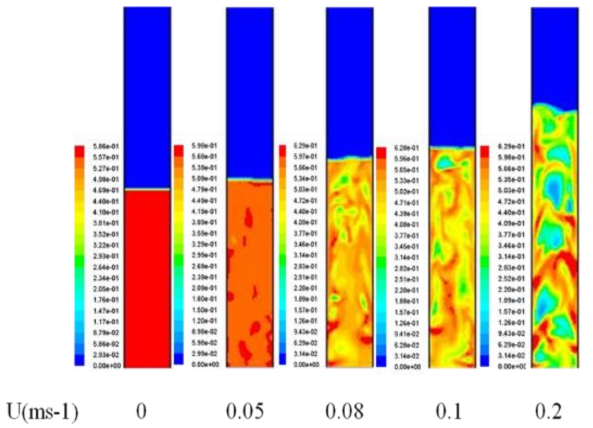

Figure 11: Contours of solid volume fraction for Ilmenite.

The minimum fluidization velocity for the particles is less than 0.05 m/s. Bubble formation and increase in bubble size occurs at the air velocity between 0.08 m/s to 0.2 m/s with significant bed expansion. The bubble formation at the velocity of 0.2 m/s shows uniform bubble distribution along the height of the bed. This indicates that the ilmenite particles can have good gas-solid mixing properties in fluidized bed reactors. This makes ilmenite an even more suitable candidate as oxygen carrier for the chemical looping combustion process.

7 Conclusion

The fluidization properties of four types of particles have been studied using an experimental cold fluidized bed cylinder with pressure sensors. The density and the size of the particles resemble possible oxygen carriers for CLC. The particles studied in fluidized bed cylinder were sand, glass beads, white ZrO and brown ZrO. The minimum fluidization velocity is lowest for sand and highest for brown ZrO.

Tests using Electrical Capacitance Tomography have been performed for glass beads to study the bubble behavior. The number of bubbles in the lower part of the bed is higher than in the upper part of the bed.

Thermo Gravitametric Analysis was performed to study oxidation characteristics of ilmenite. Ilmenite particles could not be used in the fluidized bed study because of the high moisture content in sample. The oxygen carrying capacity of the particles have been calculated using experimental results.

Computational study (2D simulations) were run using the simulation software ANSYS Fluent. 3D simulations were carried out for white ZrO. Simulations with two particle phases were carried out for glass beads.

Minimum fluidization velocities are determined by using both experimental and computational results. In the experiments, the calculation is based on the pressure drop measurements. The computational results for the minimum fluidization velocities are higher than the experimental results due to neglecting the effects of particle size distribution and particle shape in the simulations. Simulations with two particle phases give results closer to the experimental results, but it is more time consuming. The 3D simulations resulted in nearly the same minimum fluidization velocity as the 2D simulations for white ZrO. The reason may be that: although the 3D simulations are more accurate, these simulations do not account for the particle size distribution. The bed expansion are observed both in experiment and simulation and they show closer results according to the Geldart classification for particles.

References

J. Adnez, A. Cuadrat., A. Abad, P. Gayn. Ilmenite activation during Consecutive Redox Cycles in Chemical-Looping Combustion. *Energy & Fuels*.24(2):1402-1413,2010. DOI: 10.1021/ef900856d A. Cuadrat, A. Abad, J. Adánez, L.F. de Diego, F. García-Labiano, P. Gayán. Behaviour of Ilmenite as Oxygen Carrier in Chemical-Looping Combustion. *Fuel Processing Technology*. 94(1): 101-112, 2012. https://doi.org/10.1016/j.fuproc.2011.10.020

H. Fang, L. Haibin, and Z. Zengli. Advancements in Development of Chemical-Looping Combustion: A Review. *International Journal of Chemical Engineering, 2009*. http://dx.doi.org/10.1155/2009/710515

A. Fossdal, E. Bakken, B.A.Øye, C. Schøninga, I. Kaus, T.Mokkelbost, Y. Larringb. Study of inexpensive oxygen carriers for chemical looping combustion. *International Journal of Greenhouse Gas Control*.5(3) 2011. https://doi.org/10.1016/j.ijggc.2010.08.001

M. Johansson. Screening of oxygen-carrier particles based on iron-, manganese-,copper- and nickel oxides for use in chemical-looping technologies. (Phd thesis), Chalmers University of Technology, 2007.

F. G. Labiano, L. F. de Diego, J. Adánez, A. Abad, and P.Gayán. Temperature variations in the oxygen carrier particles during their reduction and oxidation in a chemical-looping combustion system. *Chemical Engineering Science*, *60*(3):851-862,2005. https://doi.org/10.1016/j.ces.2004.09.049

H. Leion, A. Lyngfelt, M. Johansson, E. Jerndal, T. Mattisson. The use of ilmenite as an oxygen carrier in chemical-looping combustion. *Chemical Engineering Research and Design*.86(9):1017–1026.2008. https://doi.org/10.1016/j.cherd.2008.03.019

A. Lyngfelt, B.Leckner, and T. Mattisson. A fluidized-bed combustion process with inherent CO2 separation; application of chemical-looping combustion. *Chemical Engineering Science*, *56*(10): 3101-3113,2001 doi:https://doi.org/10.1016/S0009-2509(01)00007-0

R. Naqvi. Overview of CLC Activities Outside ENCAP. Paper presented at the ENCAP Seminar on CLC. 2006.