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Influence of limestone addition in a 10 kW_{th} Chemical-Looping Combustion unit operated with pet coke

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ABSTRACT. Ilmenite, a natural mineral composed of FeTiO₃, is a low cost material suitable as oxygencarrier for Chemical-Looping Combustion (CLC) with solid fuels. One option when using the CLC technology with solid fuels is to introduce the fuel directly into the fuel-reactor. There the fuel is gasified and volatiles and gasification products react with the oxygen-carrier. In this study the influence of limestone addition to ilmenite as oxygen-carrier was tested in a continuous 10 kW_{th} CLC pilot for solid fuels. The fuel fed was a petcoke and the gasifying agent was steam. Tests with an ilmenitelimestone mixture as bed material were performed, and also tests using only ilmenite as bed material were carried out for comparison. Global solids circulation was varied as it is an important operational parameter, which determines the solid fuel residence time. The experiments were made at two fuel-reactor temperatures: 950°C and 1000°C. Generally, higher residence time of the fuel and higher temperature increased both gasification and combustion efficiencies. This was seen for both with and without limestone addition. The addition of limestone, gave a significant improvement of gas conversion at 950°C, which could be explained by lime catalyzing the water-gas shift reaction. Moreover, the presence of limestone significantly increased the char conversion both at 950°C and 1000°C.

Keywords: Chemical-looping combustion (CLC), Oxygen-carrier, Ilmenite, Limestone, Carbon capture, Coal.

INTRODUCTION

It is widely accepted today that carbon dioxide coming from fossil fuel combustion is the most important greenhouse gas contributing to global warming. One of the options to mitigate the anthropogenic greenhouse effect is the development of capture and storage of CO_2 emitted from large point sources such as power plants. Chemical-Looping Combustion (CLC) is nowadays an attractive option, because it is a combustion process with inherent separation of CO_2 that carries out the CO_2 capture at a low cost^{1,2} without energy losses.³

CLC involves the use of an oxygen-carrier, which transfers oxygen from air to the fuel avoiding the direct contact between them. The most typical CLC system consists of two interconnected fluidized bed reactors, designated as air- and fuel-reactors. In the fuel-reactor, the fuel is oxidized by a metal oxide in its oxidized form (Me_xO_y) that is reduced to its reduced form (Me_xO_{y-1}). The exit gas from the fuel-reactor contains, ideally, only CO₂ and H₂O. After water condensation, almost pure CO₂ can be obtained with little energy lost for component separation. The net chemical reaction is the same as in usual combustion with the same combustion heat released.

One option for the use of CLC with coal as fuel is the direct combustion, where coal is physically mixed with the oxygen-carrier in the fuel-reactor and the carrier reacts with the gas product of the pyrolysis and gasification of coal. Equations (1) to (5) express generally the reactions in the fuel-reactor. (3) to (5) are the oxygen-carrier reduction reactions with the main products of coal devolatilization and gasification. The reduced oxide is further transferred into the air-reactor where it is re-oxidized with air, following reaction (6).

$$\text{Coal} \rightarrow \text{Volatiles} + \text{Char}$$
 (1)

 $Char + H_2O \rightarrow CO + H_2 \tag{2}$

$$CH_4 + 4 Me_xO_y \rightarrow CO_2 + 2 H_2O + 4 Me_xO_{y-1}$$
 (3)

$$H_2 + Me_xO_y \rightarrow H_2O + Me_xO_{y-1} \tag{4}$$

$$CO + Me_xO_y \rightarrow CO_2 + Me_xO_{y-1}$$
(5)

$$Me_{x}O_{y-1} + \frac{1}{2}O_{2} \rightarrow Me_{x}O_{y}$$
(6)

For the good performance of this process and in order to achieve high combustion efficiencies, it is essential to get intimate contact between the oxygen-carrier particles and the volatile matter and gasification products. As part of the carrier will be removed together with the removal of solid fuel ashes, optimization of the system must be done to maximize ash separation and minimize the amount of carrier that will be extracted together with the ash removal. Furthermore, since the gasification process is the limiting step in the fuel-reactor,⁴ the stream of solids going from the fuel-reactor to the air-reactor could contain some unconverted char together with oxygen-carrier, which would lower the carbon capture. This could be avoided by a carbon stripper that separates char particles so that they are reintroduced to the fuel-reactor, thereby increasing the fuel residence time in fuel-reactor.

Suitable oxygen-carriers for a CLC process must have high selectivity towards CO₂ and H₂O, enough oxygen transport capacity, high reactivity during many reduction and oxidation cycles, high mechanical strength, attrition resistance and no agglomeration tendency.⁵ Besides, an environmentally friendly and low cost oxygen-carrier is preferable for use with solid fuels, because some oxygen-carrier will be lost

together with coal ash, which has to be removed from the reactor to avoid accumulation of ash in the system. Natural minerals such as ilmenite are therefore very interesting. Natural ilmenite is mainly composed of FeTiO₃, which corresponds to the most reduced state, when used as oxygen carrier. As for the reactivity of ilmenite with H₂, CO and CH₄, i.e. the main devolatilization and gasification products, ilmenite gave high conversion of CO and H₂ but moderate conversion of CH₄, similar to synthetic based oxygen-carriers⁶ and among the best ores or industrial residues tested.^{7,8} In addition, there is a gain in reactivity in reduction as well as in oxidation with the number of cycles and on the whole, ilmenite has shown to have good reaction rate and properties.^{9,10} Batch testing of ilmenite with coal and coal char showed that the oxygen-carrier presence increases the char gasification rate¹¹ and that the gasification rate, i.e. the char reactivity, is highly dependent on the parent fuel.¹² It is also possible to carry out this technology with CO₂ as well as with steam as fluidizing and gasification agents,¹³ although CO₂ gasification is much slower. In batch testing, as well as in continuous testing, the gasification as well as combustion efficiencies were shown to be very dependent on temperature.¹⁴ To date, continuous testing with ilmenite as oxygen-carrier has been performed with a Mexican petcoke,^{15,16} South African coal¹⁷ and Colombian bituminous coal.¹⁸

Some catalytic effect seems to occur as shown in batch reactor tests done with ilmenite as oxygencarrier and addition of calcined and sulfated limestone.¹⁹ In these experiments, it was clear that calcined limestone addition had some beneficial effect on the char conversion rate. And more important, the conversion of the gas was greatly enhanced, being unconverted $CO + CH_4$ was almost halved. Sulfated limestone particles showed a greater improvement on char conversion rate during the first cycles, but after a dozen cycles, the benefits disappeared and seemed to stabilize at a level corresponding to ilmenite only. However, the gas conversion when adding sulfated lime was similar to the gas conversion obtained when adding unsulfated limestone and it was independent on the cycle. Also, it was observed that the beneficial effect on gas conversion was seen already in the very first cycle with unsulfated lime, i.e. before any sulfate could have formed. Thus, it seems that the beneficial effect on gas conversion is largely independent on the degree of sulfation of the lime. Tests with H_2 , CO and syngas clearly indicated that the positive effect of lime could be attributed to the water-gas shift reaction, which lowers CO and raises H_2 concentration. This improves the gas conversion as H_2 is much more reactive than CO.

At high temperatures limestone (CaCO₃) can react with the released SO₂ and/or H₂S, and thereby CaSO₄ and/or CaS are formed.^{20,21} Also calcined lime (CaO) can be the reacting compound depending on the operating conditions.²² At reducing conditions CaS is stable whereas CaSO₄ is stable at oxidizing conditions. CaO is stable in between these regions, and therefore SO₂ may be released during shifts between oxidizing and reducing conditions.²⁰ At the temperatures of interest for the CLC process, the sulfidation has shown to be relatively fast for both CaO and CaCO₃.^{21,23,24} The reactions are likely affected by the sorbent characteristics.²⁵ Furthermore, the CaS formed can be expected to be oxidized to CaSO₄ in the air-reactor. Another interesting factor is that CaSO₄ formation could lead to enhanced oxygen transport, as it can act as oxygen-carrier in its reduction to CaS with much higher oxygen transfer capacity as compared to other proposed materials.^{26,27}

The aim of this work is to investigate the effect of using limestone particles as additive to ilmenite as oxygen-carrier in solid-fuel CLC, based on the positive effect of limestone addition seen in batch experiments on the CLC performance. Both catalytic effect and possible oxygen transport capacity of CaSO₄ formed from limestone were analyzed in a 10 kW_{th} CLC pilot plant.

EXPERIMENTAL

Bed material. A mixture limestone-ilmenite was used as bed material, but first, experiments were performed with 100% ilmenite as oxygen-carrier to have a base case for comparison. In this base case the total inventory in the system was 15 kg ilmenite, and the fuel-reactor inventory was about 6 kg. 4 kg limestone was later added to the CLC system.

Ilmenite is a common mineral found in metamorphic and igneous rocks. It is a cheap material, which is an advantage for its use in CLC with solid fuels, as fuel ash may significantly reduce the lifetime of the oxygen-carrier. The ilmenite used in this work is a concentrate from a natural ore from Norway with a purity of 94.3%. In the fully oxidized ilmenite, iron is in form of Fe³⁺, either as pseudobrookite (Fe₂TiO₅) or as free hematite (Fe₂O₃). In the CLC process Fe₂TiO₅ and Fe₂O₃ are reduced to ilmenite (FeTiO₃) and magnetite (Fe₃O₄), respectively. Thus, the oxygen transport capacity of ilmenite, $R_{O,ilm}$, defined as the oxygen transport capacity useful for CLC, is calculated as:

$$R_{O,ilm} = \frac{m_o - m_r}{m_o} \tag{7}$$

where m_o is the mass of the most oxidized form of the oxygen-carrier, and m_r is the mass in the reduced form. For this CLC process with solid fuels, the oxygen transport capacity of ilmenite was measured to be 3.9% by TGA analysis, being FeTiO₃ and Fe₃O₄ the reduced species. The theoretical maximum if all Fe³⁺ was reduced to Fe⁺² is 5%. The porosity was measured to be 13.5% through Hg intrusion with a Quantachrome PoreMaster 33 porosimeter. The bulk density was about 2100 kg/m³. The particle size for ilmenite was 90-250 µm.

After several redox cycles the ilmenite undergoes an activation process.^{iError! No se encuentra el origen de la referencia.} The ilmenite in this study had previously been investigated in continuous operation and batch testing with solid fuels.^{12,14-18,28,29} TGA analysis of a sample after the tests of this study was done to check the reactivity and the ilmenite was shown to have the same reaction rate as a fully activated ilmenite sample.¹⁰

To the 15 kg of ilmenite, 4 kg of a Mexican limestone which is used in the Tamuin Power Plant were added. The density was about 1900 kg/m³ and the particle size 90-200 μ m. Figure 1 shows SEM images of the general overview of a particle and a detail of the cross section inside the particles for the used limestone and ilmenite particles.

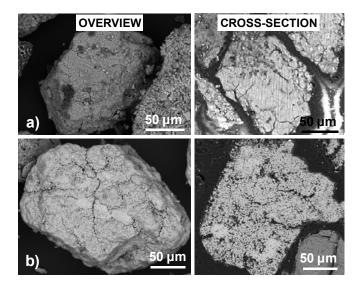


Figure 1. SEM images of the general overview of a particle and a detail of the cross section inside the particles for a) limestone particle and b) ilmenite.

Solid fuel. The fuel used in these experiments was Mexican petcoke. The proximate and ultimate analyses are given in Table 1.

С	81.3 %	Moisture	8.0 %		
Н	2.9 %	Volatile matter	9.9 %		
Ν	0.9 %	Fixed carbon	81.6 %		
S	6.0 %	Ash	0.5 %		
0	0.4 %				
Lower Heating Value: 31750 kJ/kg					

This fuel has previously been tested in this plant. Prior experience from continuous and batch tests has shown that a drawback of this plant is that the fuel feed is done by means of a fuel chute that introduces the fuel above the bed and a rather high fraction of the reducing gases escapes the fuel-reactor unconverted because they do not get in contact with the oxygen-carrier. These gases are mainly volatiles, but can also be syngas, i.e. products from the char gasification. As volatile content of petcoke is small this problem is reduced. Moreover, sulfur fraction in petcoke is quite high compared to normal coals. This low-volatile and high-sulfur fuel was chosen to be able to better see the fate of sulfur and any possible interaction with limestone. This fuel is not so reactive¹¹ with a low char gasification rate.¹²

Experimental setup. The 10 kW_{th} unit used is designed for CLC with solid fuels and located at Chalmers University of Technology. Figure 2 shows a scheme of the whole pilot plant. The reactor system consists of two interconnected fluidized beds: (a) the fuel-reactor (FR), where the fuel is gasified with steam and volatile matter and gasification products are oxidized by the oxygen-carrier, and (b) the air-reactor (AR), where the oxygen-carrier particles are oxidized. The regenerated oxidized particles are led through (c) a riser above the air-reactor, which ends up in (d) a cyclone that brings the solids flow back to the fuel-reactor. The gas velocity in the air-reactor and riser provides the driving force for particle circulation. There are also two loop-seals fluidized by nitrogen placed after the cyclone (d) and in the connection leading from fuel- to air-reactor. The task of these upper and lower loop-seals is to eliminate gas leakages between the reactors. Represented in Figure 2 are also the particle filters, as well as the fuel feeding, steam production unit and a water seal used to collect condensate and to balance the pressure in the fuel-reactor. Because of its small size, the system is not self-supporting in energy and it is therefore enclosed in an oven that keeps and controls the temperature.

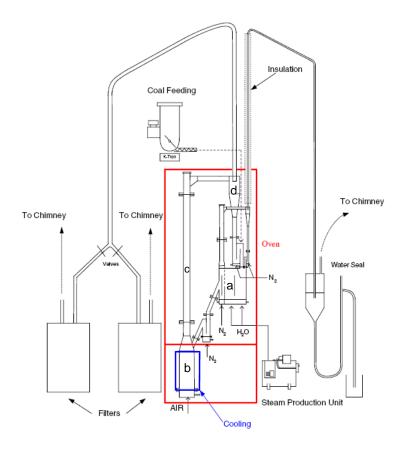


Figure 2. Pilot plant system: (a) Fuel-reactor, (b) Air-reactor, (c) Riser, and (d) Cyclone.

Figure 3 shows the layout of the fuel-reactor, which has three main sections: (1) a low-velocity section, which is operated as a bubbling bed. This chamber is divided into two parts separated by a wall with an opening at the bottom, through which the particles are forced; (2) a carbon-stripper with the purpose to separate char particles from the solids flow going from the fuel-reactor to the air-reactor; and (3) a high velocity section that gives the opportunity to increase the flow in the internal loop by increasing the elutriation of the oxygen-carrier into the riser. This option was not used in these tests.

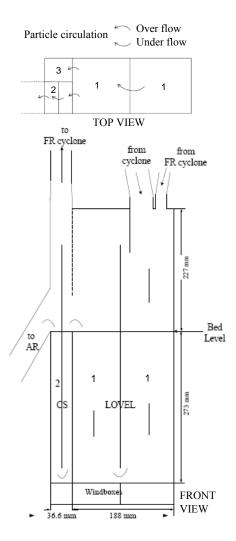


Figure 3. Main layout of the fuel-reactor, top view and front view, with the particle circulation directions, (1) the low velocity part, (2) the carbon-stripper and (3) the high velocity part.

The low-velocity section is fluidized with steam and in this bed all reactions related to char are expected to take place, that is, fuel gasification and reaction of the gasification products with the oxygen-carrier. However, as noted above, most of the volatiles are released above the bed and have little contact with the oxygen-carrier. The solids inventory in the low-velocity section is around 6 kg. A detailed description of the 10 kW pilot is given elsewhere.¹⁷

This 10 kW_{th} pilot has been already used for approximately 90 h of continuous operation with various solid fuels and ilmenite as oxygen-carrier.¹⁴⁻¹⁷

The pilot is equipped with 40 pressure transducers to monitor the pressures. The temperatures in the air-reactor, fuel-reactor and the air-reactor cyclone are also measured. Gas sampling outlets are located

on both chimneys. At the air-reactor outlet concentrations of CO, CO₂, and O₂ are measured online and at the fuel-reactor outlet concentrations of CO, CO₂, O₂, CH₄ and SO₂ are measured online with Sick Maihak Sidor analyzers and registered. The H₂ concentration could also be measured online with a Rosemount NGA2000 analyzer. Bag samples of the product gas flow from the fuel-reactor were also taken and analyzed with a gas chromatograph Varian Micro-GC CP4900; this was used to confirm the results from the other analyzers. The fluidizing gas flows are controlled and monitored by mass flow controllers. The steam flow to the low-velocity section is controlled by a steam generator.

The flows for the fuel-reactor and the loops seals were kept constant during all experiments and are shown in Table 2. F_{LOVEL} is the steam flow in the low-velocity section in the fuel-reactor with a value of 21 L_N /min, which corresponds to a gas stay time in bed of 2.9-3.0 seconds at the temperatures tested. F_{CS} is the N₂ flow in the carbon-stripper, F_{HIVEL} is the N₂ flow in the high-velocity section in the fuel-reactor, F_{HILS} is the N₂ flow in the higher loop-seal, F_{LOLS} is the N₂ flow in the lower loop-seal and F_{FRLS} is the N₂ flow in the small fuel-reactor loop-seal.

Table 2. Flows for the fuel-reactor and the loop-seals, in L_N /min.

F _{LOVEL} ((H ₂ O)	$F_{CS}(N_2)$	$F_{HIVEL}(N_2)$	$F_{HILS}(N_2)$	$F_{LOLS}(N_2)$	$F_{FRLS}(N_2)$
21		6	2	4	4	2

DATA EVALUATION

The purpose of the data evaluation is to assess the performance of the process. Since not all the fuel fed is converted to gaseous compounds, all calculations are made with the fuel fraction that is actually measured to be converted to gas. This fraction is expressed by the solid fuel conversion, η_{SF} . The carbon flow of the introduced effective coal is calculated as the sum of all carbon containing flows exiting the system: $F_{CO2,FR}$, $F_{CO,FR}$, $F_{CH4,FR}$ are the flows of CO₂, CO and CH₄, respectively, in the fuel-reactor product gas and $F_{CO2,AR}$ is the CO₂ flow from the air-reactor. $F_{C,fuel,in}$ is the carbon flow contained in the fuel feeding, $\dot{m}_{fuel,in}$, and [C]_{fuel} the mass based carbon content in fuel given by the ultimate analysis.

$$\eta_{\rm SF} = \frac{F_{\rm C,fuel,eff}}{F_{\rm C,fuel,in}} = \frac{F_{\rm CO2,FR} + F_{\rm CO,FR} + F_{\rm CH4,FR} + F_{\rm CO2,AR}}{\dot{m}_{\rm fuel,in} \cdot [C]_{\rm fuel} \cdot 1000/12}$$
(8)

The flow of each species in the fuel- and air-reactor is calculated as product of the fraction in the outgoing gas and the total fuel- and air-reactor flow, both on dry basis. Sulfur containing species and higher hydrocarbons are omitted. The total N_2 flow introduced in the fuel-reactor is the sum of the flows to the high-velocity section of the fuel-reactor and small fuel-reactor loop-seal and about 50% of the fluidizing N_2 to the upper and lower loop-seals. The N_2 to the air-reactor is sum of the N_2 in the air flow introduced in the air-reactor and half of the N_2 fluidizing the upper and lower loop-seals.

In every combustion process, to ensure enough oxygen availability is fundamental for the good performance of the process. In the particular case of this technology, this availability can be evaluated by means of the oxygen-carrier to fuel ratio, OC/Fuel, which is the amount of oxygen that can be supplied by the oxygen-carrier divided by the oxygen demand of the effective fuel feed. It depends on the oxygen-carrier circulation rate, which is given by the operation conditions and configuration of the riser in a Circulating Fluidized Bed system. For the OC/Fuel calculation only ilmenite is taken into account as the oxygen-carrier.

$$OC/Fuel = \frac{O_{2 \text{ supplied by OC}}}{O_{2 \text{ demand, fuel in FR}}} = \frac{F_{OC} \cdot R_{O,ilm} \cdot 1000/32}{\Phi_{O} \cdot (F_{CH4,FR} + F_{CO,FR} + F_{CO2,FR} + F_{CO2,AR})}$$
(9)

 Φ_0 is the oxygen carbon ratio, that is, moles of O_2 needed to fully oxidize a mass of fuel containing one mole of carbon. For this fuel Φ_0 is 1.13 moles O_2 /mole C. F_{OC} is the solids circulation rate, which can be expressed as the oxygen-carrier inventory in the fuel-reactor, m_{oc} , which was around 6 kg in this pilot for ilmenite, divided by the mean oxygen-carrier residence time, $t_{r,OC}$.

$$F_{\rm oc} = m_{\rm oc} / t_{\rm r,oc} \tag{10}$$

Although $t_{r,OC}$ is not measured in this plant, it is approximately calculated using the correlations established for this plant by Markström et al.³⁰, that use the pressure drop registered in the riser, the air-reactor total exit flow and the air-reactor temperature.

The efficiencies that indicate the performance of the process, in gasification as well for the combustion reactions, are defined as follows. The carbon capture efficiency, η_{CC} , is the ratio of the carbon that is converted to gas in the fuel-reactor to the effective carbon flow. This efficiency reflects unconverted char reaching the air-reactor and being burnt to CO₂.

$$\eta_{\rm CC} = \frac{F_{\rm CO2,FR} + F_{\rm CO,FR} + F_{\rm CH4,FR}}{F_{\rm CO2,FR} + F_{\rm CO4,FR} + F_{\rm CO2,AR}}$$
(11)

A parameter that can be also used to evaluate the carbon capture efficiency via analysis of the air-reactor is the oxide oxygen fraction, η_{OO} , defined as the amount of oxygen used to re-oxidize the oxygen-carrier in the air-reactor divided by the total amount of oxygen consumed in the air-reactor, which is the oxygen to oxidize the oxygen-carrier and the unreacted char coming from the fuel-reactor. $F_{AR in}$ is the air flow introduced in the air-reactor and $y_{CO_{2AR}}$ and $y_{O_{2AR}}$ are the CO₂ and O₂ fractions in the air-reactor.

$$\eta_{00} = \frac{F_{AR in} \cdot 0.21 - F_{AR} \cdot (y_{CO_{2,AR}} + y_{O_{2,AR}})}{F_{AR in} \cdot 0.21 - F_{AR} \cdot y_{O_{2,AR}}}$$
(12)

For Φ_0 equal to 1, η_{CC} should be equal to η_{00} under steady state. In practice the actual value of the O_2/C ratio, $\Phi_{O,act}$, is considerably lower than the theoretical of 1.13, because of the incomplete oxidation in the fuel-reactor. Therefore η_{00} should also be lower than η_{CC} . η_{00} has one important advantage as it can be calculated using only gas concentration measurements, and does not include any uncertainties arising from the calculation of the gas flows.

To evaluate the performance of the system towards combustion, the parameter oxygen demand, Ω_{OD} , is used. It evaluates the need of a later oxygen polishing step and it is the fraction of O₂ lacking to achieve full combustion of the fuel-reactor produced gas, see equation (13). The advantage of Ω_{OD} is that it does not include any flows, thus it is only dependent on gas concentrations and not on flows.

$$\Omega_{\rm OD} = \frac{O_{2\,\text{demand gases FR}}}{O_{2\,\text{demand,fuel in FR}}} = \frac{2 \cdot F_{\rm CH4,FR} + 0.5 \cdot F_{\rm H2,FR} + 0.5 \cdot F_{\rm CO,FR}}{\Phi_{\rm O} \cdot (F_{\rm CH4,FR} + F_{\rm CO,FR} + F_{\rm CO2,FR})} = \frac{2 \cdot y_{\rm CH4,FR} + 0.5 \cdot y_{\rm H2,FR} + 0.5 \cdot y_{\rm CO,FR}}{\Phi_{\rm O} \cdot (y_{\rm CH4,FR} + y_{\rm CO,FR} + y_{\rm CO2,FR})}$$
(13)

13

The reaction rate of the materials used in the reduction reaction was evaluated with TGA by means of the mass-based conversion degree, ω , defined as:

$$\omega = \frac{m}{m_o} \tag{14}$$

Being *m* the instantaneous mass of the material acting as oxygen-carrier and m_o the initial mass of fully oxidized material.

RESULTS AND DISCUSSION

The experiments were performed at two temperatures of the fuel-reactor: 950°C and 1000°C. The temperature in the air-reactor was within the range 820-980°C. The fuel flow was either 479 g/h or 1053 g/h, which corresponds to a fuel power of 4.2 and 9.3 kW_{th}. The particle recirculation between reactors was controlled by the air flow to the air-reactor, which was varied from 155 to 190 L_N /min. Operation under various conditions was performed during 8 hours, of which 4 h with the mixture of ilmenite and limestone and 4 h with only ilmenite. All the conditions tested were maintained for 30 to 60 minutes.

Continuous testing with ilmenite only. Base case. To evaluate the influence of adding limestone on the performance of the CLC process, experiments using only ilmenite as base case were done. Initially in the whole plant there was about 15 kg inventory of ilmenite with particle size of 90-250 μ m. The fuel-reactor inventory was about 6 kg.

At each tested temperature two different air flows were used for the ilmenite tests in order to change the solids circulation rate and therefore the residence time. Conditions were stable and the coal feeding rate, $\dot{m}_{fuel, in}$, was 479 g/h. Table 3 gathers the averages of gas concentrations for the experiments using only ilmenite as oxygen-carrier at the fuel-reactor temperatures and introduced air flows to the airreactor tested.

Table 3. Gas concentrations averages (dry basis) for the experiments done with ilmenite. N₂ to balance.

$F_{AR in,}L_{N}/h$	CO ₂	H_2	СО	CH ₄
190	14.8	5.9	2.2	1.2
155	19.4	7.7	3.4	1.3
190	15.2	5.7	2.4	1.3
155	16.6	6.1	2.8	1.2
	190 155 190	19014.815519.419015.2	19014.85.915519.47.719015.25.7	15519.47.73.419015.25.72.4

Figures 4 and 5 show a comparison of the main parameters which indicate the system performance. At 950°C the experiment with higher circulation rate and OC/Fuel ratio (Figure 4.a) had lower carbon capture and oxide oxygen fraction compared to the test with lower OC/Fuel (Figure 4.b). That was due to the increase in the time to gasify the char fuel. Thus, η_{CC} increased from 0.7 to 0.83 when the residence time rose from 8.1 to 13.5 minutes. The same improvement in the gasification efficiency could be seen at 1000°C: η_{CC} increased from 0.59 to 0.77 when the residence time rose from 4.9 to 9.2 minutes. The oxygen demand is not substantially influenced by the residence time within the resulting range of residence times of the tests. In all cases the OC/Fuel ratio was above 1. At 950°C the oxygen demand was 0.33 and it was 0.28 and 0.29 at 1000°C. However, there was no significant effect of the solids residence time on the oxygen demand. Thus, both gasification efficiency and gas conversion efficiency increased at higher temperature. Increased performance for higher temperatures when using only ilmenite was already seen by Cuadrat et al.¹³ and Berguerand et al.¹⁴

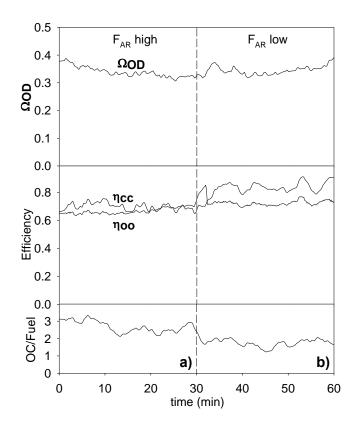


Figure 4. Comparison between the oxygen demand, Ω_{OD} , the carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , and OC/Fuel ratio for experiments at $T_{FR} = 950^{\circ}$ C using ilmenite as bed material. $\dot{m}_{fuel, in} = 479$ g/h. The dashed line shows when the air-reactor flow, F_{AR} , was lowered. a) $F_{AR} = 190$ L_N/h, b) $F_{AR} = 155$ L_N/h.

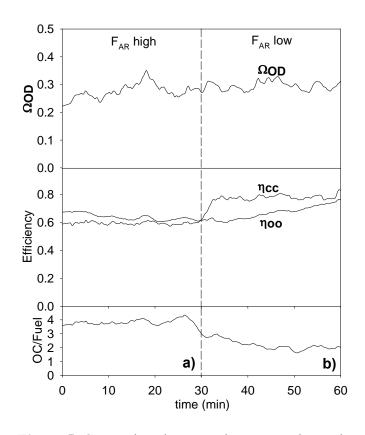


Figure 5. Comparison between the oxygen demand, Ω_{OD} , the carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , and OC/Fuel ratio for experiments at $T_{FR} = 1000^{\circ}$ C using ilmenite as bed material. $\dot{m}_{fuel, in} = 479$ g/h. The dashed line shows when the air-reactor flow, F_{AR} , was lowered. a) $F_{AR} = 190$ L_N/h, b) $F_{AR} = 155$ L_N/h.

A high fuel feed test with ilmenite was also done to compare it with the experiment at high fuel feeding after limestone addition. The petcoke feed flow was 958 g/h and the average main results obtained will be presented in the section summarizing the results.

Continuous testing with ilmenite and limestone mixture. Effect of limestone addition. After operation of the base case, 4 kg limestone of particle size 90-200 μ m was added, corresponding to 2.2 kg of burnt lime, CaO. The mass fraction of limestone in the fuel-reactor was later measured to be about 12%. Due to the fluidization properties of both types of particles, the mass fraction of limestone in the fuel-reactor was higher than in the air-reactor.

Effect of the temperature. In this section a series of experiments performed with the mixture of ilmenite and limestone as bed material with fuel-reactor temperature variation is evaluated. Figure 6

shows the measured gas concentrations in the fuel- and air-reactor for a 150 minute period. Conditions were stable and the fuel feed was 479 g/h. After 62 minutes, the fuel-reactor temperature, T_{FR} , was raised from 950°C to 1000°C. After 125 minutes the temperature was lowered back to 950°C. Similar values as previously at 950°C were obtained, indicating the reproducibility of the results.

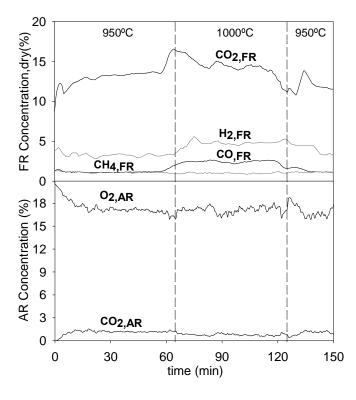


Figure 6. Measured product gas distributions in the fuel- (dry basis) and air-reactor for experiments performed with the mixture of ilmenite and limestone as bed material with fuel-reactor temperature variation: $T_{FR} = 950^{\circ}$ C and 1000°C. $\dot{m}_{fuel, in} = 479$ g/h.

At 1000°C higher amounts of H_2 , CO and CO₂ are being generated compared to the conditions reached at 950°C, which however had a better CO₂/CO ratio. The amount of CH₄ released was similar and slightly lower at 1000°C. CO₂ from the air-reactor was measured, indicating char escaping to the air-reactor. The CO₂ in the air-reactor was lower at 1000°C.

The calculated OC/Fuel ratio and mean residence time of the tests shown in Figure 6 are represented in Figure7. Note the definition of OC/Fuel, i.e. the oxygen available from the oxygen-carrier based on

mass circulation, over the oxygen needed by the fuel actually converted in the fuel-reactor. Thus, this ratio may decrease from reduced circulation or from increased fuel conversion rate.

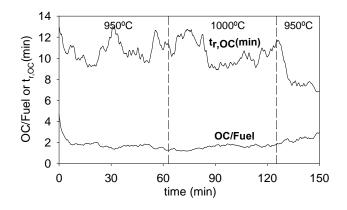


Figure 7. OC/Fuel ratio and mean residence time in the fuel-reactor for the test shown in Figure 6.

The estimated average oxygen-carrier residence time, $t_{r,OC}$, was in the range 9 to 13 minutes, corresponding to solids circulation rates of 40 kg/h to 28 kg/h. As the gasification rate for this fuel was found to be quite low, about 20 wt.%/min at this temperature range with ilmenite as oxygen-carrier,¹² and assuming that the residence time for the fuel is the same as for the oxygen-carrier, the mean residence time is insufficient to fully gasify the char. The OC/Fuel ratio was between 1.2 and 2. When the oxygen-carrier is highly converted, the reactivity decreases rapidly. Considering the reaction rate for reduction of activated ilmenite,¹⁰ the lower conversion rate could start at about a reduction conversion of 0.7-0.8, which corresponds to OC/Fuel below 1.3-1.4. This is in line with the study made by Markström et al.³⁰, who concluded that poorer conversion in this unit was obtained when the mass-based conversion degree variation is around 2.8%, which would correspond to an OC/Fuel of 1.4.

Figure 8a shows the corresponding η_{CC} and η_{OO} when using the mixture ilmenite and limestone as bed material at T_{FR} 950°C and 1000°C. At 950°C η_{CC} is about 79% and η_{OO} about 70%. For 1000°C the values are 86% and 81%. That is, the gasification rate is clearly improved by the temperature.

However, the oxygen demand at 950°C was 24%, which was lower than the oxygen demand at 1000°C, 28%. This is in contrast to the results with only ilmenite, where the gas conversion was improved by higher temperature.

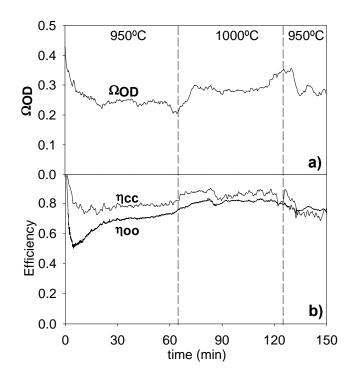


Figure 8. a) Oxygen demand, Ω_{OD} , b) Carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , for experiments with ilmenite and limestone shown in Figures 6 and 7.

Effect of the fuel feed. A test period where the fuel feed was increased to an effective value of 1053 g/h was done. The fuel-reactor temperature was 950°C. The resulting values of the most important parameters are represented in Figure 9.

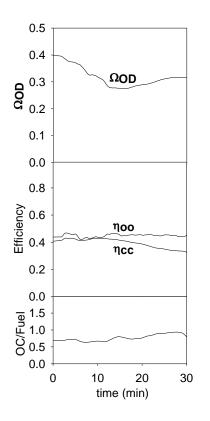


Figure 9. Oxygen demand, Ω_{OD} , the carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , and OC/Fuel ratio using ilmenite and limestone and high fuel feeding rate. $\dot{m}_{fuel, in} = 1053$ g/h. T_{FR}=950°C.

In the test performed with higher fuel flow the resulting OC/Fuel ratio dropped to 0.7 and it is not fully comparable to the other tests –tests operated with ratios over 1-, as the system was operating in substoichiometric conditions. Note that the OC/Fuel ratio should be over 1 to ensure that the circulating OC can supply enough oxygen to fully oxidize the introduced fuel.

Effect of limestone addition. The experiments with only ilmenite chosen for the comparison are those with more similar OC/Fuel ratio. Figure 10 shows the process efficiencies before and after limestone addition at a fuel-reactor temperature of 950°C. The gas conversion was higher at 950°C, as Ω_{OD} decreased from 0.33 to 0.24. η_{CC} is higher for ilmenite only in Figure 10, but this could be explained by the shorter residence time. Two tests with different residence time were made with ilmenite only, see Figure 4. By interpolation of these two tests it can be seen that η_{CC} is somewhat lower for ilmenite only, 0.76, as compared to ilmenite and limestone, 0.79, which is a slight improvement.

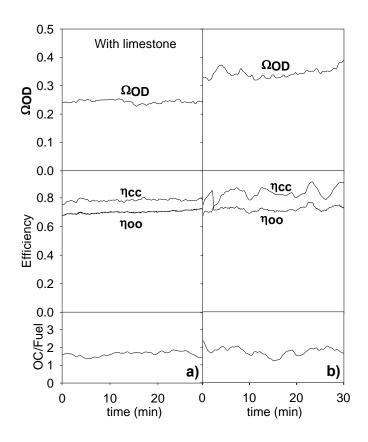


Figure 10. Comparison between the oxygen demand, Ω_{OD} , the carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , and OC/Fuel ratio for experiments at $T_{FR} = 950^{\circ}$ C using a) mixture ilmenite-limestone and b) ilmenite as bed material. $\dot{m}_{fuel, in} = 479$ g/h.

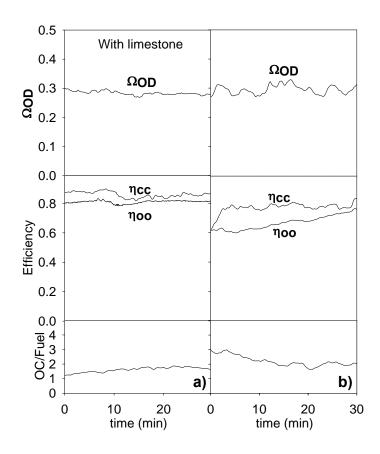


Figure 11. Comparison between the oxygen demand, Ω_{OD} , the carbon capture efficiency, η_{CC} , and oxide oxygen fraction, η_{OO} , and OC/Fuel ratio for experiments at $T_{FR} = 1000^{\circ}$ C using a) mixture ilmenite-limestone and b) ilmenite as bed material. $\dot{m}_{fuel, in} = 479$ g/h.

At 1000°C, Figure 11, there was no significant difference in the gas conversion, as Ω_{OD} was quite similar after limestone addition. However, the efficiencies related to char conversion were improved by the presence of limestone: η_{OO} increased from 0.66 to 0.81 and η_{CC} from 0.77 to 0.86. The improvement of the char conversion was also seen by the higher CO plus CO₂ flows from the fuel-reactor.

Operational overview. Table 4 shows a summary of the average values for the main experiments performed: the carbon capture efficiency, η_{CC} , the oxide oxygen fraction, η_{OO} , the oxygen demand, Ω_{OD} , the OC/Fuel ratio, the oxygen-carrier average residence time in the fuel-reactor, $t_{r,OC}$, the sum of the CO and CO₂ flows from the fuel-reactor, $F_{CO}+F_{CO2}$, and the total carbon flow in the effective coal fed, $F_{C,fuel,eff}$. The most interesting observations are related to the effect of the limestone:

- At 950°C, there is a very clear reduction in the oxygen demand, whereas no clear difference is seen at 1000°C.
- In all the cases compared there is more rapid conversion of the char in the presence of limestone, as seen in the increased flow of CO plus CO₂.

Generally, the results shown in Table 4 follow expectations and previous experiences. Thus:

- Char conversion is faster at higher temperature.
- Shorter residence time reduces char conversion in the fuel-reactor, i.e. gasification efficiency, as seen by lower flow of CO plus CO₂.

	η _{CC}	η_{OO}	$\Omega_{ m OD}$	OC/Fuel	t _{r,OC} ,min	F _{CO} +F _{CO2} , L _N /h	F _{C,fuel,eff} , g C/h	m _{fuel,in} , g/h
950°C. Mix	0.79	0.7	0.24	1.8	10.7	360	270	479
950°C. Ilm	0.7	0.67	0.33	2.6	8.1	230	210	479
950°C. Ilm	0.83	0.73	0.33	1.8	13.5	300	210	479
1000°C. Mix	0.86	0.81	0.28	1.6	10.8	445	290	479
1000°C. Ilm	0.58	0.64	0.28	3.7	4.9	255	250	479
1000°C. Ilm	0.77	0.66	0.29	2.2	9.2	350	260	479
950°C.↑Feed.Mix	0.42	0.45	0.33	0.7	8	640	870	1053
950°C.↑Feed.Ilm	0.54	0.66	0.33	1.1	8.4	420	440	958

Table 4. Summary of the average values obtained.

Operational problems. When operating with the mixture ilmenite-limestone, a substantial fraction of limestone was elutriated and left the reactor system together with the product gas. That caused some operational problems, because some $Ca(OH)_2$ was formed at the end of the outlet pipe of the fuel-reactor leading the water seal, see Figure 2. This led to partial blockage of the pipe and risk of overpressure and disturbance of the pressure balance in the system. Therefore the pipe had to be cleaned regularly. Despite these complications the unit could be continuously operated and stable conditions and values were eventually obtained. In the beginning of the tests after limestone addition, the CaCO₃ in the

limestone was calcined, and CaO was being formed with consequent CO₂ release and higher amounts of lime were lost.

Discussion of mechanisms. In order to assess the possible oxygen carrier properties of the limestone particles used in the process, a sample was taken from the fuel-reactor was reduced in TGA to evaluate whether it transferred oxygen. The sample was reduced with 5% H₂ and subsequently oxidized in TGA. There was some loss of weight and hence oxygen transfer, but it is small. Additionally to this low oxygen transport capacity of the sample, the reaction rates are much slower than the corresponding ones with ilmenite, as seen in Figure 12. The lower reactivity of CaSO₄ as oxygen-carrier with reducing gases (H₂, CO and CH₄) compared to ilmenite as oxygen-carrier has been previously seen.³¹⁻³⁴ Thus, it is unlikely that the effect seen in the gas conversion caused by limestone addition is due to its performance as oxygen-carrier. This is also consistent with the previously mentioned laboratory study by Teyssié et al.¹⁹ where the positive effect of adding CaO to ilmenite was seen already in the first cycle with fuel, i.e. before any formation of CaSO₄ is possible. Moreover, this study showed that the positive effect of using highly sulfated limestone, was only seen in the first cycles, and together with high SO₂ release. Thus, the absence of SO₂ release in the present tests is an additional indication that the CaSO₄ did not significantly contribute as oxygen carrier.

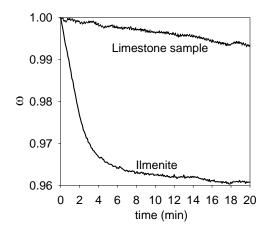


Figure 12. Mass-based conversion degree, ω , of ilmenite and limestone samples as function of time. Reduction in TGA with 5% H₂+40% H₂O for ilmenite and 5% H₂ for limestone. T = 900°C.

The study of Teyssié et al.¹⁹ also indicated that the beneficial effect of limestone addition can be explained by means of its influence on the Water-Gas Shift (WGS) reaction (see equation 15).

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 (15)

To evaluate how far from the WGS equilibrium the fuel-reactor components in the product gas are, the fraction $(F_{H2,FR} \cdot F_{CO2,FR})/(F_{H2O,FR out} \cdot F_{CO,FR})$ is calculated in each point for every experiment done. It is afterwards compared to the WGS constant, k_{WGS} , at the corresponding T_{FR} . Figure 13 shows the fraction $(F_{H2,FR} \cdot F_{CO2,FR})/(F_{H2O,FR out} \cdot F_{CO,FR})$ obtained for experiments with ilmenite-limestone and for tests done with ilmenite only at 950°C and 1000°C. The equilibrium constant k_{WGS} at the temperature considered is also represented. At both temperatures the exiting gaseous flows with limestone addition were closer to the WGS equilibrium, i.e. to higher H_2 +CO₂ formation, although the difference was much more pronounced at 950°C.

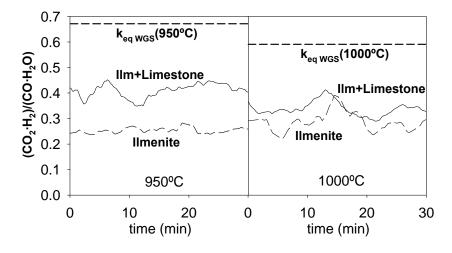


Figure 13. Fraction $(F_{H2,FR} \cdot F_{CO2,FR})/(F_{H2O,FR \text{ out}} \cdot F_{CO,FR})$ for experiments with ilmenite-limestone mixture and with ilmenite as bed material at 950°C and 1000°C.

Thus, limestone addition causes CO and H_2O to react to give CO₂ and H_2 , i.e. Ca-based compounds could act as a catalyst for the WGS reaction. This happens in the presence of an oxygen-carrier, ilmenite, which reacts faster with H_2 than with CO. Consequently, the oxidation of the gas should proceed faster, giving higher gas conversion and lower oxygen demand. This effect is clearly seen at 950°C (see Figure 10), although at a temperature of 1000°C the improvement regarding the gas conversion was residual when CaO was present in the solids mixture (see Figure 11). From results showed in Figure 13 it seems that the WGS reaction itself is fast enough at 1000°C to happen at similar extension with and without limestone addition.

The mechanism for improved char conversion is less clear. The effect seen here is different from the found in literature,^{35,36} for which calcium is known to have catalytic effects on steam gasification of coal. To obtain good catalytic activity, calcium must be atomically dispersed throughout the char, which is not the case in this process.

As compared to addition of unsulfated limestone, batch experiments with addition of sulfated limestone to an ilmenite bed at 970°C showed more rapid char conversion in the initial redox cycles and together with high SO₂ release, but the benefits as well as the SO₂ release disappeared after a dozen cycles.¹⁹ It is known that SO₂ enhances char conversion,⁴ and this is also the likely explanation to faster char conversion in the cycles where SO₂ is released from CaSO₄ decomposition. The present tests showed no SO₂ release from the fuel-reactor, and consequently the mechanism of SO₂ release would not explain the enhanced char conversion rate. Thus, the explanation for the beneficial effect on the char conversion should be found in the presence of CaO, and not CaSO₄.

Furthermore, the effect of the Water-Gas Shift equilibrium on char conversion is not clear. The general effect is to lower CO and raise H_2 . As H_2 is a known inhibitor of steam gasification this would be expected to lower char conversion, but possibly the lowered CO could compensate for this, CO also being an inhibitor of gasification.

Effect of limestone addition. Fate of sulfur. Sulfur contained in the fuel is released mainly in form of H_2S under the reducing conditions in the reactor. Previous experience with petcoke feed and ilmenite as oxygen-carrier showed that also some SO_2 can be formed when oxygen-carrier circulation is high enough.¹⁵

 SO_2 in the fuel-reactor was continuously measured online in all experiments. For the experiments done using only ilmenite the amount of SO_2 released in the fuel-reactor depended on the oxidation

conditions in the reactor. Thus, higher OC/Fuel ratios meant that more sulfur from the fuel was oxidized to SO₂. At 950°C with OC/Fuel of about 1.6, about 2% of sulfur from the fuel fed was oxidized to SO₂. For higher OC/Fuel ratio of 2.5, about 3.5% of the sulfur fed was released as SO₂. At 1000°C 2% and 9% of the sulfur fed, correspondingly, were oxidized to SO₂, as can be seen in Figure 14. The higher value of 9% is explained by a high OC/Fuel ratio. It was not possible to see any clear influence of temperature.

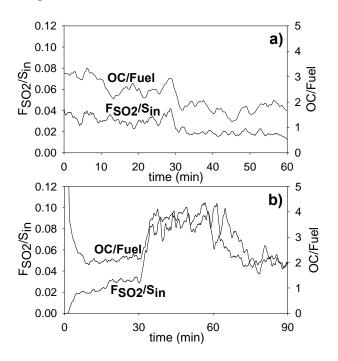


Figure 14. F_{SO2}/S_{in} ratio and OC/Fuel ratio for experiments with ilmenite as bed material at a) 950°C and b) 1000°C.

Thermodynamic simulations showed that, under these conditions, the rest of the sulfur coming from the fuel-reactor should be H_2S . The simulations confirmed that the SO_2 formed in the fuel-reactor was close to the thermodynamic equilibrium for SO_2 regarding both the CO/CO_2 and H_2/H_2O ratios for each test.

In the experiments with the mixture ilmenite-limestone the SO_2 measurement showed that there was no SO_2 generated during the 4 hours of testing.

The SO₂ analyzer was connected for some minutes to the air-reactor during experiments at 950°C and OC/Fuel ratio of 1.3 and it turned out that about 13% of the sulfur fed was being released in the air-

reactor. This sulfur was presumably coming from the combustion of char that was flowing into the air-reactor, as the carbon capture in that moment was about 62%. Considering that 38% of the effective fuel fed is converted in the air-reactor and assuming that the S released from petcoke is proportional to the carbon release, about 66% of the sulfur that would have been released in the air-reactor, was being retained by limestone. Thus, the SO₂ coming from the air-reactor was smaller than the expected release of sulfur from the fuel burning.

Sulfur and calcium mapping of a sample of limestone cross-cut particles taken from the fuel-reactor was done by SEM analysis. Sulfur was seen to be homogeneously distributed throughout the particle (see Figure 15). The mass fraction of sulfur in the particles was 4-5%.

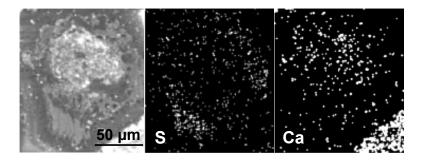


Figure 15. Image of a cross-cut particle and sulfur and calcium mapping done by SEM analysis of a sample of limestone taken from the fuel-reactor.

An additional TGA analysis was done as an approximate measurement of the calcium species present in the used limestone after these tests. A limestone sample taken from the fuel-reactor was heated up from room temperature to 900°C in a N₂ atmosphere and lost about 25% of the initial weight. This corresponded to the decomposition of the Ca(OH)₂ that would have been formed from humidity uptake by the used limestone from the fuel-reactor. Afterwards the sample was reduced with 5% H₂ and the sample lost about 3.6% mass, compared to the initial weight. This corresponded to the reduction of the CaSO₄ contained in the sample. It is presumable that there is also CaS as the other main sulfurcontaining compound. The main component in the used limestone taken from the fuel-reactor was therefore CaO. In total 95 g of sulfur were fed during the hours of tests with petcoke. In the fuel-reactor, about 0.8 kg of limestone was recovered. Considering the measured sulfur content of 4-5%, the limestone extracted from the fuel-reactor contained 32-40 g of sulfur. As there is also some limestone in the air-reactor and in the loop seals, as well as some SO₂ release from the char burnt in the air-reactor, it is likely that a major part of all sulfur released in the fuel-reactor was taken up by limestone: that is, both H_2S and SO_2 release in the fuel-reactor were reacting with limestone to form CaS.

In conclusion, most of the sulfur released seems to have been captured by the lime. Moreover, steadystate with respect to sulfur was likely not reached during the four hours of operation.

CONCLUSIONS

In this paper the effect of limestone addition in a 10 kW_{th} continuous CLC system fed with Mexican petcoke as fuel and a mixture and ilmenite as oxygen-carrier was assessed. The limestone content in the fuel-reactor bed at the conclusion of the experiments was weighed to be about 12% and the rest was ilmenite. The tests showed good agreement with previous tests and with what should be expected:

- When the residence time was higher, the gasification efficiency increased, as it was shown by e.g. the higher release of CO plus CO₂ from the fuel-reactor.
- The fuel-reactor temperature was also proved to be one of the determining variables for the performance of the process, being an increase of the temperature very positive to increase the efficiency of gasification and thus the carbon capture.

The more interesting conclusions are related to the effect of limestone addition:

 At 950°C limestone addition led to improved gas conversion, being the oxygen demand lowered from 0.33 to 0.24. At 1000 °C, however, no improvement in gas conversion could be seen for lime addition. The improvement in gas conversion can be explained by lime catalyzing the water-gas shift equilibrium, and subsequent faster reaction of H₂ with ilmenite.

- The oxygen transfer by sulfated limestone seems to be small and the improvement in gas conversion is probably explained mostly by the effect of limestone on the water-gas shift reaction.
- The char gasification rate was also improved by the addition of limestone, both at 950°C and at 1000°C, although the mechanism has not been fully clarified.
- Before limestone addition there was SO₂ and H₂S release in the fuel-reactor, and the amount of SO₂ released was higher when oxygen-carrier to fuel ratio was higher. After limestone addition, no SO₂ was measured in the fuel-reactor. SO₂ was measured in the air-reactor, coming from the unconverted char from the fuel-reactor.
- There was sulfur retention by limestone, but more hours of continuous operation would be
 necessary to ensure that limestone uptake and release of sulfur stabilized with a constant sulfur
 concentration in the particles. Although not apparent in the present test, the beneficial effects
 of CaSO₄/CaS as oxygen carrier could be different under other conditions. Firstly, the tests did
 not reach steady state, and secondly the sulfur concentrations were much lower than would
 have been the case in a real unit, i.e. with less dilution of gases in H₂O.
- For the solid-fuel CLC it is not recommended to use limestone for sulfur removal because the extraction of the used limestone would likely cause the loss of high amounts of oxygen-carrier.
- The use of some limestone in the process as additive due to its effect in the water-gas shift equilibrium has shown to be advantageous for the efficiency improvement, for gasification as well as for gas conversion.

ACKNOWLEDGMENTS

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NOMENCLATURE

AR = Air-reactor

FR = Fuel-reactor

- CLC = Chemical-Looping Combustion
- [C]_{fuel} = mass based carbon content in fuel
- [O]_{fuel} = mass based oxygen content in fuel
- $F_{AR in}$ = air flow introduced in the air-reactor, mol/s
- F_{AR} = outlet air-reactor gas flow, mol/s
- $F_{C,fuel,eff}$ = carbon flow in the effective coal fed, mol/s
- $F_{C, fuel, in}$ = carbon flow in the coal feed introduced, mol/s
- $F_{CO2,AR} = CO_2$ flow from the air-reactor, mol/s
- F_{CO2,FR}, F_{CO,FR}, F_{CH4,FR}, F_{H2O,FR out}, F_{SO2} = flows of CO₂, CO, CH₄, H₂O and SO₂, respectively, in the
- fuel-reactor product gas, mol/s
- F_{CS} = flow in the carbon-stripper, mol/s
- F_{FR} = dry basis product gas flow, mol/s
- F_{FRLS} = flow in the small fuel-reactor loop-seal, mol/s
- $F_{H2O,in}$ = water steam inlet flow in the fuel-reactor, mol/s
- F_{HILS} = flow in the higher loop-seal, mol/s
- F_{HIVEL} = flow in the high-velocity section in the fuel-reactor, mol/s
- F_{LOLS} = flow in the lower loop-seal, mol/s
- F_{LOVEL} = flow in the low-velocity section in the fuel-reactor, mol/s
- $F_{N2,AR} = N_2$ inlet flow in the fuel-reactor, mol/s
- $F_{N2,FR} = N_2$ inlet flow in the fuel-reactor, mol/s
- F_{OC} = solids circulation rate, kg/s
- $Me_xO_y = oxidized oxygen-carrier$

 Me_xO_{y-1} = reduced oxygen-carrier

m = instantaneous mass of the oxygen-carrier, kg

 m_o = mass of the oxidized form of the oxygen-carrier, kg

 m_{oc} = oxygen-carrier inventory in the fuel-reactor, kg

 m_r = mass of the reduced form of the oxygen-carrier, kg

 $\dot{m}_{fuel, in}$ = fuel feeding flow, kg/s

OC = oxygen-carrier

 $R_{O,ilm}$ = oxygen transport capacity of ilmenite

 S_{in} = sulfur flow contained in the fuel feeding (mol/s)

T = temperature, °C

 T_{FR} = temperature in the fuel-reactor, °C

 $t_{r,OC}$ = mean residence time of the oxygen-carrier, s

WGS = Water-Gas Shift

 $y_{O_{2,AR}}$, $\,y_{CO_{2,AR}}$ = fractions in the air-reactor outlet flow of O_2 and CO_2

 $y_{CH_{4,FR}}$, $y_{CO_{2,FR}}$, $y_{CO_{2,FR}}$, $y_{H_{2,FR}}$ = dry basis fractions in the fuel-reactor product gas of CH₄, CO₂, CO, H₂,

respectively

 η_{CC} = carbon capture efficiency

 η_{OO} = oxide oxygen fraction

 η_{SF} = solid fuel conversion

 ω = mass-based conversion degree

 Ω_{OD} = oxygen demand

 $\Phi_{\rm O} = O_2/C$ ratio for the fuel, mol O_2 /mol C

 $\Phi_{O,act}$ = actual O₂/C ratio for the fuel, mol O₂/mol C

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