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**Use of Manganese Ores as Oxygen Carriers in  
Chemical-Looping Combustors for Solid Fuels**

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## Use of Manganese Ores as Oxygen Carriers in Chemical-Looping Combustors for Solid Fuels

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**Abstract** –Manganese ores are highly promising oxygen-carrier candidates due to high reactivity and high availability. It has been observed that some manganese ores may be sensitive to attrition, and the challenge has thus become to find a highly reactive manganese ore, or combination of ores, with sufficient mechanical integrity. This study summarizes the operational experience with manganese ores achieved at Chalmers UT.

In an early study using Buritirama manganese ore as oxygen carrier in a 10 kW unit for solid fuels, it was shown that the gas conversion using petcoke as fuel increased from 80% with ilmenite to 85% with Buritirama. Simultaneously, there was a four-fold increase in gasification rate resulting in much higher carbon capture efficiency. However, the mechanical stability of the Mn ore was inferior to ilmenite, judged by the production of fines.

In a subsequent study, ilmenite was mixed with the Buritirama manganese ore during operation in a 100 kW unit. The mixture of ilmenite and manganese ore gave significant improvements in gas conversion in comparison to only ilmenite. The highest gas conversion observed during testing with bituminous coal was as high as 91.5%, as compared to 84% with only ilmenite during similar conditions in the 100 kW unit.

Another three manganese ores were recently investigated in the 10 kW unit. These ores appeared to form less fines as compared to Buritirama ore. All oxygen carriers showed high performance and reached more than 90% gas conversion at relevant conditions, using wood char as fuel. The estimated lifetime of the oxygen carrier based on fines production was in the range of 100 to 300 hours – a considerable improvement compared to the Buritirama ore.

The most promising of the three ores tested in the 10 kW unit, Sinfin, was selected for use in the 100 kW unit. 52 hours of operation with different fuels has been achieved with the new oxygen carrier, called Sinaus, which is similar but not identical in composition to Sinfin. Preliminary results show that gas conversion is higher, and solid-fuel conversion much higher than with ilmenite as oxygen carrier. The evaluation also shows that the lifetime is lower than for ilmenite.

## 1 Introduction

Even though developed and suggested process schemes for chemical looping differ in a range of operational parameters, a common cornerstone of the CLC technology is the oxygen carrier, which needs to have sufficient reactivity as well as mechanical and chemical stability for long periods of time in continuous CLC systems. Oxygen carrier development has been reviewed by Lyngfelt [1]. In order to find out how particles will behave over time in full-scale applications, evaluation in larger, continuous units is a vital step. The expected lifetime of the oxygen-carrying particles may be a very important parameter when it comes to process up-scaling. Lyngfelt and Leckner [2] recently proposed a design of a 1000 MW CLC system, which is very similar to a state-of-the-art CFB boiler. The authors find that the additional cost of the CLC–CFB system, relative to conventional state-of-the-art CFB technology, is around 20 €/tonne CO<sub>2</sub>. In other words, the cost of CO<sub>2</sub> capture is significantly lower as compared to other capture technologies.

Natural minerals offer a low-cost alternative for oxygen carriers, which is a desirable characteristic in CLC with solid fuels. Ilmenite is a natural mineral that has been widely used as oxygen carrier in CLC applications. Using ilmenite as oxygen carrier and bituminous coal as fuel, the expected lifetime of ilmenite particles was investigated in a 100 kW reactor system – described below – and found to be 700-800 h [3].

Compared to ilmenite, manganese ore has shown higher reactivity with syngas. This was demonstrated in a study by Sundqvist et al. [4] who investigated 11 manganese ores in a laboratory fluidized bed, and estimated the rate constant for the 8 most reactive ores to be 3-6 times higher as compared to ilmenite. Moreover, the presence of manganese ore has also been shown to give a higher rate of steam gasification of char in both lab tests [5] and a continuous unit [6]. This paper summarizes the operational experience with manganese ores achieved at Chalmers University of Technology. It should be pointed out that apart from Chalmers, only IFP in France has reported solid-fuel CLC operation with manganese ore. In 2012, 52 hours of operation was achieved with an oxygen carrier called “BMP”, which was based on manganese ore [7], in a 10 kW unit.

## 2 Experimental

### 2.1 Reactor systems

The experimental work presented here has been carried out in two solid-fuel CLC reactor systems. Both units utilize the concept of interconnected fluidized beds with an air reactor and a fuel reactor, where the gas velocity in the air reactor provides the driving force for particle circulation. Both units are enclosed in electrically heated ovens.

#### *The 10 kW chemical-looping combustor*

The reactor system (figure 1) consists of a fuel reactor (FR), where the fuel is gasified by steam, and gasification products are oxidized by the oxygen carrier, an air reactor (AR), where the particles are oxidized, and a riser, which brings particles back to the fuel reactor via the cyclone – a gas/solids separator – and the upper loop seal (ULS). The gas velocity in the AR and riser

provides the driving force for particle circulation. The upper and lower loop seals are present in the reactor system in order to eliminate gas leakages between AR and FR.

The FR is divided into two main sections; a low-velocity section (LOVEL) which is operated as a bubbling bed, and a carbon stripper which is operated between the terminal velocities of the oxygen carrier and the char, hence enabling separation of the two types of particles. The FR is also equipped with a recirculation loop, the function of which is to return elutriated char particles to LOVEL. All reactions occur in the LOVEL, which is fluidized with steam. The total solids inventory is around 15 kg, the inventory in the FR is approximately 6 kg. The LOVEL has an internal partitioning in order to give the particles a more even residence-time distribution and prevent surface by-pass. A detailed description of the 10 kW unit is given in [6].

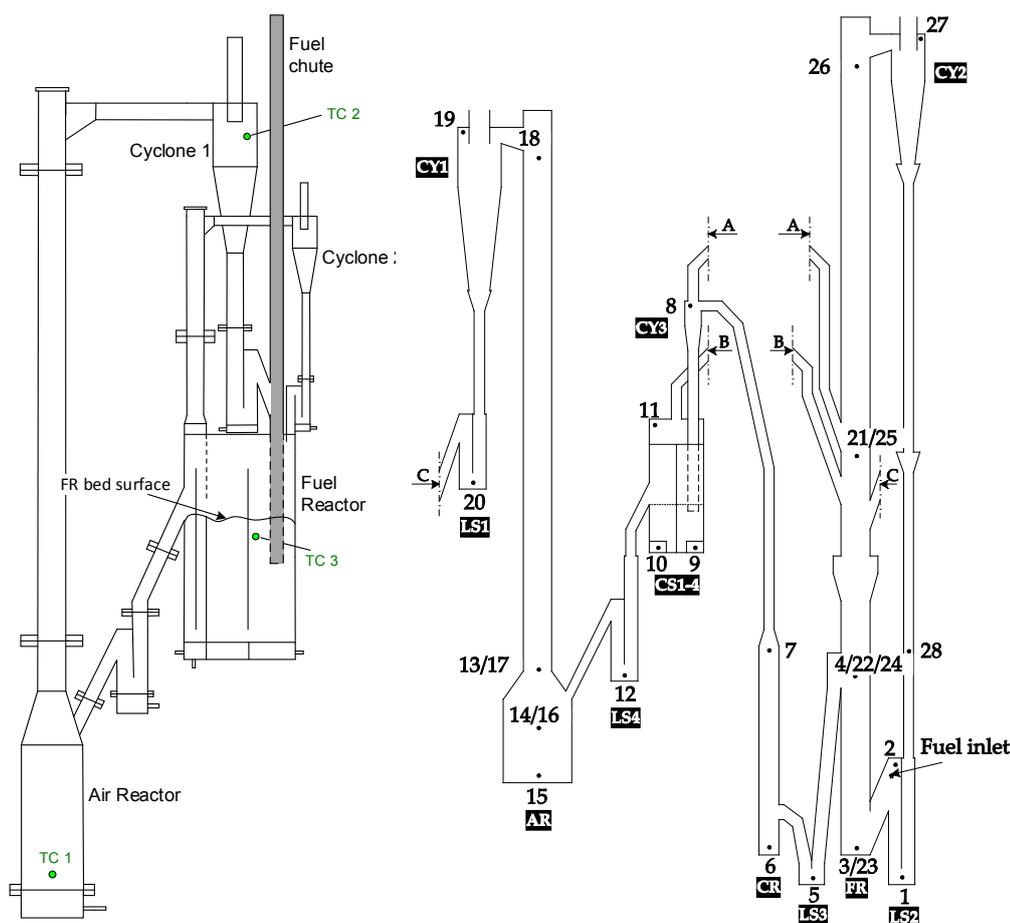


Figure 1: Chalmers' CLC units for solid fuels: 10 kW unit (left), 100 kW (right).

### The 100 kW chemical-looping combustor

The 100 kW system, also shown in Figure 1, is designed as to allow operational flexibility. The system includes two interconnected circulating fluidized beds, i.e., air reactor (AR) and fuel reactor (FR), as well as a carbon stripper. The circulating fluidized bed in the fuel reactor adds flexibility. Starting in the fuel reactor, the path of solids circulation is outlined below and is numbered from 1 to 28 in Figure 1. Gas and particles entrained in the fuel reactor enter the cyclone (CY2), fall down the downcomer to a loop seal (LS2) and enter the fuel reactor again. Particles not entrained may instead enter the so-called circulation riser (CR), which is placed in between the carbon stripper (CS1–4) and the loop seal (LS3) connected to the fuel reactor. The

circulation riser is designed to return varying mass flows of particles to the air reactor. The carbon stripper has four chambers separated by weirs. The purpose of the carbon stripper is to gasify or separate residual char in the particle flow. The particles in the carbon stripper are passed on to a loop seal (LS4), leading to the air reactor (AR). The air reactor re-oxidizes the oxygen carriers before they are transported back to the fuel reactor by passing a cyclone (CY1) and another loop seal (LS1), thus beginning a new cycle. The air reactor and fuel reactor are separated by loop seals in order to avoid gas mixing. The fuel reactor, with an inner height of 5.0 m, determines the overall height of the unit. The air reactor temperature is controlled by a mantle cooler, through which ambient air exchanges heat with the hot wall of the air reactor. Steam is used to fluidize FR, CS, CR and the loop seals. The 100 kW reactor system has been described in more detail in a study by Markström et al [8].

## 2.2 Oxygen carriers

Five manganese ores have been used in continuous CLC experiments at Chalmers. The materials were chosen with respect to chemical composition and mechanical properties such as crushing strength to cover a wide range of potential oxygen carrier materials. Important properties of the materials are summarized in Table 1. Buritirama, Mangagran and Mesa are untreated manganese ores, whereas the Sinfin and Sinaus materials are sintered ores, originally produced for the ferroalloy industry.

All materials except Buritirama and Sinaus were calcined at 950°C for 24 h. The long calcination duration is used in order to ensure fully oxidized oxygen-carrier particles and thus minimizing the risk of agglomeration during the first heat up of the material. Such a long calcination time would not likely be required in large-scale applications. During calcination, the Mesa and Sinfin materials formed soft agglomerations, which could easily be taken apart mechanically. In the case of Mesa, the particle size increased during calcination, while the density was essentially unchanged. Table 2 shows the elemental composition of the materials. As Buritirama was not heat-treated prior to use, the loss on ignition (LOI) is high.

Table 1: Characteristics of the fresh oxygen carriers used in the experiments.

Property	Units	Buritirama	Mangagran	Mesa	Sinfin	Sinaus
$\bar{d}_p$	μm	152	170	200	150	160
$\rho_{bulk}$	kg/m <sup>3</sup>	1750	1900	2000	2050	2250
Crushing strength	N	1.3	2.6	5.3	3.9	3.5

Table 2: Elemental compositions of the tested manganese materials

	Oxygen carrier				
	Buritirama	Mangagran	Mesa	Sinfin	Sinaus
<b>Mn</b>	43.6	66.4	39.9	48.9	52.3
<b>Fe</b>	5.58	2.95	13.57	5.68	8.95
<b>Si</b>	3.55	1.37	6.91	4.15	3.92
<b>Al</b>	2.86	3.11	0.42	4.76	2.47
<b>Ti</b>	0.22	0.09	0.05	0.25	0.12
<b>Ca</b>	0.14	0.08	2.48	0.29	0.89
<b>K</b>	1.57	0.69	0.75	0.98	1.05
<b>Mg</b>	0.37	0.05	0.49	0.15	0.22
<b>Ba</b>	1.61	0.27	1.11	0.21	0.48
<b>Na</b>	0.00	0.04	0.17	0.07	0.21
<b>LOI 1000°C</b>	13.40	2.40	0.80	0.00	-0.70
<b>Total element + LOI</b>	72.9	77.5	66.7	65.5	69.9

LOI: Loss on ignition at 1000°C.

## 2.3 Fuels

The fuels used in the studies are wood char, petcoke, three bituminous coals, and wood pellets, see Table 3. The wood char is produced by subjecting wood chips of both hard- and softwood to 450°C for 8 h in the absence of oxygen. The as-received wood char has a size of approximately 5 mm, but is reduced to 200-1000 μm when the fuel is passed through the primary and secondary feeding screws. The Cerrejón and Polish coals are finely ground powders with average size around 45 μm, whereas the Calenturitas coal consists of larger particles around 105 μm. Petcoke particles have an average diameter of 80 μm.

Table 3: Composition of the fuel: proximate and ultimate analyses. Maf: moisture and ash free.

Component	Wood char	Cerrejón coal	Polish coal	Calenturitas coal	Petroleum coke	Wood pellets	Comment
Fixed C	73.9	48.2	44.7	53.1	81.5	18.7	%, as received
Volatiles	16.7	29.4	29.5	29.4	10.0	74.2	%, as received
Moisture	3.9	13.8	2.3	11	8.0	6.8	%, as received
Ash	5.5	8.6	12.9	6.5	0.5	0.3	%, as received
C	86.9	84.3	80.9	78.3	88.8	53.6	%, maf
H	3.2	5.9	5.3	6.6	3.1	6.0	%, maf
O	9.5	7.4	11.2	12.7	0.5	40.3	%, maf
N	0.4	1.6	2.1	1.6	1.0	0.1	%, maf
S	0.03	0.8	0.55	0.8	6.6	0	%, maf
LHV (MJ/kg)	29.8	24.6	27.1	24.6	31.8	18.7	MJ/kg

## 2.4 Data analysis

The gas analyzers used in the experiments include an Emerson Rosemount NGA 2000, measuring CO, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub> and O<sub>2</sub>, an Emerson X-Stream, measuring NO and NO<sub>2</sub>, and a Sick Maihak S740 measuring SO<sub>2</sub>. All concentrations are measured on dry gas. It is to be noted that the measured gas concentrations do not add up to 100%. This is mainly due to dilution with N<sub>2</sub>, originating from the fuel screw, LS2 and smaller quantities from the pressure tap sweep gas.

### Performance Indicators for Fuel Conversion

The fuel fraction that is converted to gas in the entire system, *i.e.* in both FR and AR, is referred to as the solid-fuel conversion, and can be written as

$$\eta_{\text{Solid fuel}} = \frac{\dot{m}_{C,\text{fuel}} - \dot{m}_{C,\text{OUT}}}{\dot{m}_{C,\text{fuel}}} \quad (1)$$

where  $\dot{m}_{C,\text{fuel}}$  (g/min) is the mass flow of carbon in the fuel to the FR, and  $\dot{m}_{C,\text{OUT}}$  (g/min) is the mass flow of solid carbon elutriated from the reactor system.

Gaseous species produced in the FR are either volatile compounds or products of char gasification. Volatiles include mainly CH<sub>4</sub>, H<sub>2</sub>, CO and CO<sub>2</sub>. The oxygen demand,

$$\Omega_{OD} = \frac{0.5x_{CO} + 2x_{CH_4} + 0.5x_{H_2}}{\Phi_0(x_{CO_2} + x_{CO} + x_{CH_4})}, \quad (2)$$

describes the fraction of oxygen lacking to achieve complete combustion of the gas produced in the FR, where  $x_i$  is the volume fraction of gas  $i$ ,  $\Phi_0$  is the molar ratio [ $n_{O_2}$  required for combustion/kg fuel] / [ $n_C$ /kg fuel]. In this work, sulfur species have not been included in the oxygen demand.  $\eta_{\text{gas conversion}}$  describes the gas conversion efficiency in the FR, which can be defined simply as

$$\eta_{\text{gas conversion}} = 1 - \Omega_{OD} \quad (3)$$

The carbon capture efficiency,  $\eta_{CC}$ , is defined as the amount of oxygen used for oxidizing the particles in the air reactor, divided by the total amount of oxygen consumed in the air reactor. It only depends on gas concentrations in the air reactor outlet, eliminating any uncertainty due to flows. With  $x_i$  as the molar fraction of species  $i$  in the gas from the air reactor, it can be shown that

$$\eta_{CC} = \frac{0.21 - x_{O_2} - x_{CO_2}}{0.21 - x_{O_2} - 0.21x_{CO_2}} \quad (4)$$

The carbon capture efficiency is also called the oxide-oxygen efficiency,  $\eta_{OO}$ .

The oxygen needed for char combustion in the AR yields an O<sub>2</sub>/C ratio of one. The numerator in Eq. (4) represents the carbon released as gas in the FR, whereas the denominator represents the total carbon released.

#### *Lifetime of particles*

The rate of attrition, or particle degradation, can be evaluated using a measure called loss of fines,  $L_f$ , which is defined as

$$L_f = \frac{\Delta m_{\text{fines}}}{\Delta t} \frac{1}{m_I} \quad (\text{h}^{-1}), \quad (5)$$

where  $\Delta m_{\text{fines}}$  is the amount of fines produced during a period of time,  $\Delta t$ , and  $m_I$  is the total solids inventory of oxygen carrier in the system.

The lifetime of the oxygen carrier corresponding to the loss of fines can then be calculated approximately as

$$t_{\text{life}} = \frac{1}{L_f} \quad (\text{h}). \quad (6)$$

An estimation of  $t_{\text{life}}$  should preferably be based on long duration of operation using the same batch of particles, *e.g.* hundreds of hours. It should be noted that the oxygen carrier also is exposed to ash fouling which may cause loss in reactivity and ultimately particle deactivation. The rate of ash fouling is not known, but should depend on the fuel used. It cannot be ruled out that fouling leading to significant loss of reactivity occurs well before  $1/L_f$  is reached, in which case the lifetime of the carrier is governed not by the attrition rate but by the rate of fouling.

#### *Oxygen carrier conversion*

The degree of oxidation, or conversion, of the oxygen carrier can be described by  $\omega$ , which is defined as

$$\omega = \frac{m}{m_{\text{ox}}} = \frac{\dot{m}_{OC}}{\dot{m}_{\text{ox trp}} + \dot{m}_{OC}} \quad (7)$$

$\dot{m}_{OC}$  is the solids circulation and can be estimated from the method described in a study by Markström et al. [9]. The oxygen transport,  $\dot{m}_{\text{ox trp}}$ , is the amount of oxygen used to re-oxidize the oxygen carrier in the AR. It is calculated from gas flows and gas concentrations in the air reactor. The difference in oxygen carrier conversion,  $\Delta\omega$ , could be a useful indicator of the level of “chemical stress” of the particles.  $\Delta\omega$  can be calculated as

$$\Delta\omega = \omega_{AR} - \omega_{FR} \quad (8)$$

Here,  $\omega_{AR}$  is assumed to be unity, and  $\omega_{FR}$  is calculated by eq. (7).

### 3 Results and discussion

#### 3.1 Operation of the 10 kW unit: Buritirama manganese ore [6, 10]

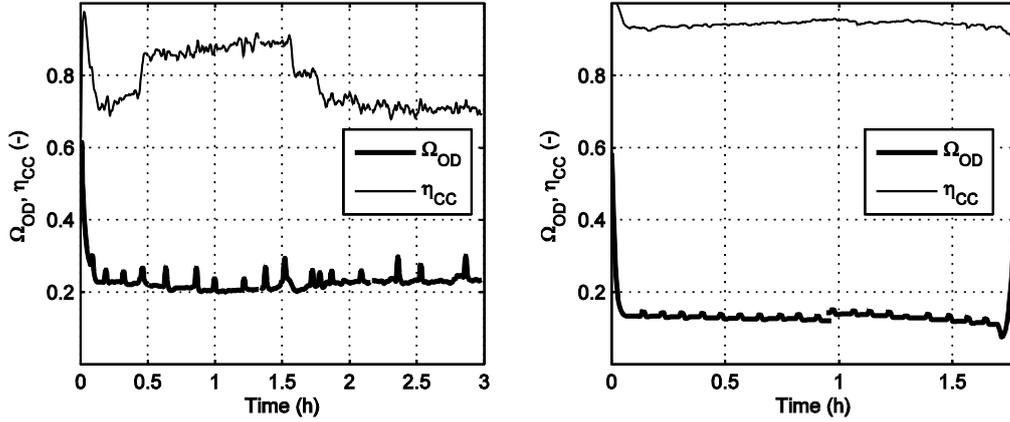


Figure 2: Using pet coke as fuel, performance with Buritirama (right) is compared to ilmenite (left).

Figure 2 compares oxygen demand and carbon capture using pet coke as fuel for similar fuel-reactor temperature, fuel power and circulation. Clearly, both gas conversion and carbon capture is higher using Buritirama as oxygen carrier. However, mechanical stability of Buritirama was inferior to ilmenite, judged by the production of fines. The estimated lifetime was 50-60 hours. In an attempt to increase the mechanical stability of the Buritirama ore, lime was added to the batch of oxygen carrier [10], but the Buritirama ore particles did not react with the lime, and the low mechanical stability remained.

#### 3.2 Operation of the 10 kW unit: Mangagran, Mesa and Sinfin [11]

As Buritirama was prone to attrition and had a short expected lifetime, other manganese ores were screened, and three ores were selected for use in the 10 kW unit.

Table 4 gives a comparison of the time-weighted averages of the performance of the three oxygen carriers tested. In these experiments, the lowest oxygen demand was achieved during operation with Mangagran, and the highest carbon capture with Sinfin. It should be observed that the performance numbers for Mesa were achieved with lower operating temperatures. At higher temperatures, this material probably would have shown better performance. However, due to recurring agglomeration problems with the Mesa ore, this was not possible to test.

Table 4: Performance comparison of all oxygen carriers.

Material	Fuel-reactor temperature °C	Fuel	$\Omega_{OD}$ (%)	$\eta_{CC}$ (%)
Mangagran	970	Wood char	7.0	90.5
Mesa	890/925	Wood char	10.1/7.4	78.1/84.7
Sinfin	970	Wood char	7.2	93.1
Sinfin	970	Petcoke	12.4	72.5

Comparing the performance with Sinfin using petcoke as fuel to previous results with Buritirama ore and petcoke, gas conversion is a somewhat higher with Sinfin, whereas the carbon capture is much lower. However, only one test was done with petcoke and Sinfin, and both fuel power and solids circulation were considerably higher than with Buritirama, thus explaining the lower carbon capture efficiency.

Based on fines production, the lifetimes calculated for Mangagran, Mesa and Sinfin were 110 h, 100 h, and 280 h, respectively. For Sinfin, this is almost six times more than what was found for the Buritirama ore, as discussed above. This was a clear indication that some manganese ores should be able to combine high gas conversion with reasonable lifetime.

### 3.3 Operation of the 100 kW unit: mixture of ilmenite and Buritirama ore [12]

Here, the potential to improve performance by mixing ilmenite with Buritirama ore was investigated. As has been described above, manganese ores may produce a lot of fines when used as oxygen carrier. Using a mixture of the two materials could therefore be preferable to using only manganese ore as oxygen carrier. In other words, the rationale for mixing the two materials is to obtain an oxygen-carrying material that has high reactivity, and yet does not produce too much fines during fuel operation. Furthermore, mixing ilmenite with more reactive manganese ore can give important reductions in costs as compared to using manganese ore only.

Operation using the mixture was stable throughout testing. The mixture of ilmenite and manganese ore gave significant improvements in gas conversion in comparison to only ilmenite. At the conclusion of the experiments, the fraction of manganese ore was approximately 8%, which was also the highest fraction during all tests. The production rate of fines was on the same order of magnitude as with only ilmenite.

Figure 3 shows the influence of fuel-reactor pressure drop on the gas conversion and the solid fuel conversion. Cerrejón coal was used Day 1 and Day 2, whereas Polish coal was used Day 3. Clearly, gas conversion increased with increasing bed level in the fuel reactor. The highest gas conversion, 91.5%, was observed on Day 2. This number should be compared to what has been accomplished with only ilmenite as oxygen carrier, 84%, during similar conditions. Furthermore, it should be noted that there is a weak trend towards increasing gas conversion efficiency from Day 1 to Day 2, and from Day 2 to Day 3. The difference in performance seen between Day 1 and Day 2 is partly due to the difference in solids inventory ( $\text{kg}/\text{MW}_{\text{fuel}}$ ). However, the main reason for the increasing performance over time is associated with the increasing fraction of manganese ore in the bed material. Since additions of manganese ore are

made several times during the total period of operation, the highest fraction of manganese ore in the bed material can be assumed to be found on Day 3.

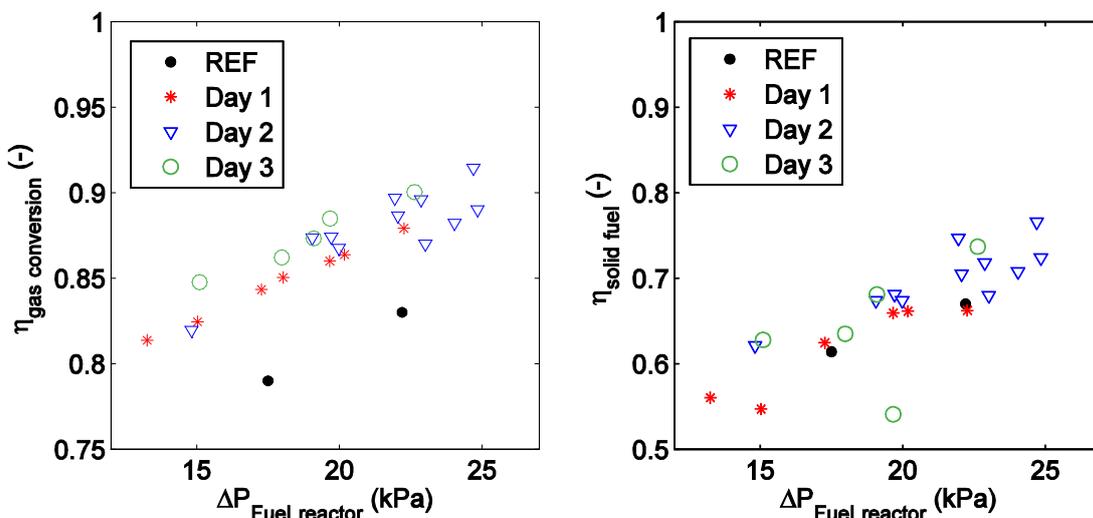


Figure 3: Gas conversion and solid fuel conversion as functions of the fuel-reactor pressure drop. Red and blue markers: Cerrejón coal. Green markers: Polish coal. Black markers indicate reference tests performed Day 1 with only ilmenite oxygen carrier.

Using wood char as fuel, the highest gas conversion efficiency was 96.3%, which is one percentage point higher than what has been accomplished with only ilmenite as oxygen carrier during similar conditions.

### 3.4 Operation of the 100 kW unit: Sinaus

Following the success of Sinfin in the 10 kW unit, a larger batch of a similar material was acquired for use in the 100 kW unit. This batch, called Sinaus, was produced in the same way as the Sinfin material, but with a different ore as raw material. The composition of the material is similar to the Sinfin oxygen carrier, *cf.* Table 2. Here we present *preliminary results* from operation with this material in the 100 kW unit.

52 hours of stable operation was achieved using wood char, bituminous coal, and crushed wood pellets as fuel. Compared to ilmenite, gas conversion was higher (i.e. oxygen demand is lower), the CO<sub>2</sub> capture was as high or higher, and the solid-fuel conversion was significantly higher. No decrease in reactivity was observed during the testing.

#### Gas conversion

Gas conversion using Sinaus was higher than with ilmenite and similar to what was observed using the mixture of ilmenite and Buritirama ore during similar operational conditions. Figure 4 shows gas conversion using Sinaus and coal as fuel versus pressure drop in the fuel reactor and OC-to-fuel ratio during approximately 6 hours of testing. Each cross represents 1 minute of operation. The temperature in the fuel reactor was 963-976°C and the fuel power was around 65 kW. The OC-to-fuel ratio describes the oxygen availability in the fuel reactor. It is defined as

$$OC / fuel = \frac{\dot{m}_{OC} \cdot R_0 \cdot 1000 / M_{O_2} \cdot V_n}{\Phi_O (F_{CO_2,FR} + F_{CO,FR} + F_{CH_4,FR})}, \quad (9)$$

where  $M_{O_2}$  (g/mole) is the molar mass of oxygen and  $R_0$  is the mass ratio of available oxygen in the oxygen carrier. Around 90% gas conversion was achieved with a high bed in the fuel reactor and high OC/fuel ratio.

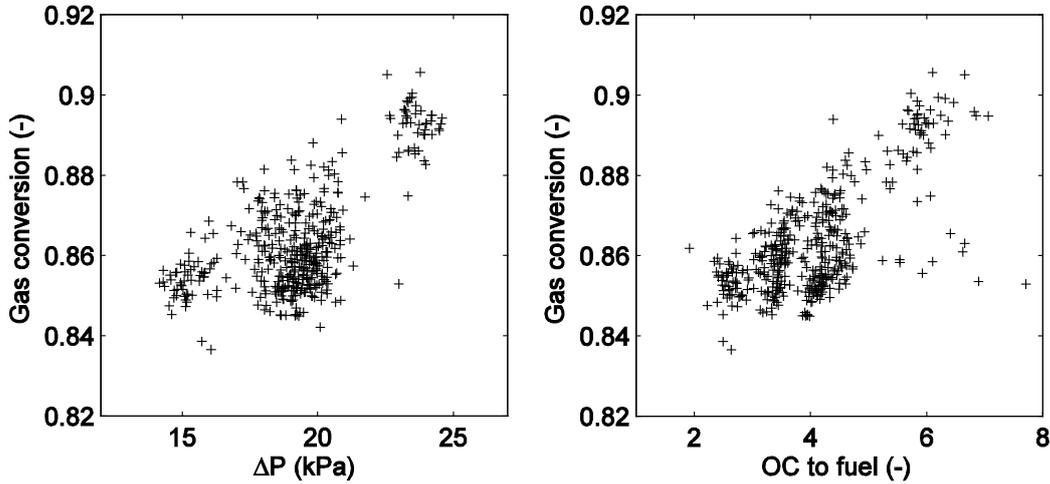


Figure 4: Gas conversion using Sinaus and Calenturitas coal plotted versus pressure drop in the fuel reactor (left) and OC-to-fuel ratio (right).

### Solid fuel conversion

The solid fuel conversion describes the fraction of solid fuel that is not converted to gas in the reactor system. It is obtained by comparing the amount of carbon introduced to the system with the fuel to the solid carbon exiting the system and ending up in the filters. Solid-fuel conversion from the 100 kW unit has been found to be 65% using ilmenite and pulverized coal [13] and 71% with Tierga iron ore as oxygen carrier and pulverized coal as fuel [14]. Using Sinaus as oxygen carrier the conversion is found to be significantly higher; for coal, the conversion was 86-95%, using wood char as fuel gave 74-98% solid-fuel conversion, and finally, the test with wood pellets resulted in 99% conversion. However, it should be noted that the size of the coal was larger during the tests with Sinfin; the average size was around 105  $\mu\text{m}$  with only 35 wt-% of the fuel passing the 90- $\mu\text{m}$  mesh sieve. Furthermore, the loss of unconverted char is expected to be significantly lower in a full-scale unit.

Solid fuel conversion was analyzed for almost all operation points during the 52 hours of testing. No correlation could be established between the solid fuel conversion and global circulation, pressure drop in the fuel reactor, or the fuel flow.

### Fate of S and N

Measurement gas from the fuel reactor is cooled and filtered before being passed through the analyzers. Steam is the main component of the FR flue gas, since a lot of steam is used to fluidize FR, CS, CR, and loop seals. Consequently, there is a substantial condensate flow from the FR sample gas. Condensate samples from the FR sample gas were collected on several

occasions during operation. By combining analysis of condensate with gas measurements using on-line instruments and Dräger tubes, it was possible to investigate the fate of fuel-N and fuel-S, as shown in figure 5. Dräger tubes were used to measure gas-phase H<sub>2</sub>S and NH<sub>3</sub>. NO and SO<sub>2</sub> are measured online. HCN was also measured but not detected. N<sub>2</sub> was measured with a gas chromatograph. It should be noted that the purge gas flow to the coal screw and pressure taps, which is normally N<sub>2</sub>, was replaced with argon. Hence, the only nitrogen entering the fuel reactor was fuel-N.

Each data point represents approximately one hour of stable operation without parameter changes. As can be seen in figure 5 for both nitrogen and sulfur, more reducing conditions leads to formation of more NH<sub>3</sub> and H<sub>2</sub>S. In these experiments, where coal was used as fuel, 5-10 wt-% of the fuel-N exited the reactor system with unconverted char and was found in the filtercake. The fulfilment of the nitrogen mass balance was 84-97%. 15-23% of the fuel-S was found in the filtercake and the fulfilment of the sulfur mass balance was 57-105%.

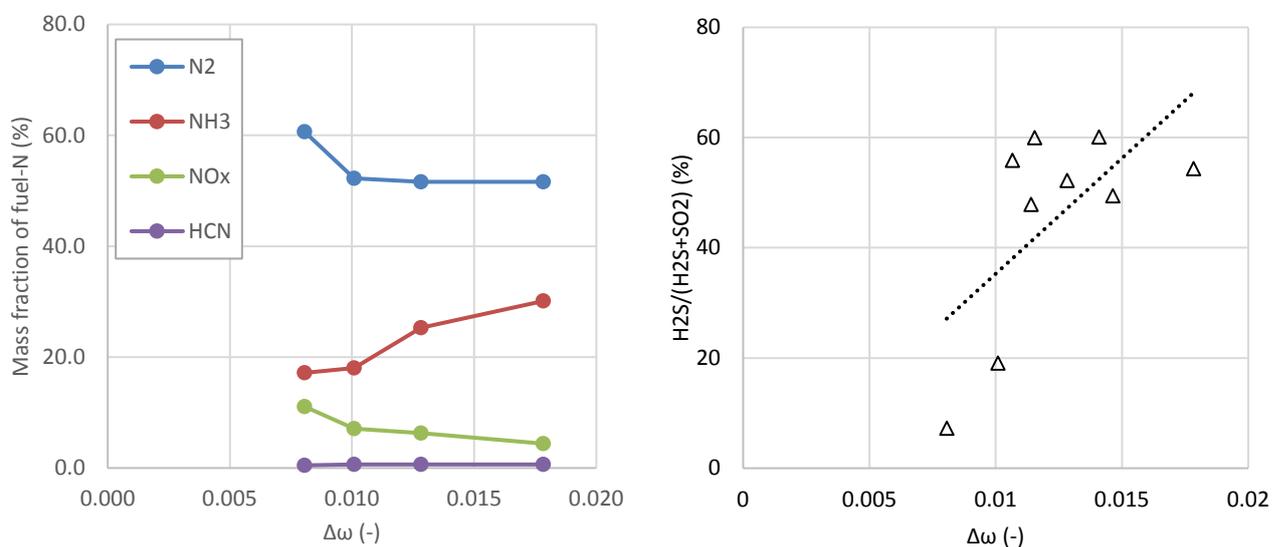


Figure 5: Fate of N (left) and S (right) during operation with Sinaus.

### Lifetime of the oxygen carrier

The lifetime of the Sinaus oxygen carrier as calculated from the production of fines during hot operation – with and without fuel – is shown in figure 6 as a function of the change in oxygen carrier conversion. There is a clear trend that higher oxygen turnover results in more production of fines, i.e. shorter particle lifetime. Each marker represents stable operation during 40-90 minutes. The markers on the y-axis correspond to operation without fuel, i.e. fully oxidized particles. There is a significant variation in fines production without fuel, which is not associated with, for example, circulation or gas flow in the air reactor. Directly after fuel operation is terminated, the production, or at least the elutriation, of fines, is higher than what would be expected, for a period of up to 30 minutes. Figure 6 shows data from operation with all fuels except the wood pellets. The expected lifetime of the Sinaus particles is hence 100-250 h, depending on the operational setting. This should be compared to what was found using ilmenite oxygen carrier, 700-800 h [13], and Tierga iron ore, 280-375 h [14]. However, those two studies concerned only one test each, whereas the data presented here represents more than

30 tests, hot operation during 55 h, and operation with fuel for more than 40 h. In summary, Sinaus has shorter expected lifetime than previously investigated iron-based oxygen carriers, but still probably sufficient for large-scale operation [2].

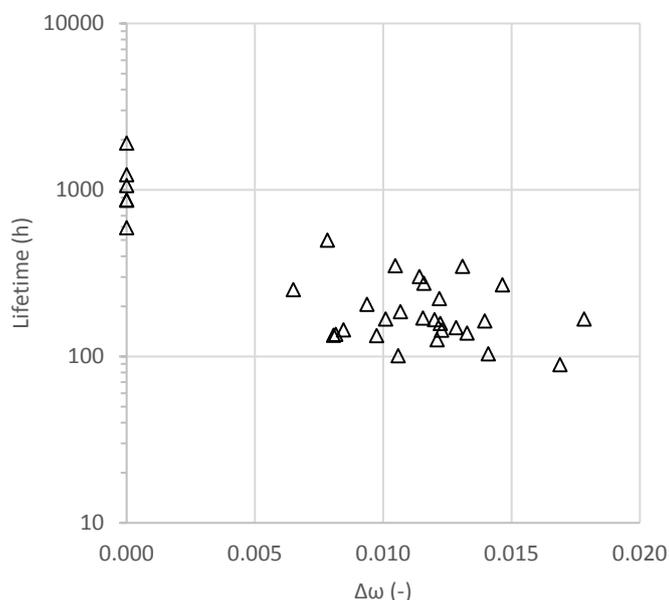


Figure 6: Expected lifetime versus change in oxygen carrier conversion.

#### Operation with wood pellets

Wood pellets (cf. Table 3) have not previously been used in the 100 kW unit. During 55 minutes of stable operation (figure 7), the only parameter variation was the fuel flow. A low fuel flow corresponding to a fuel power of 40 kW was employed during the first 28 minutes. This period was followed by a higher (60 kW) fuel flow. The oxygen demand was 23-27% during the lower fuel flow, and 28-30% during the higher fuel flow. This actually corresponds to a surprisingly high gas conversion, given that the fuel contained 74% volatiles and that the reactor system is not designed for using high-volatile fuels. The CO<sub>2</sub> capture was 95-98%. No higher hydrocarbons were detected.

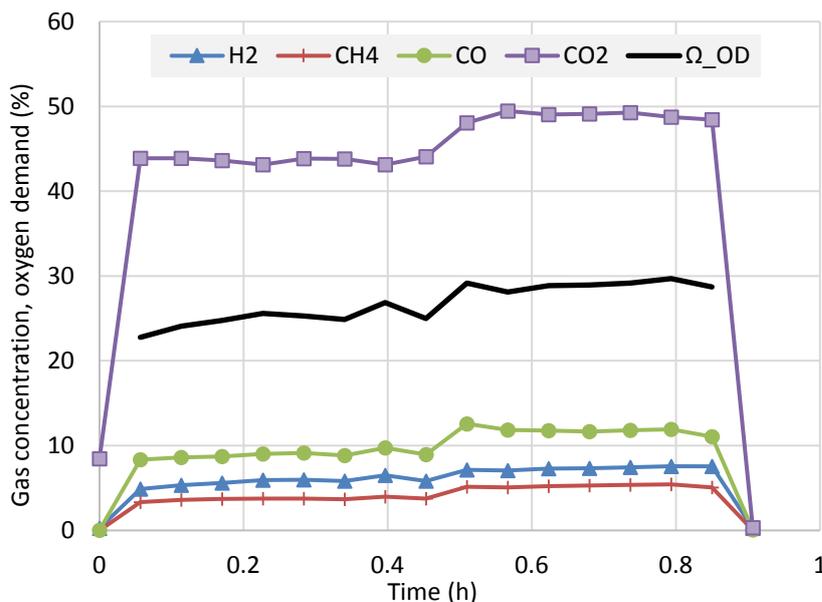


Figure 7: Operation with Sinaus using wood pellets as fuel: gas concentrations and oxygen demand versus time of operation.

## 4 Conclusions

In this paper we have described operation with manganese ores as oxygen carrier in the Chalmers CLC pilots. Performance as regards gas conversion, carbon capture and solid fuel conversion is better or much better compared to ilmenite as oxygen carrier. The drawback of these materials is the mechanical stability.

A new oxygen carrier called Sinaus was tested in the 100 kW unit. It showed high reactivity and gave high carbon capture – up to 99.7%. Furthermore, the solid fuel conversion was much higher than what has been observed in any previous operation with coal in the 100 kW unit. However, this result is probably largely due to the appropriate choice of fuel size.

The expected lifetime of the Sinaus material was found to be 100-250 h, which is not as high as previously tested iron-based oxygen carriers, but most likely sufficiently high for use in full-scale CLC applications.

An alternative to using only manganese ore as oxygen carrier is mixing with a more durable material. Here we have shown that mixing mechanically stable ilmenite with more reactive manganese ore can give important improvements reduction in fines production, and still give significantly increased gas conversion as compared to ilmenite.

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