# Högeffektiv syrebärare av billiga råvaror för användning i kemcyklisk förbränning av biomassa

Highly efficient oxygen carrier from cheap raw materials for use in chemical-looping combustion of biomass

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#### **Summary**

Chemical looping combustion is a novel combustion method that can capture carbon dioxide ( $CO_2$ ) without any costly and energy consuming gas separation. Thus, the technology has a unique potential for a radical decrease in the cost of carbon dioxide capture. This is possible because combustion air and fuel are never not in contact with each other. Instead, the oxygen is transferred from the air to the fuel by means of an oxygen carrier that circulates between two interconnected fluidized beds, the air reactor and the fuel reactor. The oxygen carrier constitutes the bed material and the air reactor largely resembles a normal circulating fluidized bed boiler. The exhaust gas from the fuel reactor consists of the combustion products, i.e. carbon dioxide and steam. The latter is easily removed by condensation, thus providing a stream of  $CO_2$ .

The goal of the project is to show that it is possible to use simple manufacturing methods to create a highly efficient oxygen carrier with cheap raw materials. Previous experiments have shown that the gas conversion when burning biomass increases dramatically when calcium manganite is used as bed material. Calcium manganite, CaMnO<sub>3-8</sub>, has several properties that make it very suitable as an oxygen carrier. Common oxygen carriers react with combustible gases to form carbon dioxide and water, while calcium manganite, when it reaches the fuel reactor, spontaneously releases oxygen in gaseous form. Combustible gases can then be burned by this oxygen, which facilitates the conversion in the fuel reactor. Trials in a pilot plant for chemical cyclic combustible gas by a factor of ten with calcium manganite compared to manganese ore. Furthermore, calcium manganite should be possible to produce from cheap natural materials, namely limestone and manganese ore.

In the first stages of the project, different manganese ores, production methods and production conditions including sintering temperature were examined. The resulting calcium manganite materials were evaluated with respect to physical and chemical properties, to assess the integrity of the material as well as the reactivity. This resulted in a selection of ore and conditions of production that were used to produce a batch of 1 kg for examination in continuous CLC operation in a 300 W CLC pilot unit.

The investigation in the 300 W reactor system involved CLC operation using syngas and methane as fuels. A total of more than 30 h of operation with fuel was performed, in addition to experiments showing the oxygen release when adding inert gas to the fuel reactor. Operation was successful, i.e. neither agglomerations, significant attrition nor any loss in reactivity was observed. The formation of fines was higher initially, but gradually fell to a low level, below 0.1%/h. The decrease is likely an effect of rounding effects, as the initial particles were highly non-spherical. The operation with both syngas and methane showed high conversion. Post-operation reactivity tests in a batch fluidized bed reactor, showed that the reactivity after 29 h of operation was the same, both for syngas and for methane. XRD verified that the material was composed of mainly CaMnO<sub>3</sub>.

In conclusion, the project was quite successful and provided good evidence that low-cost raw materials, and a simple production method, can be used to manufacture an oxygen carrier of high reactivity and high material integrity, i.e. with low attrition and no chemical deterioration of the material.

## Introduction

Chemical-Looping Combustion (CLC), is a fundamentally novel principle for oxidizing gaseous, solid or liquid fuels. CLC has a unique advantage in being able to create an essentially pure  $CO_2$  stream, ideally without any costly and energy demanding gas separation. The concept involves the transfer of oxygen from air to fuel by means of metal oxide particles, "the oxygen carrier", which circulates between two fluidized beds, i.e. the air and the fuel reactor, Figure 1. Because the air and the fuel are being kept separate, the combustion products, i.e. carbon dioxide and steam ( $CO_2$  and  $H_2O$ ), are achieved in a separate stream. Thus,  $CO_2$  and  $H_2O$  are not diluted by the nitrogen ( $N_2$ ), and remaining oxygen ( $O_2$ ), from the air used in combustion. The steam is easily removed by condensation, hence an essentially pure carbon dioxide is uniquely obtained without any costly gas separation. This is possible because fuel and combustion air are never mixed.



Figure 1. CLC principle.

The technology has large similarities to conventional combustion of solid fuels in circulating fluidized-bed (CFB) boilers, and the reactor system is essentially identical to thermal gasification in dual fluidized beds. For the application to solid fuels, like biomass, the cost of  $CO_2$  capture with CLC has been estimated to 10-30  $\notin$ /tonne of  $CO_2$ , and energy penalty is also small compared to established  $CO_2$  capture technologies <sup>1</sup>.

The cornerstone of the technology is the oxygen-carrier, which must meet a number of criteria to be relevant. These include adequate reactivity, fluidizability, sufficient lifetime, reasonable cost and low risk with respect to health, safety and environment (HSE). Oxygen-carriers can be subdivided into two main categories, 1) cheap natural minerals and industrial waste materials and 2) manufactured materials. The first category includes ores of ilmenite, manganese and iron. The second category involves manufactured materials based on oxides of nickel, copper, manganese and iron, as well as combined oxides. Nickel materials are costly and come with significant risks with respect to health. Copper materials are also costly. Most attractive materials from a reactivity point of view are copper and combined manganese oxides. This is because these materials do not only react with combustible gases, but also have the ability to spontaneously release oxygen, which is normally referred to as the Chemical-Looping with Oxygen Uncoupling (CLOU). Looking at the criteria noted above, calcium manganite is very attractive as it can be produced from low-cost minerals, has shown high lifetime and even full conversion in CLC pilots <sup>2</sup> and has small HSE risks. It also has CLOU properties, which explains why it can reach full gas conversion in pilot operation.

# Method

The general manufacturing scheme is shown in Figure 2



Figure 2: The manufacturing process visualized with a flow chart

Starting with raw materials, such as different manganese ores, limestone and PVA (polyvinyl acetate), the raw materials had to be prepared for granulation. The manganese ore was crushed into smaller pieces and limestone was calcined to get calcium oxide. Both manganese ore and lime/limestone were then ball milled and sieved to get the preferred sizes. Smaller sizes are desirable since there is an increased contact area per volume and therefore the reactivity between the calcium and the manganese ore is higher. PVA powder was mixed with water and was heated until it dissolved. This PVA solution was used as binder for the manganese ore and calcium oxide in the granulation. The granulation process involves the mixing and forming needed for the ingredients to combine into particles. Two simple granulation procedures, batch added material (BaM) and continuously added material (CaM), where used. In BaM the dry ingredients were added first to a food processor, and the binder was sprayed unto the material while stirring, whereas in CaM the dry particles were added in portions with addition of the binder with spraying in between, again under continuous mixing.

The granulated particles were then sintered at high temperature to form calcium manganite. Lastly the oxygen carriers were sieved to obtain a size range of 90-300 µm.

Testing the physical attributes of the oxygen carriers involved examining the density, the crushing strength and the attrition rate. The crushing strength gives some indication of the ability of a material to withstand mechanical breakdown. The jet-cup attrition rate shows mechanical breakdown of particles subjected to a high velocity air jet at ambient temperature and gives a first indication of the risk for mechanical breakdown under actual chemical-looping operation. Although helpful for initial screening, crushing strength and jet-cup attrition are only moderately correlated to the performance in actual operation at high temperature and with reactions taking place. Thus, the only safe assessment of the particle integrity is many hours of actual pilot operation. After sieving and weighing the oxygen carrier, the wt% was calculated for each size range and the result was taken into consideration when choosing the best manufacturing process. The size range is important because of the size constraints for fluidization. The particles cannot be too small, or they will be elutriated and leave the reactor system with exiting gas. Further, they should not be too large as this would reduce circulation and reactivity.

Furthermore, reactivity of samples were investigated in a fluidized-bed batch reactor, described in <sup>3</sup>. Here, the sample was subject to alternatingly oxidizing and reducing conditions, with a period of inert gas during the shifts to prevent oxidizing and reducing gases to mix. As oxidizing gas with 5 or 10%  $O_2$  in  $N_2$  was used while the reducing period involved fuel gas, either a gas of 100% methane (CH<sub>4</sub>) or syngas containing 50% CO and 50% H<sub>2</sub>. In addition the oxygen release was examined by using inert gas instead of fuel in the "reducing" period.

Further, samples were examined using SEM (Scanning Electron Microscopy), EDX (Energy Dispersive X-ray analysis) and XRD (X-Ray Diffraction). EDX was used to identify elemental composition and XRD to verify the presence of calcium manganite, CaMnO<sub>3-δ</sub>.

Images of the oxygen carrier particles were taken in the SEM (Scanning Electron Microscopy) to see if any agglomerations, pores or cracks could be seen. In addition images by light microscope were used to study the shape of the particles.

Based on these results, a production method, production parameters and an ore were finally selected and a batch of 1 kg was produced for investigation in extended CLC operation in a 300 W pilot.

## Results

#### Stage 1. The manufacturing process results

This stage involved a first study of the manufacturing process using the South American manganese ore Buritirama and resulted in 9 different samples. The samples were examined with respect to physical properties, i.e. attrition, crushing strength and size distribution, and, based on this, one method, BaM, was selected for the next stage.

## Stage 2. Selection of manganese ore

In stage 2 three manganese ores were used in the manufacturing, i.e. Eramet HM, Braunite and Buritirama, the first originating from Gabon and supplied by Eramet and the second of unknown origin supplied by Sibelco. In this stage different sintering temperatures were investigated in an iterative process. In total 12 samples were produced. The first 4 samples were totally agglomerated during sintering and had to be discarded and lower temperatures were used in the following.

In this stage crushing strength, attrition, density, and particle structure were examined, as well as chemical properties. Chemical properties were examined in a fluidized-bed batch reactor and involved both oxygen release and reactivity with both methane and syngas. Based on physical parameters, three samples, S8-S10, were selected for batch reactor testing. Table 1 shows the ability of the material to release oxygen, and sample S8 showed the best performance. Further, the reactivity with syngas is shown in Figure 3, again indicating that sample S8 is superior. S8 showed lower conversion with methane than S9 and S10, but on the other hand it showed lower attrition than these. In fact, it showed the lowest attrition of the 8 samples investigated. Further, XRD verified that CaMnO<sub>3-δ</sub> was the main component of S8. Based on these results, Eramet, from which sample S8 was produced, was selected, and the production parameters for sample S8 were the starting point for the next iteration.

	Met	hane	Synga	s used	Syngas fresh		
Sample	Pre reaction	Post reaction	Pre reaction	Post reaction	Pre reaction	Post reaction	
S8	22.8%	22.5%	22.5%	22.5%	22.8%	22.8%	
S9	18.0%	17.7%	17.7%	11.3%	18.0%	12.0%	
S10	23.5%	21.0%	21.0%	21.9%	23.5%	21.3%	

Table 1. Oxygen uncoupling ability in wt%



Figure 3. Syngas conversion versus oxygen carrier mass-based conversion ( $\omega$ )

#### Stage 3. Selecting production parameters

In the third stage Eramet was used for making calcium manganite using the CaM method. The CaM scheme involved limestone or CaO, two different particle sizes and at two different sintering temperatures, Table 2. For comparison two samples were made by extrusion, using Eramet, limestone and sintering temperatures of 1240°C (Ex1) and 1265°C (Ex2). Thus, nine samples were made, of which one, SP4, failed, being so hard to crush that no particles could be made from this sample.

Sintering temperature	1265°C	1265°C	1240°C	1240°C
Size raw material	<90 μm	<45 μm	<90 μm	<45 μm
Limestone	SP1	SP2	SP5	SP6
CaO	SP3	SP4		SP7

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First crushing strength was measured, showing good results for all particles tested. Then attrition was tested and all samples except Ex1 and SP7 had acceptable attrition rates, Table 3.

	SP1	SP2	SP3	SP4	SP5	SP6	SP7	Ex1	Ex2
Attrition rate (%/h)	1.12	1.44	1.28	-	1.32	1.4	2.48	3.28	0.84

Two samples, SP2 and SP6, were rejected due to a very small amount of particles in the right size range. Then, six samples were examined in a batch fluidized-bed reactor for oxygen release and reactivity versus methane and syngas. CLOU behaviour and reactivity tests were made at 950°C and 1050°C and then again at 950°C. An example of results is shown in Figure 4, showing gas conversion versus oxygen carrier mass-based conversion. The two samples produced by extrusion had the highest conversion, closely followed by SP3 and SP5, all having a conversion above 90%.



Figure 4. Gas conversion of syngas versus mass-based oxygen carrier conversion at 950  ${
m C}$ 

A summary of the ranking of the samples based on O<sub>2</sub> release and reactivity with methane and syngas is seen in Table 4. Here, SP1 and SP3 show higher oxygen release, while SP5 and SP7 have better reactivity with methane and syngas, and SP5 is best for both methane and syngas. Although Ex2 was

a bit more reactive and showed lower attrition than the others it was not considered, as it was the purpose of this project to investigate a simpler manufacturing method and extrusion was only included for comparison.

Table 4. Ranking of reactivity/oxygen release. Cycling tests were done at 950  $^{\circ}$  (before), then at 1050  $^{\circ}$  and then again at 950  $^{\circ}$  (after). (Experimental difficulties prevented the case: "skipped")

Sample	950 before [methane]	1050 [methane]	950 after [methane]	950 before [syn]	1050 [syn]	950 after [syn]	950 before [O2]	1050 [O2]	950 after [O2]
SP1	4:th	3:rd	3:rd	4:th	4:th	3:rd	2:nd	2:nd	1:st
SP3	3:rd	4:th	4:th	1:st	2:nd	_skipped	1:st	1:st	2:nd
SP5	2:nd	1:st	1:st	2:nd	1:st	1:st	4:th	4:th	3:rd
SP7	1:st	2:nd	2:nd	3:rd	3:rd	2:nd	3:rd	3:rd	4:th

From the four materials, it was possible to exclude SP1 because of very low reactivity, figure 4, and SP7 for having much higher attrition than the others, Table 3. Noting that SP3 and SP5 have almost similar attrition, SP5 is obviously the better one, having the highest reactivity, Table 4.

Based on these results one production scheme was selected and 1 kg of oxygen carrier was produced.

# Stage 4. Manufacture of 1 kg of material

In stage 4, 1 kg of material has been manufactured using the production parameters for SP5. To summarize this method, it meant that the raw materials, manganese ore Eramet HM and limestone, were crushed and milled to a size  $<90 \ \mu\text{m}$  and mixed to a homogeneous blend with the mass ratio 1.25/1. Then the material was granulated according to the CaM method and sintered at a temperature of 1240°C. The sintered material was easily crushed and then sieved to a size range of 90-250  $\mu\text{m}$ .

The material was used in continuous operation in a 300 W CLC pilot in Stage 5. A photo of the particles produced is seen in Figure 5. A comparison to particles previously made in spray-drying is shown to the right.



Figure 5. Left, particles from the 1 kg batch. Right, example of spray-dried calcium manganite from previous work <sup>4</sup>

As can be seen the 1 kg batch had significantly lower sphericity than the spray-dried material. The cause for this is likely a combination of the production method, sintering and crushing, and rather large particle size of the raw material used in manufacturing.

Documentation of stages 1-4 involves two reports, <sup>5,6</sup>.

# Stage 5. Validation of material through operation in 300 W CLC pilot

After a one-year delay, this work was started. The results are evaluated and a first draft of a coming publication presenting the results has been made <sup>7</sup>. The work will also be part of a PhD thesis <sup>8</sup>.

The material was investigated in a 300 W CLC pilot shown in Figure 6. Circulation is driven by particles being elutriated from the bed of the air reactor (blue), then falling down in the widening top part and being led into the upper loop seal (green) leading into the fuel reactor (red). The circulation increases the bed height of the fuel reactor creating the pressure needed to drive the circulating flow of particles back into the air reactor via the lower loop seal (green). A more detailed description of the 300 W unit and how it is operated is given in <sup>9</sup>.

The small size of the reactor system is a great advantage for long-term testing of oxygen carrier materials.



Figure 6. The 300 W CLC pilot. Left: Air and fuel reactors. Right: Reactor system including top section, pipes for pressure measurements, thermocouples, and introduction of gas

# Oxygen release experiments.

Prior to fuel operation as well as after and in between periods fuel operation periods oxygen release was examined by operating the system with inert gas in the fuel reactor. Oxygen is then absorbed in the air reactor and spontaneously released in the fuel reactor. The oxygen concentration in the fuel reactor was 2-5% at 850°C and 3-8% at 950°C, with the higher numbers seen just after temperature increases, whereas lower numbers were predominant for more stable operation.

Examination of oxygen release in a fluidized-bed batch reactor showed a somewhat higher release at higher temperature, Figure 7, and a comparison of fresh material with used material, i.e. material after 29 h of fuel operation in the 300 W unit, showed that the oxygen release capacity decreased a bit after operation.



*Figure 7. Oxygen uncoupling in an inert atmosphere of the batch reactor as a function of conversion of 15 g calcium manganite oxygen carrier under varying temperatures.* 

In Figure 7, the release is shown versus the mass-based conversion,  $\omega$ . It can be noted that the release ends at a  $\Delta\omega$  of around 0.003, which means that the oxygen released corresponds to 0.3% of the mass of the oxygen carrier. In actual operation, the expected cyclic conversion would be much larger, with a  $\Delta\omega$  of up to 2%. This also means that the majority of the fuel conversion would not be from oxygen released but through the direct reaction of gas species with the oxygen carrier.

#### Fuel operation in 300 W

The fuel operation involved two batches of material, the first was operated 2 h with syngas. i.e. a 50/50 mixture of CO and H<sub>2</sub>, and second batch was operated 29 h with methane (CH<sub>4</sub>).

Different temperatures and fuel flows were used, and the  $CO_2$  yield, i.e. the conversion to  $CO_2$ , is shown in Figure 8. Here the fuel flow is represented in the x-axis as the "specific bed mass", i.e. the ratio of the fuel reactor bed mass to the fuel flow in terms of thermal power.

It can be seen that syngas was completely converted to  $CO_2$  and  $H_2O$  at 915°C even though high fuel flows were used. Full conversion was also seen for most of the operation at 850°C. Only at the very highest fuel flow the conversion dropped to 99.4%.

At the higher temperature the conversion of methane was high, and even complete at low fuel flows. A most distinct decrease with temperature is seen. The results shown by stars are averages from long term operation and reflect a falling conversion that can be explained by a gradual decrease in bed mass, as measured by falling pressure drop over the beds. The decrease in bed mass is associated with elutriated material and causes the circulation to decrease. As will be shown below, it is not associated with any loss in reactivity.



Figure 8. Gas conversion in 300 W operation. Red: syngas, 850 ℃ filled circles and 915 ℃ empty circles. Other colours: methane 850-950 ℃.

## Attrition

Elutriated fines were recovered in filters downstream of the reactors, see Table 5. The common filter is located after the mixing of the gas flows from the air and the fuel reactor. The AR and FR filters collect fines going into the gas analyzers, whereas the FR water seal is where the condensate from the steam produced in the fuel reactor is collected. Batch one was only in fuel operation for 2 h with syngas, and the corresponding attrition was around 1%/h. Data for the first 8 h with methane show a lower loss, around 0.3%/h. As can be seen the loss falls with time of operation. This is expected and can be explained by rounding off of the not so spherical particles, as well as breakage of weak particles. But apart from the initial hours, the attrition is low, below 0.1%/h in the later part of operation.

Initial	Test	Common	AR	FR	FR	Total	Fuel	Attrition	Average	
OC		filter (g)	filter	filter	water	loss	operation	(wt%/h)	attrition	
load			(g)		seal	(g)	time (h)		(wt%/h)	
(g)					(g)					
300.0	Syngas_Day 3	4.8	1.3	0.1	-	6.2	2	1.03	1.03	
	CH <sub>4</sub> Day 2-4	2.0	0.6	0.2	3.7	6.5	8	0.27		
200.0	CH <sub>4</sub> Day 5	0.0	0.1	0.0	1.7	1.8	5	0.12	0.15	
300.0	CH <sub>4</sub> Day 6	0.0	0.3	0.1	1.0	1.4	5	0.09	0.15	
	CH <sub>4</sub> _Day 7,8	0.1	0.3	0.1	0.6	1.1	5.6	0.07		

Table 5. Attrition of calcium manganite in the 300 W reactor.

In Figure 9 it is clearly seen that a rounding off of the particles has increased the sphericity after 29 h of operation.



Figure 9. Left: fresh material. Right: material after 29 h of operation in 300 W unit.

## Post operation analysis

Firstly, the reactivity of the oxygen carrier particles after 29 h of operation with methane, were compared with the fresh material. This was done in a batch reactor of quartz with an inner diameter of 22 mm. The material was subject to cycles of oxidizing and reducing conditions. Oxidizing conditions involved a flow of 900 mL<sub>n</sub>/min of 5% oxygen in nitrogen, and the reducing cycles involved either 450 mL<sub>n</sub>/min of methane or 900 mL<sub>n</sub>/min of syngas. Between oxidizing and reducing conditions inert gas, that is N<sub>2</sub>, was introduced to safely avoid any mixing of reducing and oxidizing gases. For methane tests 15 g of oxygen carrier was used, whereas 2 g of oxygen carrier diluted in 13 g of sand was used for the syngas experiments, to compensate for the much higher reactivity. An example of a reduction period with methane is shown in Figure 10.



Figure 10. Batch reactor test with methane at 950  $^\circ$  showing reduction period.

Note the time delays reflecting the time needed for the gas to reach the analyzers. The oxygen curve has been manipulated by subtracting the oxygen concentration versus time for similar experiments done with an inert sand bed instead of oxygen carrier. Thus, the oxygen concentration curve only shows oxygen released. Further, it can be added that the hydrogen peak is an artifact caused by the inbuilt correction for  $CO_2$  and  $CH_4$ . Thus, the hydrogen peak can be explained by the correction for  $CO_2$  being much faster than the actual effect of  $CO_2$  on the H<sub>2</sub> analyzer. Experiments with adding various gases to the analyzer clearly shows that changes in gas concentrations are accompanied by positive or negative peaks in H<sub>2</sub> that disappear after some time of stable operation, clearly indicating that the inbuilt correction works well under stable conditions. There is also back-mixing which affects the shape of the curves.

As can be seen there is high conversion of methane initially, with methane concentration increasing as the material is converted. Figure 11. shows gas conversion of methane versus time. The curves start after the initial lowering of  $\omega$  associated with oxygen release under the inert phase and the initial transient in concentrations. The increase in conversion at the end of the curve is likely an artifact caused by uncertainties associated with measuring low gas concentrations at the end of the transient. As can be seen the reactivity of the material increases very significantly with temperature. It can also be seen that the curves for used and spent material are rather similar, the conversion of the spent material is even slightly higher except for the lowest temperature. Thus, 29 h of operation has no negative effect on the reactivity of the material.



*Figure 11. Methane conversion of material used in 29 h of operation as compared to fresh material versus mass-based conversion of the oxygen carrier.* 

Figure 12 similarly shows the conversion of syngas for fresh and used material. The same artifact as observed with methane is seen at the end of the conversion. For syngas a similar positive effect of temperature is also seen, albeit much smaller, and the curves of the three highest temperatures are very close. Notable is also the insignificant differences between fresh and used material. Thus, it can

be safely concluded that the reactivity has not been reduced during the 29 h of operation, neither for syngas nor methane.



Figure 12. Syngas conversion of material used in 29 h of operation as compared to fresh material versus mass-based conversion of the oxygen carrier.

## Discussion

The mass to fuel ratio of the methane tests in the batch fluidized-bed is 56 kg/MW, and, for the syngas tests the mass to fuel ratio is 23 kg/MW. This is much lower than in the operational tests that were conducted in the range 150-800 kg/MW. Despite the low mass to fuel ratio, syngas conversion is 100% at  $\omega$ =0.99 and temperatures from 900°C and more. For methane, conversion at  $\omega$ =0.99 and 950°C is 50%. If this number is extrapolated to, for example, 200 kg/MW, the conversion would be above 90%. Thus, it can be concluded that conversion is much higher in the batch reactor.

This can be explained in terms of the two-phase theory of fluidization, according to which only a small fraction of the gas will move upwards inside the dense particle phase of a bubbling bed, whereas the majority of the gas will travel upwards in a dilute phase at high velocity, the consequence being poor contact between gas and solids. At the lower bed height of laboratory batch reactor, the two-phase flow is less developed, thus giving better contact.

However, in the full scale, assuming a fuel reactor designed similar to the riser of a circulating fluidized-bed (CFB), the conditions are much different from a bubbling bed. In such a riser, perhaps 40-50 m high, bed material would be transported upwards providing good contact between gas and solids. The bed mass typically used in commercial circulating fluidized-bed boilers is 150-350 kg/MW<sub>th</sub>. Thus, the results obtained in the batch reactor with 23-56 kg/MW, clearly indicate that high gas conversion should be expected under conditions expected for the full scale.

## Conclusions

Using natural manganese ores in the production of calcium manganite was investigated in order to see whether such ores of low cost would be suitable raw material in the production of high-performance oxygen carriers. Several iterations were made involving testing of different ores and two granulation methods and the variation of the parameters of production, e.g. sintering temperature. Based on this, a selection of method, raw materials and procedure was made and a batch of 1 kg was produced. The subsequent investigation of this material in a 300 W CLC unit during more than 30 h of operation showed:

- Operation was successful with no operational difficulties, no agglomerations, small attrition and no loss in reactivity.
- Formation of fines was higher initially, up to 1%/h, but gradually fell to a low level, below 0.1%/h. The decrease is likely an effect of rounding effects, as the initial particles were highly non-spherical. This was likely an effect of the raw material, after crushing and ball milling, still containing rather large particles, i.e. up to 90 µm. After 29 h of operation particles were more spherical but were nevertheless still quite non-spherical. A modification of the production method to give more spherical particles would likely have resulted in even lower attrition.
- Operation with both syngas and methane showed high gas conversion.
- Post-operation reactivity tests in a batch fluidized bed reactor, showed that the reactivity after 29 h of operation was the same, both for syngas and for methane.
- XRD verified that the material was composed of mainly CaMnO<sub>3</sub>

In conclusion, the project was quite successful and provided good evidence that low-cost raw materials and a simple production method can be used to manufacture an oxygen carrier of high reactivity and high material integrity, i.e. with low attrition and no chemical deterioration.

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