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Chemical-looping Combustion CO₂ Ready Gas Power

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Abstract

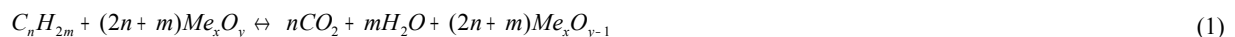
This paper presents results from a 30-month project devoted to taking the chemical-looping combustion (CLC) technology to the next level of development. The project is part of the EU's Sixth Framework programme with support from the CCP (Carbon Capture Project) and has mainly focused on the critical issues for an up-scaling of the technology. In an earlier project the CLC technology was demonstrated successfully for the first time for 100 h using Ni-based oxygen carrier particles using natural gas as fuel. The current project has built on these experiences and: i) established industrial-scale NiO particle production with suitable commercial raw materials. Oxygen carrier particles have been produced with both spray-drying and impregnation and investigated extensively with respect to parameters important for CLC operation, such as reactivity in batch and continuous operation, strength, defluidization phenomena, operation at high temperatures and effect of impurities such as H₂S in the fuel; ii) extended operational experience in long term tests of particles in the available 10 kW prototype for more than 1000 hours combustion and iii) successfully scaled-up and operated the process in a 120 kWth combustor using syngas and natural gas. Further, the project has included extended and verified modelling of the reactor system for scale-up in addition to process and technology scale-up and economic assessment. The paper will present the main results of the project.

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1. Introduction and methodology

Chemical-looping combustion (CLC) is a combustion technology where an oxygen carrier is used to transfer oxygen from the combustion air to the fuel, thus avoiding direct contact between air and fuel. The technique involves the use of metal oxide particles with the purpose of transferring oxygen from an air reactor to a fuel reactor. In the fuel reactor, the fuel in gaseous form reacts with the metal oxide according to reaction (1) and in the air reactor the reduced metal oxide is reoxidized according to reaction (2);



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The total amount of heat evolved from reaction (1) plus (2) is the same as for normal combustion where the oxygen is in direct contact with the fuel. However, the advantage with this system compared to normal combustion is that the CO₂ is inherently obtained in a highly concentrated stream ready for sequestration and there is no costs or energy penalties for gas separation. CLC uses well-established boiler technology very similar to circulating fluidized bed boilers, which also means that costs can be assessed with great accuracy. Thus, CLC could play a significant role in achieving large reductions in emissions of CO₂ and hence combating global warming.

The critical issues that need to be addressed for an up-scaling of CLC technology for gaseous fuels to a demonstration step have been identified together by the industrial and university/research partners. It was the objective of the CLC Gas Power project to establish and validate solutions to these topics, thereby enabling a future demonstration phase:

- 1) Identify process suitability of raw materials commercially available at competitive prices.
- 2) Establish commercial particle production techniques for up-scaling from laboratory freeze-granulation.
- 3) Adapt alternate particle production paths with potentially lower production costs, such as impregnation.
- 4) Investigate possible effects of gas impurities on particles, primarily sulfur.
- 5) Perform long term testing to confirm mechanical and chemical integrity of particles.
- 6) Modify an existing CFB rig to intermediate CLC demonstration unit at 100-200 kWth scale.
- 7) Extend and verify modelling capability for process performance optimisation and scale-up.
- 8) Perform process and technology scale-up to prepare for industrial 20-50 MWe demonstration unit.

The project is part of the phase II of CCP (CO₂ Capture Project via Shell), and has been carried out in close collaboration between universities, research institutions and industry: i) Chalmers University of Technology, (Chalmers), Sweden, ii) Consejo Superior de Investigaciones Científicas (CSIC), Spain, iii) Vienna University of Technology (TUV), Austria, iv) Tallinn University of Technology (TUT), Estonia, v) ALSTOM Power Boilers (APB), France and vi) Shell Global Solutions International BV, Netherlands.

This paper will present the main results of the project with special focus on the oxygen carrier development and testing. It is important to develop an oxygen carrier which has characteristics important for use in a CLC unit, such as high reactivity, resistance towards attrition and which can be produced in large quantities at reasonable cost.

2. Oxygen Carrier Production and Evaluation

In the first phase of the project approximately 40 different oxygen carriers based on NiO with NiAl₂O₄ were prepared by freeze granulation. Here different commercially available NiO and α- Al₂O₃ powders were used in

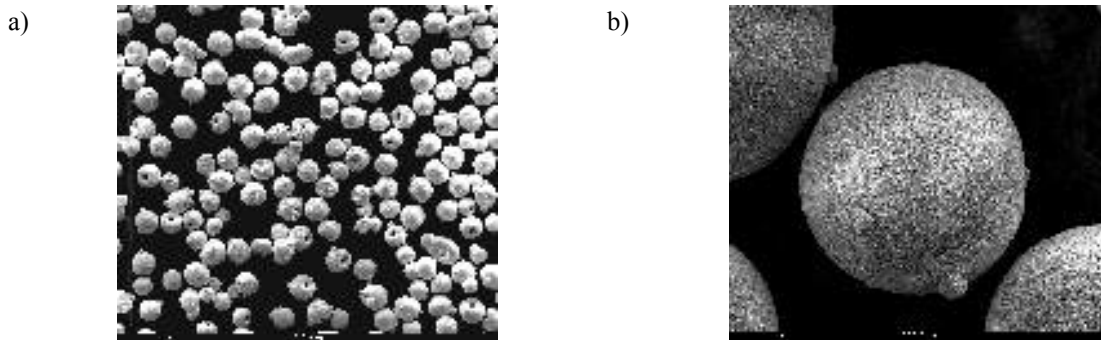


Figure 1. Scanning electron microscope image of some spray-dried particles

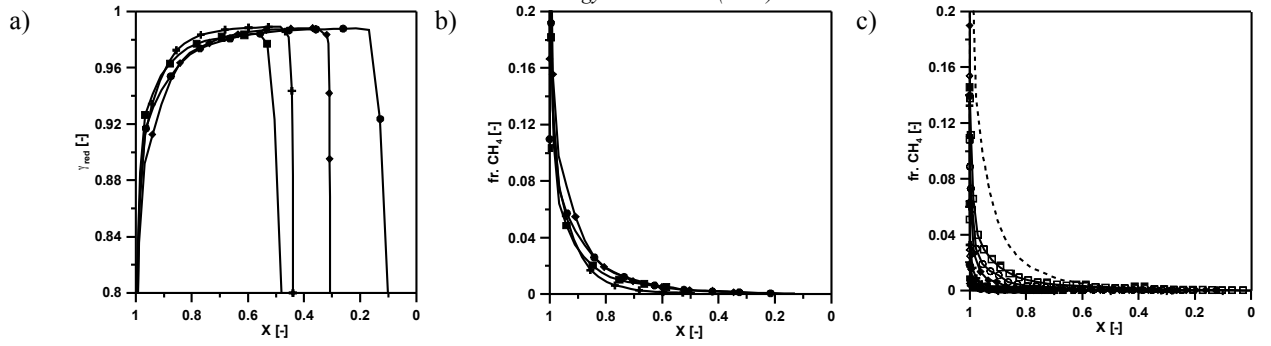


Figure 2. a) The gas yield to CO₂ for Ni-based material based on Novamet refractory grade, sintered at different temperatures (N-VITO), b) the methane fraction from the outlet for the particles in Fig. 2a and c) the methane fraction for some oxygen carriers doped with MgO. The dashed line indicates the conversion for the N-VITO particle. For a description of the actual Mg-doped carriers, see the work by Jerndal et al.

the preparation stage. The oxygen carrier materials were investigated with respect to parameters important for CLC, such as reactivity under alternating oxidizing and reducing conditions, mechanical strength and defluidization phenomena. The most promising materials were then prepared using spray-drying, a commercial method of particle production. In parallel, oxygen carriers were prepared by the impregnation technique, a common method of preparing commercial catalysts.

2.1. Particle production using industrial methods

Oxygen carrier particles with high sphericity, good free-flowing properties and homogeneity on the micro-scale, were prepared by the industrial spray-drying method, using commercial raw materials. In order to do so, a powder mixture of NiO, α -Al₂O₃ or MgAl₂O₄ and/or MgO and/or Ca(OH)₂ were dispersed in deionised water with the necessary organic additives. A further description of the raw materials used can be found in the papers by Jerndal et al. Appropriate amounts of the above materials were weighed before suspending in deionised water. The suspension was homogenized either by milling in a planetary ball mill for small quantities or by means of an horizontal attrition mill for larger amounts. The water-based suspension was continuously stirred with a propeller blade mixer while being pumped to the 2-fluid spray dry nozzle, positioned in the lower cone part of the spray drier (type 6.3-SD, Niro, Denmark). After spray drying, the fraction between 106 and 212 μ m were separated from the rest of the spray dried product by sieving the chamber fraction. In order to obtain oxygen carrier particles with sufficient mechanical strength, sintering was performed in air at at top temperatures in the range of 1300°C to 1500°C for 4 hours, using high temperature furnaces (Entech, Sweden; Bouvier)

In addition to the spray-dried particles, a new oxygen carrier was prepared by hot incipient wet impregnation at CSIC using NiO as active phase and α -Al₂O₃ as support. Commercial γ -Al₂O₃ particles of 100-300 μ m were sintered in a furnace at 1150°C for 2 hours to obtain the support. The oxygen carrier was prepared by addition over the hot α -Al₂O₃ (80°C) of a volume of a saturated solution (6 M) of Ni(NO₃)₂·6H₂O at 60-80°C. An oxygen carrier with a NiO content of 18% was obtained by applying two successive impregnations followed by calcinations at 550°C, in air atmosphere for 30 minutes. Finally, the oxygen carrier was calcined for 1 hour at 950°C, obtaining a material with adequate properties to be used as oxygen carrier.

2.2. Oxygen carrier screening

The oxygen carriers prepared by freeze granulation and spray drying were tested with respect to physical properties, chemical composition, gas conversion under reducing and oxidizing conditions as well as rate of reduction. The reactivity investigation was carried out in a batch fluidized bed reactor where the oxygen carriers were exposed to alternating CH₄ and 5% O₂. The oxygen carriers prepared by spray-drying displayed a remarkable similarity when compared to oxygen carriers prepared from the same starting material by freeze-granulation. Almost all of the oxygen carriers prepared showed very high reactivity with methane. The mechanical strength and defluidization behavior varied between the tested materials. The defluidization of these oxygen carriers was most likely to occur for highly reduced particles, at low fluidizing velocities. The apparent density and crushing strength of the oxygen carriers could be increased by increasing the sintering temperature. However, the fraction of unreacted CH₄ was fairly unchanged when the sintering temperature was increased. The apparent density and crushing strength could also be increased by increasing the sintering time. Further, increasing the sintering time resulted in a clearly improved conversion of CH₄. A material based on Novamet refractory grade NiO and Almatix 3000SG Al₂O₃ was chosen to be produced for initial large scale production. This material, referred to as N-VITO had a combination of high reactivity with methane, high mechanical strength and low tendency for defluidization. Figure 2a shows the gas yield for some of these types of oxygen carriers sintered at different temperatures. The fraction of methane from the outlet of the reactor is seen in Figure 2b. It was also found that the addition of MgO or the use of MgAl₂O₄ as the 'inert' improved the methane conversion, see Figure 2c, where a series of different Mg-based materials were investigated. Hence a larger batch of material was produced, which was similar to the N-VITO oxygen carrier, but with 5wt% MgO added during the preparation stage, hence the nomenclature N-VITOMg.

2.3. Investigations in small continuous reactors

Two small continuous CLC reactors at Chalmers and CSIC were used to investigate reactivity of particles under continuous conditions. The first reactor, a 300 W unit at Chalmers was used to evaluate the performance of the the N-VITO oxygen carrier, sintered at 1450°C, which was found to have promising behavior, see Figure 2a,b. The possibility to optimize the methane conversion while retaining the oxygen transport capacity was evaluated by mixing different Ni-based oxygen carriers with better methane cracking. As was seen in the batch reactor investigation, it was found that the N-VITO particle had good oxygen transport characteristics, but had relatively poor methane conversion. The particle with 5 wt% MgO addition, on the other hand, showed excellent methane conversion, but with poor oxygen transport capability, especially at the lower temperature. The mixture of the two particles resulted in a potent oxygen carrier mixture with the desired qualities. Three experimental series were conducted in the 300 W CLC unit: i) using only the first reference spray-dried particle, N-VITO ii) a combination of the reference particle and the MgO based particle, N-VITOMg, and iii) using the previous mixed oxide system together with a small quantity of the high-surface area impregnated oxygen carrier based on NiO and Al₂O₃ prepared at CSIC. It was shown that the methane conversion to CO₂ is dependent primarily on the solids flux in the reactor system, but also on the temperature in the fuel reactor. Experiments at 315 W were conducted during a total of 59 h of fuel operation. Results showed that the operation was more stable and that it was possible to obtain better fuel conversion when the mixtures of two or three different oxygen carrier particles were used. With these mixtures, the methane fraction could be brought down to <0.1% while still maintaining a low CO fraction at the outlet of the fuel reactor.

The 500 Wth CLC plant at CSIC was used to analyze the behavior of the impregnated oxygen carrier prepared at CSIC during continuous operation as well as to know the effect of different operating conditions (fuel gas flow, solids circulation rate, and fuel reactor temperature) on the combustion efficiency. An important advantage of this installation was the possibility to control and measure the solids circulation rate at any moment by the use of a solids valve located above the FR. The prototype was successfully operated during 100 h, of which 70 h were at combustion conditions. No methane was detected at the FR exit, with CO and H₂ being the unconverted gases. Efficiencies as high as 99% were obtained at temperatures in the range 800-880°C, and a solid inventory of 600 kg per MWth. No signs of agglomeration or carbon formation were detected and the main properties of the particles did not vary. It was found that both the NiO and the NiAl₂O₄ were active to transfer oxygen, although the reactivity of the later was much lower than that of NiO.

2.4. Effect of impurities

Gaseous fuels (natural gas, refinery gas or synthesis gas from coal gasification) used in a CLC process may contain different amounts of impurities, primarily sulfur compounds (H₂S, COS, etc.) and light hydrocarbons. The presence of these compounds could affect the behavior of the oxygen carrier and may result in the adoption of important modifications in the CLC process. The effect of the presence of sulfur and light hydrocarbons (ethane and propane) was tested during CH₄ combustion in the 500 Wth CLC plant at CSIC using the Ni-based oxygen carrier prepared by impregnation.

The effect on the oxygen carrier behavior and combustion efficiency of several operating conditions such as temperature and H₂S concentration (100 to 1000 ppm H₂S) was analyzed. Nickel sulfide, Ni₃S₂, was formed at all operating conditions in the FR, which resulted in oxygen carrier deactivation and lower combustion efficiencies. However, the oxygen carrier recovered their initial reactivity after a certain time without sulfur addition. The sulfides were transported to the AR where SO₂ was produced as the final gas product. Agglomeration problems derived from the sulfides formation were never detected during continuous operation.

The experiments carried out in presence of light hydrocarbons (ethane and propane) demonstrated the feasibility of use of these fuels in CLC because neither unburnt hydrocarbons, nor carbon formation, nor agglomeration problems were detected at any experimental condition.

Based on the experimental carried out, it was concluded that no major problems are expected during CLC operation in presence of light hydrocarbons, and neither in presence of sulfur if realistic content values in refinery fuels in the near future (< 20 ppm H₂S) are considered.

2.5 Detailed kinetic testing

The kinetic of the reduction and oxidation of the oxygen carrier selected for operation in the 120 kW plant and prepared by spray-drying was determined through thermogravimetric tests. The oxygen carrier exhibited a high reactivity in both reactions. The reaction times for complete conversion at 950 °C were lower than 1 minute for the typical concentrations existing in the fuel and air reactors. Using the changing grain size model to describe the reactions, activation energy values from 34 to 109 kJ/mol were found for the different reactions of the oxygen carrier with CH₄, O₂, CO, and H₂.

The use of these kinetic parameters into the mathematical model developed to describe the CLC process was useful to understand the experimental data obtained in the 120 kWth CLC plant, as well as to optimize the process operation.

2.6 High temperature experiments

It is important that the oxygen carriers have the ability to withstand high temperatures. Hence, thermal resistance of several of the most promising carrier samples were tested using a ceramic fluidized bed reactor. It was shown that in reducing atmosphere the spray-dried N-VITO particles started to agglomerate at 1125°C and defluidized at 1150°C. The particle doped with 5% of MgO, i.e. N-VITOMg, showed increased temperature resistance and no defluidization was observed at any temperature tested, i.e. up to 1175-1190°C.

3.Integrity testing in 10 kW gas fired CLC units

3.1 Long term integrity testing in a 10 kW reactor

From the screening phase of the project the N-VITO particle sintered at 1450°C was selected to be investigated for long-term operation (> 1000 h) with natural gas and study changes with respect to reactivity and physical characteristics of the particle. This study was performed in Chalmers 10 kW unit, and 1016 h of fuel operation were achieved. The first 405 h were accomplished using a single batch of particles (N-VITO). The last 611 h were achieved using a 50/50_{mass}-mixture of the first batch, i.e. particles taken from the previous 405 h of operation, and a second batch (N-VITOMg), which was very similar in composition but with an addition of MgO, as described above. The gas conversion was generally high, see Figure 3. However, the CH₄ was between 2-4% before the second batch was added, but decreased to around 1% after addition of the new particles.

No decrease in reactivity was seen during the test period. No gas leakage between the reactors was detected. Agglomeration of particles occurred on some occasions. The agglomerates were soft, and could be crushed and re-introduced into the reactor system.

During the 1016 h of experiments in the 10 kW unit, the loss of fines decreased slowly throughout the test period. An estimated particle life time of 33000 h was calculated from the loss of fines. However, if the micro-agglomerates formed during operation were to be incorporated in this measure, the resulting lifetime would be significantly reduced.

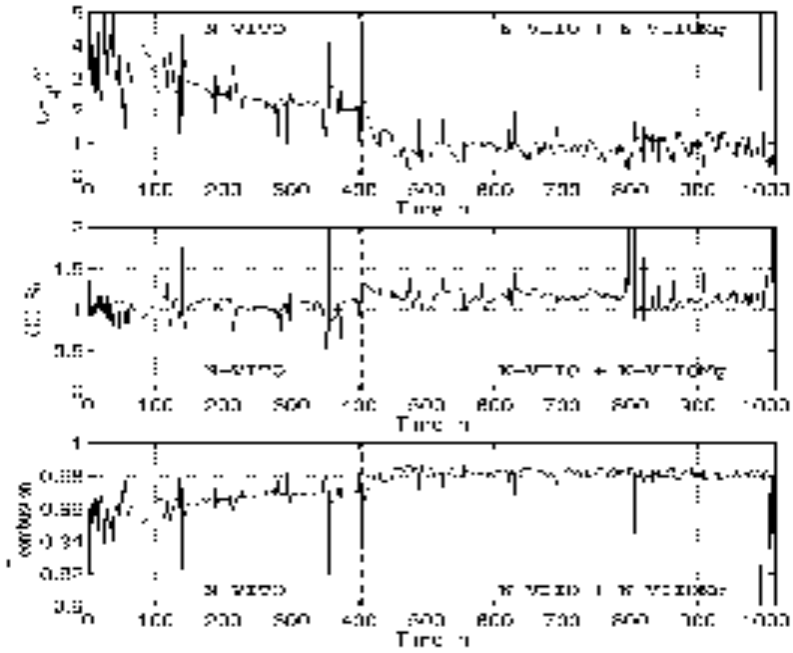


Figure 3. Fractions of CH₄, CO₂ and η_{comb} as functions of time for long term integrity tests in 10 kW reactor at Chalmers.

3.2 Integrity testing in a hot bench scale CLC unit

A specific hot integrated pilot has been designed and built by ALSTOM to study the attrition behavior of oxygen carriers. A preliminary test rig in ambient operating conditions was also constructed in order to optimize the final design. The 15 kWt rig is composed of two interconnected circulating fluidized bed and it is operated with natural gas. Four different oxygen carriers have been tested with the main part of the tests performed with the N-VITO particle. Carbon conversion up to 97% has been obtained during experimental investigation. A limited attrition of particles has been observed.

4. Scale-up and investigations in 120 kW CLC unit

At Vienna University of Technology, a dual circulating fluidized bed (DCFB) reactor system has been designed and built for CLC operation with natural gas at a fuel power of 120 kW. The concept is shown in Figure 4. The pilot rig design allows operation at high solids circulation, low solids inventories and low solids residence time. The chosen DCFB reactor system has a high potential for scale up. Therefore, the results obtained can be assigned to large plants to some extent. Details on the design of the reactor system have recently been reported elsewhere.

About 100 hours of CLC and CLR operation experience with Ni-based oxygen carriers at different bed inventories have been reached at the test rig between May and August 2008. The unit has been fuelled with CH₄, CO, H₂, C₃H₈ or mixtures of these gases and can be operated with different oxygen carriers. The two Ni-based oxygen carriers (N-VITO and N-VITOMg) are compared and discussed for natural gas (CH₄) fuelled operation. Generally, a very low temperature difference between air reactor and fuel reactor of only 5–20°C, already indicates relatively high solids circulation rates. Based on solid samples taken directly out of the loop seals in the global loop, the solids circulation rate can be determined with great accuracy. The results show air reactor entrainment rates between 10 and 90 kg/(m²s).

Also in the DCFB rig the particles achieve high CH₄ conversion and high CO₂ yield. Figure 5 reports temperature variation data for natural gas and propane operation using the N-VITOMg particle. At lower temperatures the slip of unconverted fuel, CO and H₂, out of the fuel reactor is increased while the (primary) conversion of CH₄ seems to be less dependent on temperature. For high temperatures and high global air/fuel ratios the CH₄ conversion even tends to decrease (not shown in Figure 5). This is most likely caused by reduced catalytic activity due to reduced presence of metallic nickel at the surfaces of more oxidized particles. Interestingly, the global degree of oxidation of the circulating particles is rather low. This indicates that the air reactor reaction limits the process, which is an interesting finding with some relevance for larger scale CLC units, where high circulation rates and low solids inventories may reduce operating costs. No problems with carbon deposition on oxygen carrier particles were found.

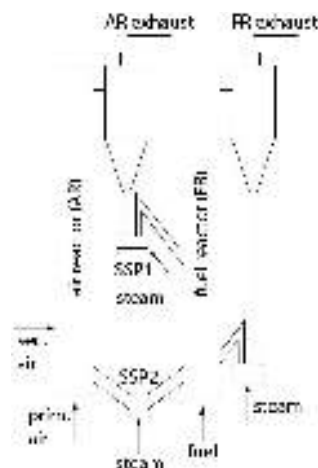


Figure 4. Dual circulating fluidized bed reactor concept (SSP1&2 indicate solids sampling points).

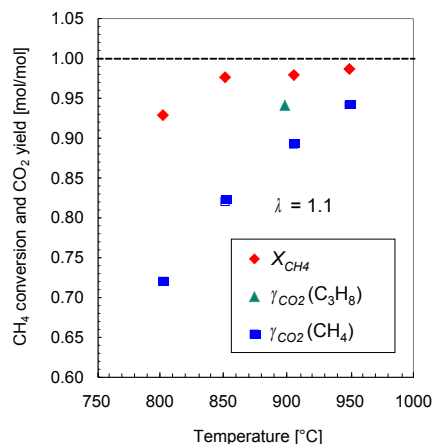


Figure 5. CH₄ conversion and CO₂ yield for N-VITOMg at the DCFB rig as a function of fuel reactor temperature (global air ratio

5. Modelling for future scale up

5.1. Mathematical modelling

Mathematical modelling of the CLC reactor system provides cheap and easy solution for optimisation and scale-up of the process. In this work, a mathematical model describing the behavior of the 120 kWth CLC pilot plant located at Vienna University of Technology has been developed. The global model includes the submodels describing the FR and the AR.

The FR model considers all the processes affecting the reaction of the fuel gas and the oxygen carrier such as the reactor fluid dynamics, the reactivity of the oxygen carrier and the reaction pathway. The reaction mechanisms and reactivity depends on the pair fuel gas/oxygen carrier, whose kinetic data has been previously determined, whereas the fluid dynamics is linked to the design and operational conditions of the reactor.

The main outputs of the model are the axial profiles of gas composition and flows (CH₄, CO, H₂, CO₂ and H₂O), gas composition at the outlet, solid conversion, profiles of solid concentration and flows in the dilute zone.

5.2. Technology scale up and costing

The critical issues for a future demonstration step of the CLC process have been addressed. These include, among others, the up-scaling of the technology to an industrial demonstration unit. As part of this an environmental assessment has been done to ensure the process meets (future) high standards of environmental performance and workplace safety.

Potential HSE (Health, Safety and Environment) show-stoppers and major challenges have been identified. It entailed: a) Occupational health & safety (workers) and environmental health & safety (outside the fence), b) environmental issues (biodiversity, ecosystems etc), c) social issues (jobs, economic impact etc). No outright show-stoppers could be identified. The most important issue identified was the nickel containing particles emissions from the plant, which deserve special attention. As a follow up, recommended particle air emission should be kept as low as possible, requiring the design of an as tight a system as can be attained. Well known technology will have to be implemented to insure the tightness of the system.

Further, the issue of permitting was addressed; this novel technology might not fit into the existing permitting regime and finally scale-up of the technology from pilot to full size plant may reveal issues, which were not apparent at a smaller scale. These and other risks/recommendations need to be addressed in the next development phase of this technology.

An update of the cost model developed in the former EU project GRACE has confirmed that Chemical Looping technology is offering a competitive CO₂ mitigation cost. [The preliminary design for a 10 MWe demonstration unit has been prepared as a deliverable.](#)

6. Summary

The work performed in the CLC Gas Power project has taken the chemical-looping technology for natural and refinery gas to the next level of development. The project has demonstrated that production of oxygen carriers which exhibit excellent properties with respect to important parameters for CLC can be produced with commercial materials and production methods. The effect of higher hydrocarbons and sulfur on the oxygen carriers do not present any major complications. Integrity tests for one Ni-based carriers for >1000 h of combustion showed good reactivity and limited attrition. Further, within the project the world largest CLC reactor has been constructed and operated successfully with some of the developed oxygen carriers.

7.Acknowledgements

This work was part of the EU financed project Chemical Looping Combustion CO₂-Ready Gas Power (CLC Gas Power, EU contract: 019800) led by Chalmers University of Technology. The project is also part of phase II of CCP (CO₂ Capture Project) via Shell.

8.References