

Design, hydrodynamic testing and scale-up recommendations of a conceptual large-scale chemical-looping combustion power plant

B. Kronberger^{1*}, C. Beal², J.-X. Morin², H. Hofbauer¹

¹ Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, A-1060 Vienna;

² Alstom Power Boilers, BP74 – F - 78141 Velizy – Villacoublay cedex.

* corresponding author: tel. +43 1 58801 15955, fax. +43 1 58801 15999, e-mail:

bkron@mail.zserv.tuwien.ac.at

Abstract

Chemical-looping combustion (CLC) is a novel combustion technology with inherent separation of the greenhouse gas CO₂. The technique involves the combustion of gaseous fuel using a metal oxide as an oxidant instead of air. The system consists of two reactors, a fuel reactor and an air reactor, and an oxygen carrier in the form of a metal oxide that transports oxygen from the air to the fuel. Direct contact between fuel and combustion air is avoided, and the products from combustion are kept separated from the rest of the flue gases, e.g. nitrogen and any remaining oxygen.

In this paper a conceptual design of a large-scale CLC demonstration system is outlined. The power plant concept was developed in the framework of the EU/CCP cofunded GRACE project. The system is based on the Grangemouth refinery scenario (200MW thermal power, fuel: refinery gas) and an atmospheric circulating fluidized bed (CFB) boiler design.

A down-scaled cold flow model based on the large-scale design was built using hydrodynamic similarity rules. An intensive test program with variations of key operating parameters was performed. Analysis of results particularly in respect of solids circulation rate and gas leakage rates between the reactors, confirms the suitability of the conceptual design.

Based on experimental findings and mathematical modeling analysis, scale-up recommendations for CLC were developed. The study confirms that chemical-looping combustion is appropriate for new units and for retrofitting existing atmospheric CFB boilers.

1 Introduction

From the large number of fuel conversion technologies currently being developed for CO₂ – capture and separation, a considerable technical and commercial potential is anticipated for advanced concepts such as the advanced zero emission power plant (AZEP), carbonization/calcination cycles, and fuel cells. These concepts are all relatively new and are characterized by a lack of process operating experience. They also bear considerable risk associated with process scale-up when compared to state of the art/benchmark technologies like MEA absorption. There is a need for continued research and development and demonstration for all these advanced concepts.

Chemical-looping combustion is a prominent representative of the group of advanced concepts. The technology integrates the separation of air into the combustion process and fuel oxidation products subsequently consist mainly of CO₂ and water vapor from which the CO₂ can be readily

separated for storage. CLC based around fluidized bed technology currently appears to be one of the most promising candidates from this portfolio of advanced concepts.

The uncertainties in process and CLC - reactor scale-up were a main focus for the development of chemical-looping combustion throughout the GRACE research project between December 2001 and December 2003. Further, the design and operation of a prototype reactor and the development of oxygen carriers were conducted and a techno-economic assessment of the technology was undertaken (Lyngfelt et al., 2004).

2 Chemical-looping combustion

Chemical-looping combustion is a relatively new technology, which integrates air separation into the combustion process and produces a separate $\text{CO}_2/\text{H}_2\text{O}$ flue gas stream for CO_2 capture. The principle is to separate the fuel oxidation process from the air stream by carrying oxygen to the fuel in the form of a metal oxide. In oxidizing the fuel in a "fuel reactor" the metal oxide is reduced and then transported to an "air reactor" where it is re-oxidized by contact with air, leaving an oxygen-depleted air stream. The oxide is then returned to the fuel reactor. The scheme is illustrated in Figure 1.

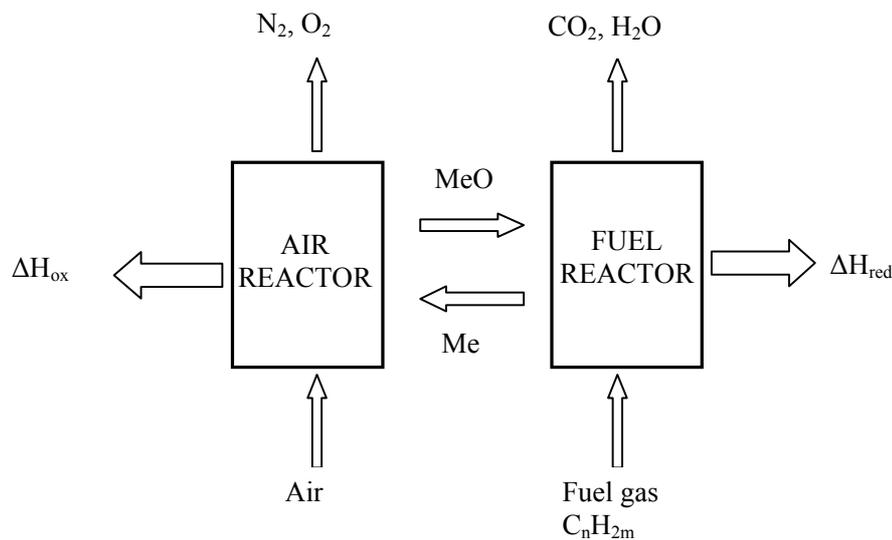


Figure 1: Principle of chemical looping combustion (MeO = metal oxide)

Basic requirements for the oxygen carrier are high surface area for fast reaction and suitable physical properties such as crushing strength and attrition resistance. This can be achieved by supporting the various metal oxide types (Fe, Cu, Ni, Mn, Co, Cd) on an inert such as alumina or titania dioxide.

In order to balance the temperature levels in the reactors the metal oxide also acts to carry heat around the system. The required solids flow is determined from mass and energy balances. Calculations by Kronberger et al. (2004) show that a solids flow between 2 and $8 \text{ kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{MW}^{-1}$ provides a feasible operating range.

The major advantage of this system is that CO_2 and H_2O are separated inherently from the rest of the flue gases without the need of extra energy for the separation as the net energy release of the reduction and oxidation reaction is equal to the heat of combustion. For the metal/metal oxide

systems considered, the heat of reaction (ΔH_{ox} , ΔH_{red}) is different in the air and fuel reactor and most or all of the exothermicity occurs in the air reactor, which gives special requirements for the power cycle integration of CLC.

Another beneficial characteristic of the combustion process is that the formation of nitrogen oxides is suppressed. The relatively low combustion temperatures of about 900-950°C, highly dependent on the selection of the type of oxygen carrier, give no rise for formation of thermal NO_x. Fuel NO_x formation in the oxidation reactor is eradicated since air and fuel pass through different reactors and metal oxidation is independent of the fuel used.

3 GRACE– project objectives and main achievements

A project was developed and carried out to take the technology to the proof of concept stage over a period of two years from December 2001 to December 2003. The project targets were to demonstrate a laboratory chemical-looping combustor with metal oxide particles and to develop an outline design and economic analysis for an industrial plant based on the refinery boiler scenario as described below. For these tasks the GRACE team was assembled from across Europe (Table 1).

Table 1: The GRACE project - partners and work packages

Institution	Work-package
BP, Sunbury, UK	Project co-ordination
Chalmers University of Technology, Gothenburg, Sweden	Particle development and screening tests Comprehensive testing of carrier materials Construction and testing of a lab-scale CLC unit
Consejo Superior de Investigaciones Cientificas, Instituto de Carboquimica, Zaragoza, Spain (CSIC)	Particle development and screening tests Comprehensive testing of carrier materials
Vienna University of Technology, Austria (TU-Vienna)	Reactor fluidization conditions, mathematical modeling and reactor scale-up
Alstom Power Boilers SA, Velizy-Villacoublay, France	Design criteria and economic evaluation for the conceptual Grangemouth CFB design

The project was cofunded by the European Commission (ENK5-CT-2001-00571) and the CO₂ Capture Project (CCP). The CCP is an organization comprising eight international energy companies (BP, EnCana, ENI, ChevronTexaco, Norsk Hydro, Shell, Statoil and Suncor Energy), who's role is to develop and evaluate new technologies aimed at reducing the cost of capture and storage of CO₂ from combustion.

The main achievements of the GRACE partners/work packages are summarized below. Detailed description of the work packages can be found in the CCP book (CCP, 2004).

3.1 Particle Development

More than 240 different types of particles were prepared and screened by CSIC and Chalmers University. The objective of this task was to develop oxygen carriers for use in a chemical-looping combustion system. The particles should be capable of maintaining their chemical, structural and mechanical properties following a large number of reduction-oxidation cycles. A test matrix was developed for the oxygen carriers. Selection was based on best aggregate performance for the key particle characteristics including: crushing strength, attrition, agglomeration tendency and reactivity during successive reduction-oxidation cycles.

The three most promising oxygen carriers were selected for testing in a pilot plant: NiO-Al₂O₃, Fe₂O₃-Al₂O₃, and CuO-TiO₂.

The effect of the main operating variables, including temperature, gas composition, gas concentration, etc., on the oxidation and reduction rates were analyzed in a TGA and the kinetic parameters of the selected carriers were determined (Cho et al., 2002, Mattisson et al., 2004, Adanez et al., 2004).

3.2 Reactor design and GRACE prototype

A 10 kWth prototype for chemical-looping combustion has been designed, built, and run successfully with nickel-based oxygen-carrier particles (Lyngfelt et al., 2004). A total operating time of more than 100 h was accomplished with the same batch of particles, i.e. without adding fresh, unused material. No decrease in reactivity or particle strength was seen during the test period.

A high conversion of the fuel was reached, with approximately 0.5% CO, 1% H₂ and 0.1% methane in the exit stream. There was no detectable leakage between the two reactor systems. Therefore it is possible to achieve an almost pure stream of CO₂ from the fuel reactor, with the possible exception of unconverted fuel, or inert compounds associated with the fuel, e.g. N₂.

4 Development of a conceptual design of a large scale application

A key objective of the GRACE program was the development of a conceptual design and economic evaluation of a large scale application of chemical-looping combustion. The task was lead by Alstom Power Boilers and the technical work was conducted in cooperation with TU-Vienna.

The design scenario chosen for this work was developed by the CCP and was taken from one of four real scenarios used by the CCP to facilitate a comparison of new capture technologies. The methodology developed by the CCP for economic comparison was also adopted for this work. The selected scenario is based on BP's Grangemouth refinery and petrochemical complex and utilizes CLC to replace existing power boilers. Total boiler fired duty is 200 MW producing 227 tonne/hour of superheated steam for co-generation of power and process steam. The study uses refinery gas as fuel to the boiler, which is in contrast to the laboratory based prototype work, which utilized methane gas as fuel. The refinery fuel gas specification is given together with steam parameters and terminal point conditions for the carbon dioxide and the exhaust gas situation in Table 2.

Table 2 Industrial Plant Design Criteria

Refinery gas composition			Steam parameter	
methane	CH ₄	68.16% vol	Temperature	515°C
ethane	C ₂ H ₆	9.47% vol	Pressure	126 bar
ethene	C ₂ H ₄	0.02% vol	Steam flow	227tonne/h
propane	C ₃ H ₈	7.46% vol	Feedwater	
propene	C ₃ H ₆	0.01% vol	Temperature	122°C
isobutane	C ₄ H ₁₀	1.08% vol	Pressure	150bar
n-butane	C ₄ H ₁₀	3.14% vol	Flue gas conditions	
hydrogen	H ₂	7.91% vol	Excess air	15%
nitrogen	N ₂	0.75% vol	Flue gas temperature at stack	190°C
carbon dioxide	CO ₂	2.02% vol	Ambient conditions	
hydrogen sulfide	H ₂ S	0.08% vol	Ambient Temperature	12°C
			Air humidity	80%

4.1 Boiler layout and process flow diagram

ALSTOM Power Boilers has developed a design concept for large-scale chemical-looping combustion boiler, taking advantage of its leading experience in this field (Marchetti et al., 2003). Earlier studies (Lyngfelt et al., 2001) determined that a combustor design based upon a circulating fluidized bed (CFB) technology can satisfy the crucial characteristics of chemical-looping combustion. These are as follows:

- ◇ The solid circulation rate is a very sensitive parameter in system operation because the solids act simultaneously as oxygen and an energy carrier between the two reactors.
- ◇ Gas leakage between the two zones must be prevented to maximize CO₂ capture efficiency.
- ◇ Residence time of gas must be sufficient to ensure essentially complete fuel gas conversion.

The concept for the large-scale combustor uses mainly existing CFB technology with fluid bed heat exchangers. The work includes the main process flow diagrams, process design calculations, equipment sizing and layout, and estimates of capital and operating costs.

One key difference is immediately apparent on inspection of the process block flow diagram, given in Figure 2. The chemical-looping combustor requires two separate backpass boiler lines, each one for the fuel and the air reactor. This split backpass system, however, is similar to existing practice for reheat control.

The combustor itself is based on a conventional CFB concept (cf. Figure 3) and, as for the design of the prototype, the riser section was selected as the metal oxidizer. The air is fed to the unit as primary air at the bottom of the riser and as secondary air in the lower section of the riser. The lower region is refractory lined and the top area is enclosed by water cooled tubes. The possibility of secondary air injection is justified by the improved load control and possibility for adjustment of the riser pressure profiles. The bed material is entrained through the exit, which is designed as T-shape exit allowing adequate particle circulation flow and at the same time an adequate solid residence time in the oxidizer section. The return leg is formed by: a single cyclone, the loop seal solid splitter, and the downcomers. For the solids separator the particle size distribution of the oxygen carrier has been reviewed for compatibility with large scale industrial cyclones.

One major difference from conventional CFB technology is the integration of the fuel reactor within the solids return system. The gas streams must be prevented from mixing and this requires the development of a novel loop seal with three solids outlets. Solids can be directed either via a straight return to the riser, extracted to fluid bed heat exchanger (FBHE) or to the fuel reactor for closing the oxygen carrier flow loop.

Since there is an optimum temperature range for the oxides operation, load follow-up requires close temperature control of the air riser loop, which has lead to the installation of the fluid bed heat exchanger allowing adjustment of the heat duty removed from the solids loop. The FBHE allows incremental duty by passing some amount of recycle solids to the bundles.

The main downcomer returns the particles into the fuel reactor where the reduction of the oxygen carrier by the gaseous hydrocarbon fuel takes place. The operating conditions in this reactor are determined by a superficial gas velocity of 1.5 times the terminal velocity, which corresponds to a bubbling fluidized bed regime. The outgoing flow is higher than at the inlet due to the fuel gas volume expansion resulting from the oxidation reaction. The expansion factor of 3 is likely to result in high elutriation rates, and an analysis of the compatibility of the particle characteristics with the required solids loading for the fuel reactor, shows that additional cyclones are required.

For this the Fi-Circ™ system of ALSTOM Power Boilers as presented e.g. by Goldbach (2001) is considered.

The fuel reactor is directly connected to the air reactor. The chemical-looping boiler concept from ALSTOM Power Boilers includes gas barriers between the fuel reactor and the air reactor, which are crucial for the interconnected reactor performance.

Because of high velocity in the riser section an additional bed material is believed to be necessary for achieving the required mean particle residence time. Also part load operation down to 35%/40 % of the nominal power output is facilitated by this.

The most crucial design parameter for a chemical-looping combustor is the type of oxygen carrier. The encouraging results of the GRACE prototype test runs (Lyngfelt et al., 2004) form the basis for the use of nickel-based oxygen-carrier particles also for the large scale scenario. An air-to-fuel ratio of 1.15 was selected, which represents a typical value for industrial applications and the operating temperature is assumed as 950°C. The resulting heat and mass balances were reviewed and required solids circulation rates as well as resulting solids conversion were determined for the CLC boiler arrangement.

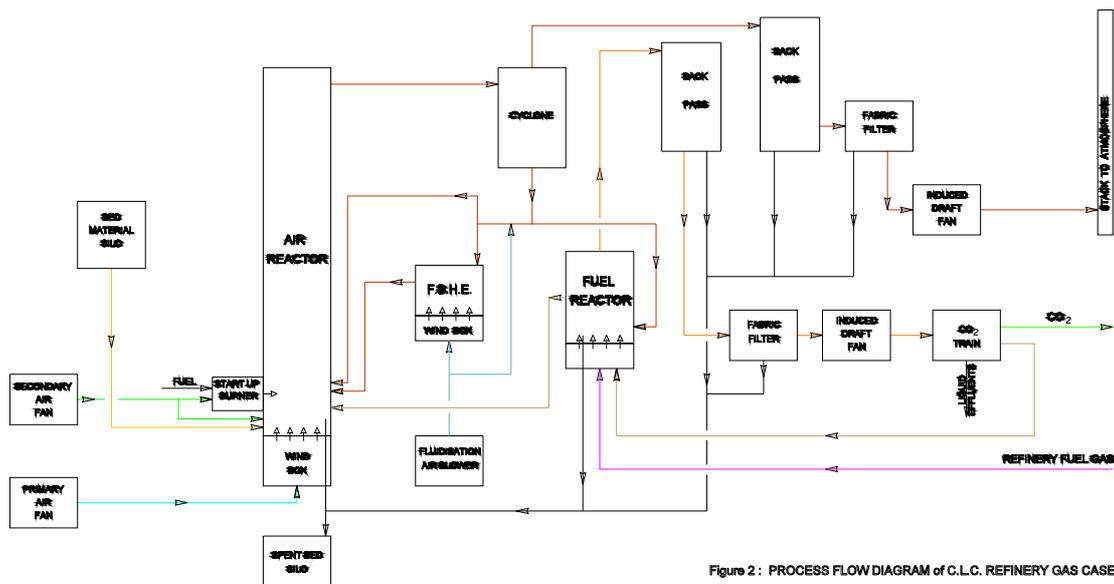


Figure 2 : PROCESS FLOW DIAGRAM OF C.L.C. REFINERY GAS CASE
ALSTOM Power Boilers

Figure 2: Process flow diagram of CLC refinery gas case

5 Hydrodynamic testing of the chemical-looping combustor concept

After the industrial case data (Grangemouth refinery) and the main design outline were fixed a cold flow model made from Perspex was designed, built and tested.

5.1 Design of the cold flow model

The major deviation between the Grangemouth case and the hydrodynamic testing is given by the size of the arrangement. Because of space limitations and restrictions for downscaling, the unit is

smaller by a factor 20, i.e. the nominal thermal power is 0.5 MW. A scaled cold flow model of this 0.5MW was built and operated according to the simplified scaling laws of Glicksman et al. (1993), which resulted in the use of bronze powder representing oxygen carrier particles with a mean particle diameter of $200\mu\text{m}$ and a density of $2250\text{kg}\cdot\text{m}^{-3}$.

Figure 3 presents the design and photograph of the cold flow model based on exact default dimensions from the outline of the large scale system. A few modifications were made in comparison to the large-scale CFB unit in order to simplify the design and the testing program. These include

- ◇ the scaling of the height of the unit
- ◇ neglect of an internal solids return system
- ◇ neglect of the short-circuit between the solid splitter and the riser
- ◇ neglect of the external fluid bed heat exchanger.

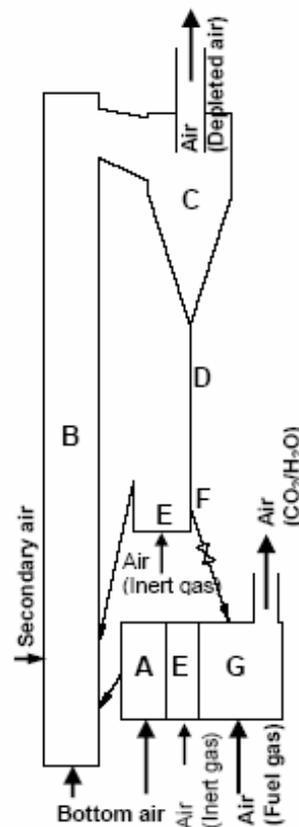


Figure 3: Design layout of dual fluidized bed system cold flow model with (A) air reactor , (B) riser, (C) particle separator, (D) downcomer, (E) loop seal, (F) solid splitter, (G) stationary bed (fuel reactor). Gases for large scale CLC unit are given in brackets.

5.2 Experimental results

Cold flow modeling gives valuable insight into the hydrodynamic behavior and such into the performance of a circulating fluidized bed system. Furthermore it forms the basis for material and energy balances in the system and also for reaction kinetics. To this end a number of parameters have been studied focusing on

- ◇ stability and control of the dual-fluidized bed system
- ◇ system pressure situation
- ◇ solids circulation rate
- ◇ degree of gas mixing between the reactors
- ◇ mean residence time of particles and gases in the reactors

Throughout the entire experimental program stability of the system and an effective control of the unit simulating start-up, part load, and turn down operation was found. The pressure balance determines the solid inventory distribution and for chemical-looping combustion it is particularly important in determining the amount of gas leakage. The following graph (Figure 4) shows the results of pressure measurements across the system at typical settings for riser velocity, solid inventory and secondary air ratio.

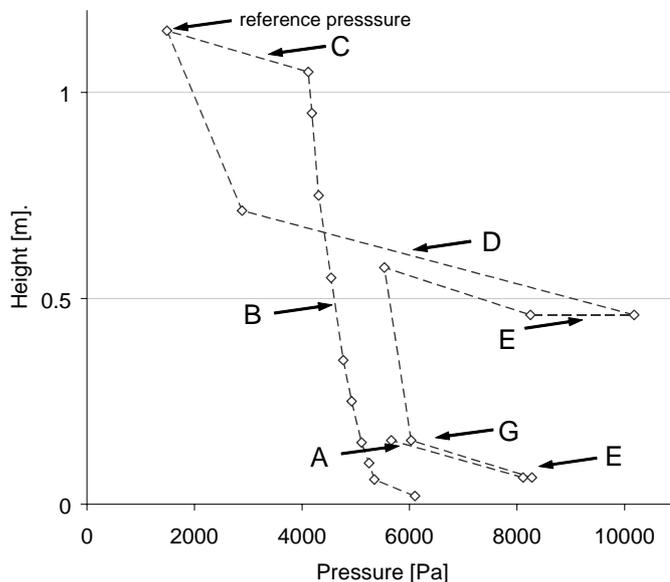


Figure 4: Pressure profile of demo-scale unit at standard operating conditions. Letters refer to Figure 3.

It can be seen that the highest pressure in the system is in the upper loop seal (E) at the side of the downcomer, whereas the lowest pressure is given by the pressure drop of the dust filter at the exit of the cyclone (reference pressure). Letter B indicates the pressure profile of the riser and letters E represent the pressure drop of the horizontal solid flux in the loop seals. The high absolute pressures in the loop seals together with the small pressure difference between air reactor (A) and fuel reactor (G) give the conditions for very low gas mixing between the reactors.

Solids circulation rate measurements were carried out at different total solid inventories, riser velocities, and ratios of bottom air to secondary air. As can be seen from Figure 5, the total solid inventory and the velocity in the riser strongly influence the specific solid circulation rate. It can also be observed that for a constant secondary air addition a wide range of the solids flux can be achieved in the system, which corresponds to variations of the thermal load of the CLC-unit.

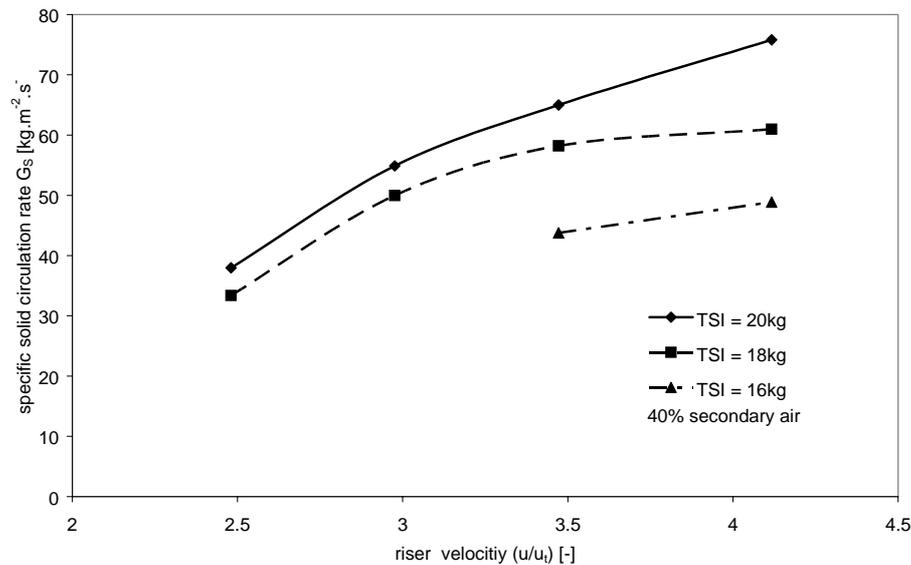


Figure 5: Specific solids circulation rate for variation of riser velocity and total solids inventory for 40% secondary air

Variations of the secondary air fraction were carried out for simulation of process control during part load operation and simplified start-up and shut-down procedure. Heat transfer may also be varied in certain riser sections. It can be shown that this is a very effective measure as the solid circulation rate can be varied over a wide range.

Gas leakage and solids circulation rate are the most important factor determining the performance of the CLC process. Additional gas flows, introduced for fluidization of the gas seals, are diluting the exit gas flows and it is of particular interest to trace the direction of the flows for prediction of the exit gas compositions. Numerous measurements at variations of the pressure balance between the reactors, the solids flow, and different fluidization velocities were carried out.

The results confirm that, for both novel gas seal designs developed by this project, very good seal performance can be achieved. The relative gas leakage values are well below 0.5% and the consumption and type of fluidization gas for the loop seal were optimized.

6 Scale-up issues in the CLC system

The scale-up (or scale-down) of fluidized bed reactors usually requires to scale-up three distinguishable sub-processes: Fluid dynamic gas to solid contact, heat and mass transfer, and chemical reactions. For successful execution the interaction of these sub-processes has to be considered. From the design point of view the major scale-up technical challenges are with four major components of CFBs: the combustor, the cyclones, the backpass, and the fluid bed heat exchangers. However, the dual- fluidized bed combustor concept coupled by the solid flow gives a rather large degree of freedom for each single reactor.

The *hydrodynamic scale-up* of the CFB system is primarily determined by the fluidization regime of the reactors, in particular the CFB riser. The fluid dynamic behavior of the transport reactor determines the solid circulation rate, which, in turn, is crucial for the heat balance of the system and the oxygen transport between the reactors.

With regard to process economics it is desired to minimize the bed material and to optimize the solid circulation rate as this influences the overall energy consumption of the fluidization. However, with regard to the design of a robust process some margin of safety is advisable as it may give some additional operating flexibility.

The test results of the cold flow models of the GRACE program were evaluated in view of scale-up effects on solids elutriation. It has been concluded that all correlations used indicate that basic scale-up criteria should focus on the use of a constant ratio of specific solid circulation rate and specific fuel mass flow rate.

The *air reactor* design can be handled without major difficulties. From determination of reactivity of the various metal oxide types and the fuel gas composition the required particle residence time is determined directly. For scale-up constant mean particle residence time is required.

From the reaction engineering point of view the main focus is to be given to the *fuel reactor*. Similar fuel gas conversion can only be obtained when the gas solid contacting is similar at different scales. Reaction rate constants and order of reaction are determined by reactivity tests and, as a consequence of the required gas residence time, the reactor mass is given for a certain thermal power and fuel type. Constant gas residence time has been used as the key scale-up criteria for this issue. For a more general case, however, the mass transfer coefficient X (dimensionless interphase mass transfer) and the dimensionless reaction rate k^* as proposed by Grace (1986) are suitable scale-up criteria.

Detailed analysis of the fuel reactor performance was carried out by means of mathematical fuel reactor models by CSIC and TU Vienna. As a result these tools can be used as scale-up instruments for fuel reactor optimization. A summary of the scale-up criteria is given in Table 3.

An additional technical challenge for the process scale-up is given for the cyclone. In scaling-up, a point is reached where the cyclone size gets so large that oxygen carrier particle losses are increasing significantly. Scale-up to larger size cyclones has been gradual and like the conventional CFB, as the unit size increases, cyclone size is increased or cyclones are added as required to maintain optimum gas velocities, and then optimum cyclone fractional collection efficiency.

Table 3: Scaling criteria for chemical-looping combustion

Scaling criteria for CLC reactor systems	
CFB reactor system	$\frac{\text{specific solid flow rate}}{\text{specific fuel mass flow rate}} = \text{const.}$
Air reactor	$\frac{\text{fuel mass flow rate}}{\text{air reactor bed mass}} = \text{const.}$
Fuel reactor	$\frac{\text{fuel mass flow rate}}{\text{fuel reactor bed mass}} = \text{const.}$ interphase mass transfer coefficient = <i>const.</i> dimensionless reaction rate constant = <i>const.</i>

7 Techno-economic evaluation of the large scale-concept

In the previous section it has been shown that the concept for a large scale chemical-looping combustor developed during this project is suitable for the refinery case. From the technical point of view the key issues were addressed and satisfactory results were found. In the following section further technical aspects relevant for the set-up of a complete CO₂ capture unit are dealt with and results of the economic evaluation are presented.

7.1 Further technical issues

Incomplete fuel conversion

The tests with the prototype reactor within this project showed that almost complete fuel conversion can be reached. A limitation, however, is given for the nickel-based oxygen carrier as thermodynamics do only allow about 99% fuel conversion.

The best way to treat the unconverted fuel is not clear although it is believed that it can be separated from the liquefied CO₂ at a reasonable cost and recycled to the process. Wilkinson and Boden (2001) have presented estimations for such a phase separation close to the triple point for an Oxyfuel system, whereby for comparative conditions a cost reduction for elimination of the inerts removal process a net reduction of CO₂ capture cost of \$1.7/tonne is given. The number, however, does not consider that parts of the removed gases are combustibles and can be returned into the process as in our case.

Dust emissions

The use of CFB processes raises the possibility of particle emissions to the atmosphere. It should be kept in mind that the regulations demand very high standards, which are even higher when it comes to dust emissions of heavy metals like nickel. This issue has been considered in the economical evaluation for this project but no detailed analysis was made of its potential impact.

7.2 Economic evaluation

An economic evaluation of the scenario was carried out during the project by Alstom Power Boilers. It should be underlined that the reference case does not show the technology to its best advantage as it utilizes a small size boiler, expensive fuel and low pressure steam parameters when compared to typical utility class boilers.

Two CLC systems, a possible and a conservative basis, were analyzed based on equal assumptions and terminal conditions as specified within the GRACE project. The results show that cost and performance of the oxygen carrier are a significant cost factor. Based on detailed calculations made by Lyngfelt et al., (2004) the costs for the oxygen carrier were derived. For the lifetime the number obtained from the GRACE prototype was used, which suggests a durability of the solids up to 40 000hours. The mass requirement is calculated from reactivity data determined throughout this project. The different assumptions suggest oxygen carrier cost in the order of 1 €/tonne of CO₂ captured. As the assumptions are conservative the concern that cost of the particles might be a show-stopper for this technology appears unlikely, but much more testing is required.

Table 4: Economics of entire CLC system

		CLC boiler (conservative case)	CLC boiler (possible case)
CO ₂ mitigation cost (without CO ₂ compression)	€/tonne CO ₂	20.8	16.7

In Table 4 it can be seen that in comparison to the reference case the cost of electricity increase by about 20%. The CO₂ mitigation cost per tonne CO₂ (conditions as specified in Table 2) are in the range of €16.7 to €20.8, which indicate that CLC technology is a promising option for CO₂ capture.

8 Future Development and Conclusions

A concept for an industrial chemical-looping combustion boiler has been developed, sized, and detailed costing was conducted. An extensive hydrodynamic testing program was carried out and confirmed the suitability of the concept. Scale-up issues have been analyzed and it appears that there are no difficult points in terms of technology, in particular as the process reuses mostly existing CFB technology.

Research in the GRACE project has moved the development of suitable oxygen carriers forward and nickel-oxide particles have been tested in the GRACE prototype reactor successfully. Safety and environmental aspects of the proposed design have been considered throughout the program, particularly with respect to the selection of particle materials and the minimization of emissions.

In terms of cost and durability the oxygen carrier is the main issue. Costing carried out by Alstom Power Boilers and the CCP indicates that the CO₂ capture cost could be substantially below that for existing capture technologies if the targeted particle performance is achieved.

The successful results of this project form the basis for future development. One priority is intensive particle development and long term durability testing. Further, demonstration at pilot scale in long term prototype operation (10 kWth and 1 MWth) is suggested. As the steam cycle is representative of the reference industrial boiler and not of utility type boiler (400 MWe) such a process could be built using CLC with much higher steam conditions (600/650°C) then offering better cost attractiveness.

CLC technology using CFB boilers should appear as a leading technology in terms of competitiveness for CO₂ removal and quick access to the market after a demonstration unit operation (40/50 MWe class).

9 Acknowledgements

The contribution of the partners of the collaborative project to this paper, the support of the European Commission's FP-5 program (ENK5-CT-2001-00571) and the CO₂ Capture Project (CCP) are gratefully acknowledged.

10 References

J Adánez, L F de Diego, F García-Labiano, P Gayán, A Abad, J.M. Palacios Selection of oxygen carriers for chemical looping combustion. *Energy & Fuels* 18 (2004) 371-377.

P Cho, T Mattisson, A Lyngfelt. Reactivity of iron oxide with methane in a laboratory fluidized bed - application of chemical-looping combustion. 7th International Conference on Circulating Fluidized Beds, Niagara Falls, Ontario, 2002. p. 599-606

L R Glicksman, M Hyre and K Woloshun Simplified Scaling Relationships for Fluidized Beds", *Powder Technology*. 77, pp. 177 – 199, 1993.

G Goldbach and M Tanca, Firing Coal Washing Wastes in a FI CIRC™ Steam Generator - Redbank Project (ALSTOM Power) 16th International Conference on Fluidized Bed Combustion, Reno 2001.

J R Grace Fluidized Beds as Chemical Reactors, in *Gas Fluidization Technology*, Geldart, D. (Ed.), John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore, 1986.

B Kronberger, G Löffler and H Hofbauer. Simulation of Mass and Energy Balances of a Chemical-Looping Combustion System. *International Journal on Energy for a Clean Environment*. 2004. (accepted).

A Lyngfelt, B Leckner and T Mattisson, A Fluidized-Bed Combustion Process with Inherent CO₂ Separation; Application of Chemical-Looping Combustion, *Chemical Engineering Science*, 56, 3101-3113, 2001.

A Lyngfelt, B Kronberger, J Adanez, JX Morin, P Hurst, The GRACE project. Development of oxygen carrier particles for chemical-looping combustion. Design and operation of a 10 kW chemical-looping combustor. to be presented at The Seventh International Conference on Greenhouse Gas Control Technologies (GHGT-7), Vancouver, Canada 5-9 September 2004.

M M Marchetti, T S Czarnecki, J C Semedard, S Devroe, J-M Lemasle, Alstom's Large CFBS and Results, Proceedings of FBC 2003, 17th International Fluidized Bed Combustion Conference, May 18-21, 2003, Jacksonville, Florida USA.

T Mattisson, M Johansson, A Lyngfelt, Multi-cycle reduction and oxidation of different types of iron oxide particles - application to chemical-looping combustion" 2004, accepted for publication in *Energy & Fuels*.

M B Wilkinson and J C Boden, CO₂ capture via Oxyfuel Firing: Optimisation of a Retrofit Concept for a Refinery Power Station Boiler, in Proceedings of the First National Conference on Carbon Sequestration, Washington DC, May 15-17, 2001.

The CCP book, The CO₂ Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations for Climate Change Mitigation, Volume 1 – Capture and Separation of Carbon Dioxide from Combustion Source. Chapters 29-32 to be published end 2004.