

# **Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO<sub>2</sub> Capture Project**

**Capture and Separation of Carbon Dioxide  
from Combustion Sources**

*Edited by*

**David C. Thomas**

*Senior Technical Advisor*

*Advanced Resources International, Inc.*

*4603 Clearwater Lane*

*Naperville, IL, USA*

*Volume 1*



**ELSEVIER**

2005

Amsterdam – Boston – Heidelberg – London – New York – Oxford  
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

**Elsevier Internet Homepage – <http://www.elsevier.com>**

Consult the Elsevier homepage for full catalogue information on all books, major reference works, journals, electronic products and services.

**Elsevier Titles of Related Interest**

AN END TO GLOBAL WARMING

L.O. Williams

ISBN: 0-08-044045-2, 2002

FUNDAMENTALS AND TECHNOLOGY OF COMBUSTION

F. El-Mahallawy, S. El-Din Habik

ISBN: 0-08-044106-8, 2002

GREENHOUSE GAS CONTROL TECHNOLOGIES: 6TH INTERNATIONAL CONFERENCE

John Gale, Yoichi Kaya

ISBN: 0-08-044276-5, 2003

MITIGATING CLIMATE CHANGE: FLEXIBILITY MECHANISMS

T. Jackson

ISBN: 0-08-044092-4, 2001

**Related Journals:**

Elsevier publishes a wide-ranging portfolio of high quality research journals, encompassing the energy policy, environmental, and renewable energy fields. A sample journal issue is available online by visiting the Elsevier web site (details at the top of this page). Leading titles include:

*Energy Policy*

*Renewable Energy*

*Energy Conversion and Management*

*Biomass & Bioenergy*

*Environmental Science & Policy*

*Global and Planetary Change*

*Atmospheric Environment*

*Chemosphere – Global Change Science*

*Fuel, Combustion & Flame*

*Fuel Processing Technology*

All journals are available online via ScienceDirect: [www.sciencedirect.com](http://www.sciencedirect.com)

**To Contact the Publisher**

Elsevier welcomes enquiries concerning publishing proposals: books, journal special issues, conference proceedings, etc. All formats and media can be considered. Should you have a publishing proposal you wish to discuss, please contact, without obligation, the publisher responsible for Elsevier's Energy program:

Henri van Dorssen

Publisher

Elsevier Ltd

The Boulevard, Langford Lane

Kidlington, Oxford

OX5 1GB, UK

Phone: +44 1865 84 3682

Fax: +44 1865 84 3931

E.mail: [h.dorssen@elsevier.com](mailto:h.dorssen@elsevier.com)

General enquiries, including placing orders, should be directed to Elsevier's Regional Sales Offices – please access the Elsevier homepage for full contact details (homepage details at the top of this page).

ELSEVIER B.V.  
Radarweg 29  
P.O. Box 211, 1000 AE Amsterdam  
The Netherlands

ELSEVIER Inc.  
525 B Street, Suite 1900  
San Diego, CA 92101-4495  
USA

ELSEVIER Ltd  
The Boulevard, Langford Lane  
Kidlington, Oxford OX5 1GB  
UK

ELSEVIER Ltd  
84 Theobalds Road  
London WC1X 8RR  
UK

© 2005 Elsevier Ltd. All rights reserved.

This work is protected under copyright by Elsevier Ltd, and the following terms and conditions apply to its use:

#### Photocopying

Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: [permissions@elsevier.com](mailto:permissions@elsevier.com). Requests may also be completed on-line via the Elsevier homepage (<http://www.elsevier.com/locate/permissions>).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

#### Derivative Works

Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

#### Electronic Storage or Usage

Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.

Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

#### Notice

No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2005

#### Library of Congress Cataloging in Publication Data

A catalog record is available from the Library of Congress.

#### British Library Cataloguing in Publication Data

A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

**Volume 1:** Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

**Volume 2:** The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

© The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).

Printed in The Netherlands.

Working together to grow  
libraries in developing countries

[www.elsevier.com](http://www.elsevier.com) | [www.bookaid.org](http://www.bookaid.org) | [www.sabre.org](http://www.sabre.org)

ELSEVIER

BOOK AID  
International

Sabre Foundation

## Chapter 35

# CHEMICAL-LOOPING COMBUSTION—REACTOR FLUIDIZATION STUDIES AND SCALE-UP CRITERIA

Bernhard Kronberger, Gerhard Löffler and Hermann Hofbauer

Institute of Chemical Engineering, Vienna University of Technology, Austria

### ABSTRACT

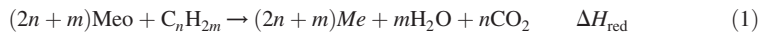
This chapter is aimed to report the results of the work package of Vienna University of Technology in the GRangemouth Advanced CO<sub>2</sub> CapturE Project (GRACE). The GRACE project is an EU founded research project under the specific programme for research on “energy, environment and sustainable development”. The work of Vienna University of Technology is concerned with the design and scale-up of a CLC reactor concept by investigations of the fluidization conditions. Detailed modelling was carried out experimentally in cold flow models at different scales. The experimental findings were integrated into mathematical models on the kinetics and hydrodynamics. The derivation of scale-up guidelines of the CLC process was carried out and recommendations are given. Clearly, the dual fluidized bed reactor concept coupled by the solid flow is well suitable for chemical-looping combustion. Scale-up issues can be overcome and a demonstration of the technology is recommended.

### INTRODUCTION

Oxyfuel combustion is amongst the technologies currently under investigation for CO<sub>2</sub> capture. Out of a number of options for burning fuel in oxygen instead of air chemical-looping combustion (CLC) is certainly amongst the most novel concepts. A CLC system consists of two reactors and the combustion is split into separate oxidation and reduction reactions. An oxygen carrier in the form of a metal oxide cycles between an air reactor and a fuel reactor and transports oxygen from air to the fuel.

In the reduction reactor a metal oxide is reduced by gaseous fuel and subsequently transported back to the air reactor where it is regenerated by air. The flue gas from the fuel reactor consists of carbon dioxide and water, while nitrogen and non-reacted oxygen exits from the air reactor.

According to the scheme shown in Figure 1 the gaseous fuel introduced to the fuel reactor reacts with the oxygen carrier according to Eq. (1).

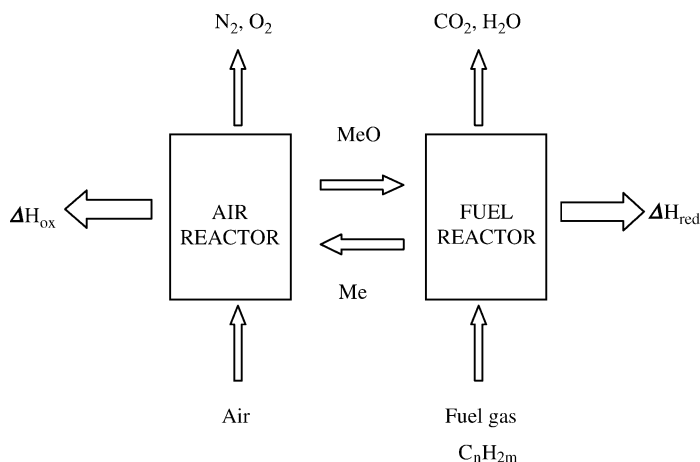


In second step the reduced metal is circulated to the air reactor where it is oxidised and thus, regenerated (Eq. (2)).



The flue gas from the air reactor contains N<sub>2</sub> and any non-reacted O<sub>2</sub>. Reaction (1) is, depending on the metal oxide type, often endothermic and reaction (2) is always exothermic [1]. The net chemical reaction over the two reactors, however, is the same as for normal combustion with an equal amount of heat released [2]. Also, the total amount of heat evolved is equal to normal combustion of the same fuel (Eq. (3)).

$$\Delta H_c = \Delta H_{\text{ox}} + \Delta H_{\text{red}} \quad (3)$$



**Figure 1:** Principle of chemical-looping combustion (CLC). MeO and Me denote oxidized and reduced oxygen carriers.

Therefore, the major advantage of this system is that  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are separated inherently from the rest of the flue gases and no additional energy is required for this separation. This is in contrast to the common techniques for separating carbon dioxide from flue gas, where large amount of energy and expensive equipment are necessary [4] that reduce the thermal efficiency. Also, CLC decreases the destruction of fuel exergy upon combustion as reported by Richter [3] and Anheden [5].

Research in this novel technology so far can be grouped into three distinct areas:

Techno-economic evaluations of the system were carried out, e.g. by exergy analysis [5,6], and the potential for different options of integration of the process into power plant concepts were demonstrated by Copeland [7,8] and Wolf [9]. Wolf attributed a combined cycle efficiency of 52–53% at an optimum working pressure of 13 atm to pressurized CLC systems. Main focus has been given to the experimental development of oxygen carrier materials. Adánez [10], Cho [11,12], Ishida [13–17], Jin [18–21], Mattisson [22–25], Ryu [26–28], Song [29] have tested different materials by cyclically exposing them to fuel gas and air. Promising candidate materials are Fe, Ni, Mn, Cu, Co as metal oxides and for support materials like  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  are considered. The experiments show that the rates of reaction for both the oxidation and the reduction are fast enough for practical applications.

So far, very limited work has been carried in the design of a CLC reactor system. Batch experiments and general feasibility analysis of Lyngfelt [30] showed that a fluidized bed reactor concept is suitable for CLC. Johansson [31,32] has presented cold flow modelling results of different layouts of small laboratory scale reactor systems for CLC. Ryu [33,34] has presented a preliminary design of a 50 kW unit based on a pressurized fluidized bed technology.

Fundamental knowledge of fluid dynamic behaviour of the two-phase flow is essential for an optimized design and operation of a chemical-looping combustor. The crucial CLC characteristics can be satisfied for a CLC design based upon a circulating fluidized bed (CFB) technology:

- solid circulation rate is a very sensitive parameter in operating the system because the solids act as oxygen and heat carrier between the two reactors.
- gas leakage between the two zones has to be prevented as it reduces the  $\text{CO}_2$  capture efficiency and/or dilutes the exhaust gas enhancing the  $\text{CO}_2$  capture expense.
- residence times of gas and solids in both reaction zones have to be sufficient to ensure high conversions.

## EXPERIMENTAL/STUDY METHODOLOGY

For assisting the design process of the GRACE prototype and scale-up of the CLC process a two-step strategy was chosen. Two laboratory scale and one bench scale designs were developed and corresponding cold flow models were built and tested. Their hydrodynamic performances were evaluated in respect to variation of operation parameters. In second step the results of the experimental work were integrated in mathematical models. In this way information for the design of the laboratory scale chemical looping reactor, fluid dynamic restrictions for the choice of oxygen carrier material, and scale-up guidelines for a bench scale atmospheric demonstration plant were developed.

### *Basic CLC Reactor Concept*

The choice of the type of reactor system is a key issue in CLC considerations. For the heterogeneous nature of the reaction, the required solid transport between the fuel reactor and the air reactor, a CFB concept is the preferred reactor type. Dual fluidized beds are used in a multitude of process such as biomass pyrolysis [35] and gasification [36] where good contact between solids and gas is required. The proposed dual fluidized bed concept is built up by a transport reactor acting as riser and a stationary fluidized bed. The riser gives the driving force for the solid material circulation, which has to fulfil two main objectives: First, it shall provide sufficient oxygen carrier capacity for complete conversion of the fuel gas in the stationary bed. Secondly, the mass flow shall supply the energy transfer needed for balancing the temperatures between the oxidation and the reduction reactor. Calculations by Kronberger [1] show that for most of the considered different metal oxide types (Cu, Fe, Ni, Mn) it is determined by the heat balance and a solid mass flow of  $0.005 \text{ kg s}^{-1} \text{ kW}^{-1}$  is sufficient. The choice for using the stationary fluidized bed as fuel reactor and the faster fluidized zone as air reactor respectively was based on the experienced smaller reaction rates of the metal oxides with air whereas the reaction with fuel gas demands a higher residence time. The separation of the bed material and exit gas stream is performed by a cyclone, designed acc. [37]. The dimensions of the downcomers and the loop seals are based on considerations of expected solid flows and acceptable particle velocities.

### *GRACE prototype reactor*

Basic requirement of the laboratory scale prototype unit is to create the possibility to operate the unit at different power (5–10 kW) and temperature levels (800–1000 °C). This allows the simulation of part load behaviour in large-scale units but more importantly performance tests of oxygen carrier types. A number of different metal oxides and/or physical properties (particle size, density) of the oxygen carrier shall be tested and long-term behaviour evaluated. To this end a very flexible unit is designed to fulfil the requirements but also to create safety margin for uncertainties in the design.

The basic layout of the CLC prototype reactor system and the declaration of the sections can be seen in Figure 2a. Particularities of the dual fluidized bed system are particle residence time in the fuel reactor (G) that can be varied almost independently by adjusting the bed height. In contrary, the particle residence time in the air reactor (A) is primarily determined by the total material solid inventory and the material circulation rate. Since this would result in low particle residence times for this reactor a widened bottom section was chosen. This is aimed to support the formation of a dense bottom bed, although it is clear that it would reduce achievable circulation rates [35]. The fuel reactor is designed with a conical section in order to take into account the volume increasing oxidation reaction of methane, used as model fuel for the Grangemouth refinery gas.

An alternative design for a CLC bench-scale unit with an advanced option for particle circulation control was additionally developed in this project. The basic concept is based on the GRACE prototype but by modular design different particle separator design and solid flow systems were tested.

### *Bench scale CLC demonstrator*

Main difference from the prototype unit and the demonstration unit is the scale. The demo unit (Figure 2b) was designed for a power of about 0.5 MW (fuel: refinery gas) and the concept is based on conventional atmospheric CFB boilers (e.g. Ref. [38]). The boiler arrangement was modified for the CLC system and can be easily adapted to a large-scale combustor of a thermal power of 200 MW as foreseen in the Grangemouth advanced CO<sub>2</sub> capture (GRACE) project scenario (CCP [39]).

The air fed to the unit is as primary air at the bottom of the riser (B) and as secondary air in the lower section of the riser. 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, designed as T-shape exit and separated from the deleted air stream by a cyclone (C). The solid flow exiting via the cyclone dipleg passes the downcomer (D) and a loop seal—solid splitter (E, F) combination. A novelty of this concept is that the solid flow is split inside the loop seal into three separate streams, whereby the flow of two of them is controlled by mechanical valves. One is being returned into the fuel reactor another through an external fluidized bed heat exchanger (H) for achieving the heat duty. The third leg forms a short-cut for easier power control of the unit. The fuel reactor (G) is directly connected to the air reactor (A). A loop seal (E) is preventing the mixing of gas flows from the reactors. In contrary to the CLC-prototype design, a separate air reactor (A) is planned for a large-scale CLC unit in order to allow for sufficient mean particle residence time.

TABLE 1  
STANDARD OPERATING CONDITIONS AND MAIN DIMENSIONS OF  
THE TESTED CLC SYSTEMS

Parameter	Operating parameter and design factors	
	GRACE-lab-scale prototype	Bench-scale demo unit <sup>a</sup>
Thermal power (kW)	5–10	500
Fuel type	Methane	Refinery gas
Air to fuel ratio	1.2–2.6	1.2
Operating pressure (Pa)	$1 \times 10^5$	$1 \times 10^5$
Reactor temperatures (°C)	950	950
Particle density ( $\text{kg m}^{-3}$ )	2500–5400	2300
Mean particle diameter (m)	$100 \times 10^{-6}$ – $200 \times 10^{-6}$	$220 \times 10^{-6}$
Gas fluidization velocity in the riser	$4-10u_t$	$4u_t$
Gas fluidization velocity in the air reactor	$1.2-3u_t$	$0.7u_t$
Gas fluidization velocity in the fuel reactor	$5-15u_{mf}$	$0.7u_t$
Loop-seal gas fluidization velocity	$1.2-4u_{mf}$	$2u_{mf}$
Total reactor system height (m)	2	7

Data for hot reactors.

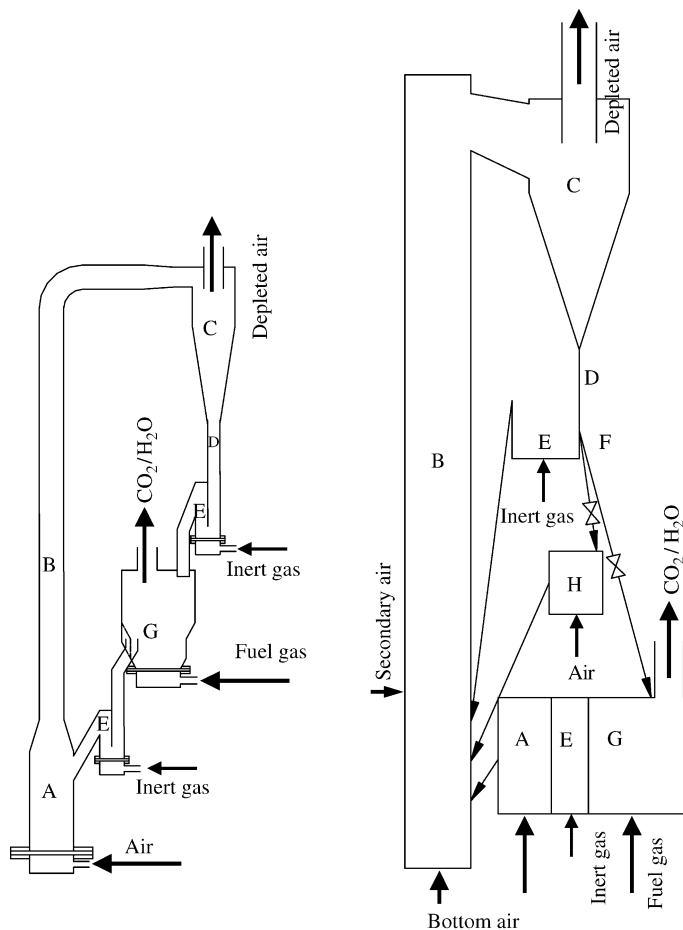
<sup>a</sup> Standard operating condition at nominal thermal power.

The standard operating conditions and main dimensions of the both systems are given in Table 1. It can be seen that for the prototype the fuel reactor velocity is above terminal velocity, which causes high solid entrainment. Further, the outgoing flow is due to the increase in gas moles higher by a factor of about 3 and therefore an internal return of particles by means of internal cyclones is required. For this the Fi-Circ™ system of ALSTOM Power as, e.g. presented by Goldbach [40] is considered.

#### Cold Flow Model—Scaling Laws and Design

It has proved worthy to study fluid mechanics in fluidized beds in cold flow models, as they provide the advantages of being cheap and allowing easy changes in geometry. Moreover, operation at ambient conditions makes measurements easier and cheaper than in reactors operated at higher temperature and/or pressure. In order to ensure similar fluid mechanic behaviour as in the corresponding reactor the cold flow models have to be designed and operated according to similarity rules. The scaling of the hydrodynamics of the CLC units dimensions into the scaled cold flow model was pursued by applying the scaling rules of Glicksman [41] (Eq. (4)) and Glicksman [42].

$$\text{Fr}, \text{Re}_p, \frac{L}{d_p}, \frac{D}{d_p}, \phi, \text{PSD, bed geometry} \quad (4)$$



**Figure 2:** Design layout of dual fluidized bed system with (A) air reactor, (B) riser, (C) particle separator, (D) downcomer, (E) loop seal, (F) solid splitter, (G) stationary bed (fuel reactor) (H) fluidized bed heat exchanger (FBHE).

Application of the scaling laws shows that for the material properties selected as standard parameters it is difficult to develop reasonable scaling factors. Thus, two different systems were obtained and operating conditions as well as idealized relationships between the hot units and the CFM are presented in Table 2.

As can be seen for the cold flow model of the bench scale unit air and for the prototype a gas mixture of helium and nitrogen is required as fluidization gas. Because of the high gas flows for He/N<sub>2</sub> a gas recycling loop was set up [43]. The scaled model of the demo unit was operated with air. As bed material glass beads and bronze powder were selected and for diminishing electrostatic charges small amounts of an anti-static power (Larostat<sup>®</sup>) were added.

In general the design of the cold flow models are similar to the hot reactors. The scaled models are built from acrylic glass and operated according to the scaling laws of fluid dynamics. Some simplifications were made



TABLE 2  
IDEALIZED RELATIONSHIP BETWEEN COLD FLOW MODELS AND CLC REACTOR SYSTEMS

Parameter	Scaling relationships			
	GRACE-prototype	CFM prototype	Demo-unit	CFM demo-unit
Temperature (°C)	950	25	950	40
Pressure (Pa)	$1 \times 10^5$	$1 \times 10^5$	$1 \times 10^5$	$1 \times 10^5$
Fluidization gas type (riser)	Air	He/N <sub>2</sub>	Air	Air
Solid material type	Oxygen carrier	Glass beads	Oxygen carrier	Bronze powder
Mean particle diameter (m)	$120 \times 10^{-6}$	$67.5 \times 10^{-6}$	$220 \times 10^{-6}$	$54 \times 10^{-6}$
Particle size distribution (m)	$120 \times 10^{-6}$	$40-80 \times 10^{-6}$	$220 \times 10^{-6}$	$32-63 \times 10^{-6}$
Solid density (kg m <sup>-3</sup> )	2550	2550	2300	8750
Particle sphericity	~ 1	1	~ 1	1
Mass	1	0.17	1	0.144
Length	1	0.55	1	0.33
Area	1	(0.55) <sup>2</sup>	1	(0.33) <sup>2</sup>
Velocity	1	0.74	1	0.58
Volume flow	1	0.22	1	0.063
Solid circulation rate	1	0.23	1	0.25

for the cold flow model in particular on the demonstration system. The FBHE and the internal particle return system for the fuel reactor will not give any additional information and installation was therefore omitted. Instead, the pressure drop at the fuel reactor exit was simulated by a pressure relief valve and variations were carried out to study the effect on the pressure balance of the system. Further, the gas distributor systems were simplified and perforated plates were used for the riser. Fuel reactor and loop seals are equipped with porous glass plates for simplicity reasons.

#### Supply Equipment and Measurement Techniques

All in- and outgoing gas flows of the CFM were measured. Instruments were mass flow controllers (Type MKS flows 5-200l<sub>N</sub>/min (basis nitrogen) and a commercial diaphragm gas meter (Type Elster BK). For very low gas flows and for calibration purpose also a gas bubble meter was utilized. The pressures were determined by a total number of 20 pressure transducers, type Honeywell, Micro Switch.

The solid circulation rate was determined by short interruption of the fluidization of one particle lock. Repeated measurement of the time necessary to fill a dedicated volume in the downcomer allows the determination of the solid flux. Measurement accuracy was determined being below  $\pm 8\%$ .

For the residence time distribution (RTD) test a tracer measurement technique of Rhodes [44] was adapted. A pulse function of sodium chloride was injected into the solid flow and bed material samples are taken at the downcomer of the fuel reactor particle overflow at given time step. The concentration of the solid sample is determined by a conductivity method [45] and the RTD distribution function is derived by standard methods.

The gas leakage measurements were carried out by using a tracer gas method. Propane was added alternately to the inlet air in succession in all four fluidization gas flows. The concentration of propane was measured with a flame ionization detector at the incoming as well as at the outgoing gas flows from the cyclone and the fuel reactor. Solving the mass balances of this over-determined set of equations leads to the leakage gas flows of each particle lock.

For the operation of the prototype and a potential CLC demonstration unit it is important to keep the loss of solids very low. The performance of the particle separator (cyclone) was therefore determined by the fractional separation efficiency.

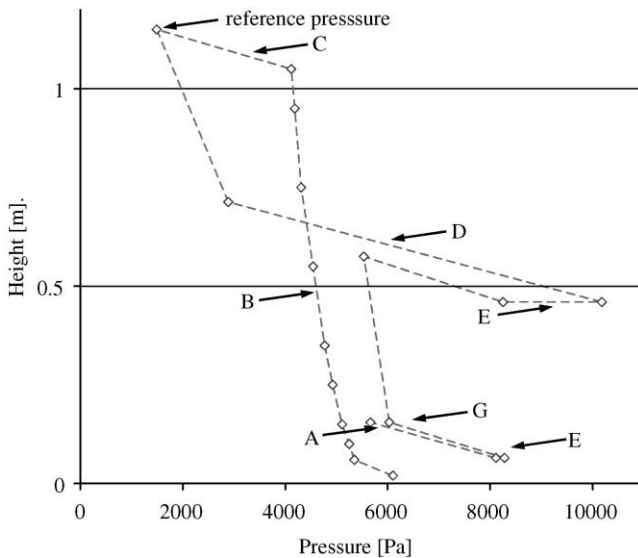
## RESULTS AND DISCUSSION

During the first experimental phase the general suitability of each concept was assessed. Both, the scaled model of the prototype and the demonstration unit performed at operation without difficulties. The solid splitter valve of the demonstrator model can be operated such that the solid flow can be split into ratios between the two downcomers enabling good part load and turn down behaviour. Further, a number of design improvements were carried out, which lead to the final designs as presented in Figure 2a and b.

### System Pressure Balance

Pressure measurements have long been used to monitor operating conditions in industrial fluidized-bed chemical reactors. A detailed look on the static pressure balance of the CLC demo unit at standard operation condition is presented in Figure 3. A very similar behaviour of the pressure loop, however, is obtained for both concepts. Letter (B) indicates the riser profile with a steeper gradient at the bottom zone. This is equivalent to larger solid inventory caused by the split of the total riser gas flow (S/T) into 35% secondary air. An examination of the riser profiles show that for the different operating conditions a mathematical model concept based on a core-annulus flow structure [46] with a simple exponential correlation for the axial voidage profile in the transport zone [47] gives good agreement with measurement data.

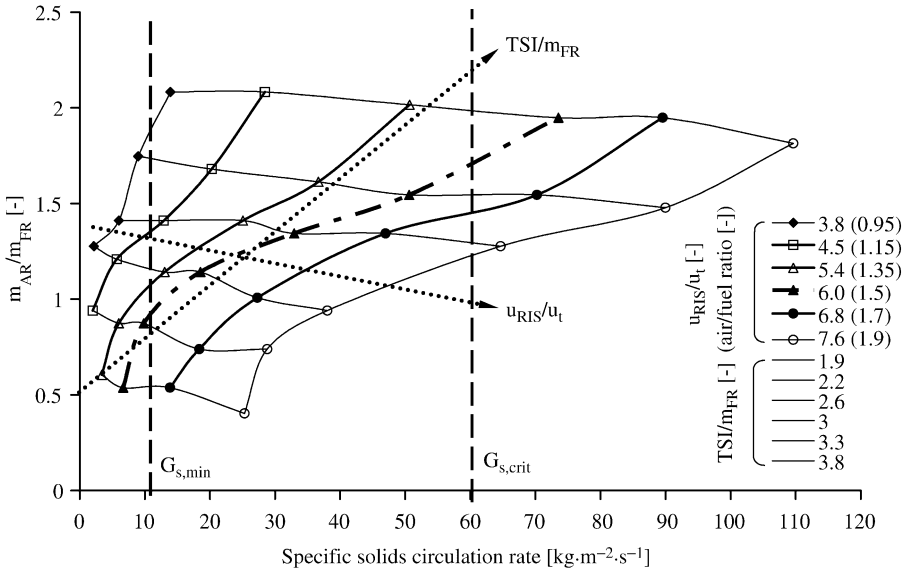
For the prototype a similar effect is achieved by the widened bottom section. At top of the curve the pressure drop of the riser exit and the cyclone (C) is apparent. The pressure drop of the downcomers (D) is caused by the material column at the inlet of the loop seals. Large differences appear for the two loop seals (E) that are caused by the different geometry. However, analysis showed that the pressure drop of the horizontal connection can be correlated in analogy to laminar flow of fluids as suggested by Venderbosch [48] and Hofbauer [49]. For both concepts it was found that the J-type loop seals between cyclone and reduction reactor are well designed to balance the different pressures. The pressure in the air reactor and fuel reactor were kept at the same level, which was assumed as standard operating conditions. Variations on this were carried out additionally for simulating the variable pressure drop of the particle recirculation system of the fuel reactor exit.



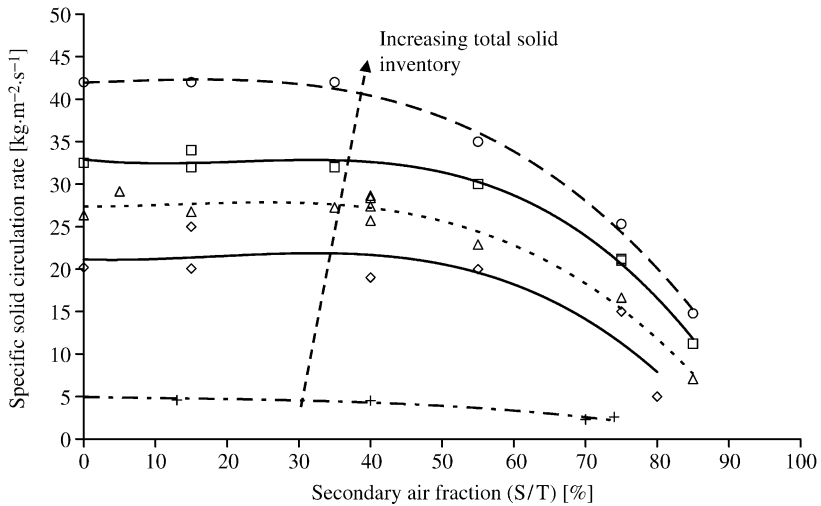
**Figure 3:** Pressure profile of demo-scale unit at standard operating conditions. Letters refer to Figure 2b.

**Solid Circulation Rate**

Measurements of the solid circulation rate were carried for a huge variety in operating conditions, material properties and geometry variations. In Figures 4 and 5 design charts for the solid circulation rate applicable to the hot reactors are depicted at standard condition according to Table 1.



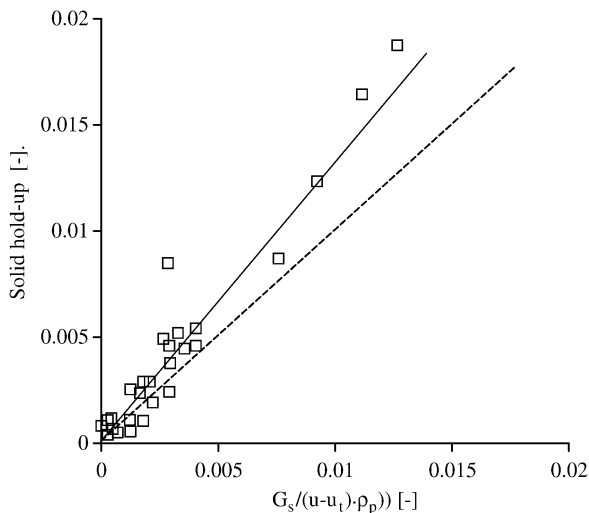
**Figure 4:** Specific solid circulation rate of GRACE prototype reactor. Parameters: riser velocity ( $u_{RIS}/u_t$ ), air reactor bed mass ( $m_{AR}/m_{FR}$ ), total solid inventory( $T_S/m_{FR}$ ) and air/fuel ratio.



**Figure 5:** Specific solid circulation rate of bench scale unit vs. S/T and total solid inventory at standard operating conditions.

The solid flux is specific to the cross section of each riser and minimum required flow at nominal thermal unit power. The chart of the prototype allows determination of the bed mass inventory in the air reactor, the specific circulation rate at given total solid inventory and air/fuel ratio or riser velocity, respectively. Clearly, the mass flux satisfies the needs of the system. A limitation is given by the flow capacity of the downcomers indicated by the bend of the curve at a flux of  $G_{s,crit} = 60 \text{ kg m}^{-2} \text{ s}^{-1}$ .

It has been mentioned that one of the additional requirements of the demonstrator is the possibility for improved load control of the solid flow by secondary air injection in combination with total air flow. The solid flux has been found almost linearly proportional to the riser velocity. Further, Figure 6 shows the solid flow vs. the fraction of secondary air to total air (S/T), which confirms that air splitting as an effective measure. This behaviour also can allow for different metal oxides having very fast oxidation reaction omitting the separate air reactor.



**Figure 6:** Solids hold-up vs. dimensionless specific solids circulation rate for prototype unit.

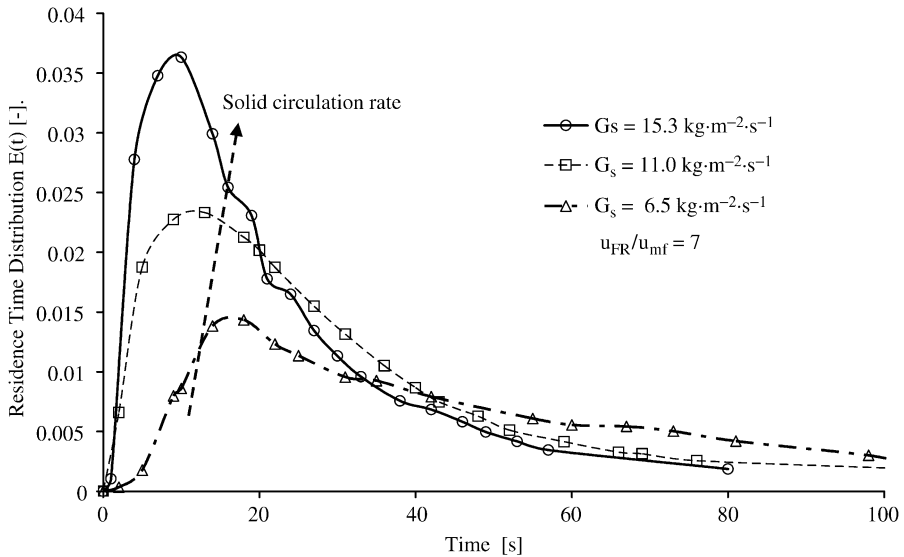
#### *Determination of the solid circulation flow from pressure measurements*

Measurements of the solid flow of the different CLC reactor types are not only important for assessing the performance and optimization of the CFB system. As the solid flow can only be measured in a hot unit with difficulties it is valuable to have an indirect technique. Hartge [50] compared solids hold-up derived from pressure drop and from  $\gamma$ -ray absorption measurements and found good agreement between the results obtained with both techniques. Although the pressure drop at the top of the riser is very low and such causes higher measurement inaccuracy the results are satisfactory. The use of this correlation gives good agreement between the solids hold-up detected in the upper portion of the riser (calculated from pressure measurements) and the specific circulation as presented in Figure 6. The method used for predicting the solids circulation rate of the demonstration unit is based on work by Patience [51] and Gupta [52] who take into account the riser exit effects on the solids circulation rate.

#### **Particle Residence Time Distribution**

The particle RTD in fluidized bed reactors of the CLC system can provide vital information for system designers and operators. RTD is of enormous importance in particular when the gas solid reaction is the limiting factor. The particle age distribution in the fuel reactor influences the kinetics of the fuel oxidation and thus, the conversion. The gas conversion itself is crucial for high thermal efficiency and for environmental concerns else require recycling of combustibles in the flue gas. Therefore, it is essential to accurately configure the geometry of the fuel reactor to the needs of the fuel gas.

The RTD in the fuel reactor of the prototype was determined by a solid tracer method. The sodium chloride method presented by Rhodes [44] was applied as described earlier. The results of variation of the solid mass flow on the RTD of the reactor is shown in Figure 7 as mass fraction of particles having a certain residence time in the reactor. The mode of the distribution shifts towards longer time with decreasing solid flow whereas the mean residence time decreases. The shape shows strong deviation from the common assumption of ideal mixing of a fluidized bed reactor as proposed, e.g. by Krishnaiah [53].



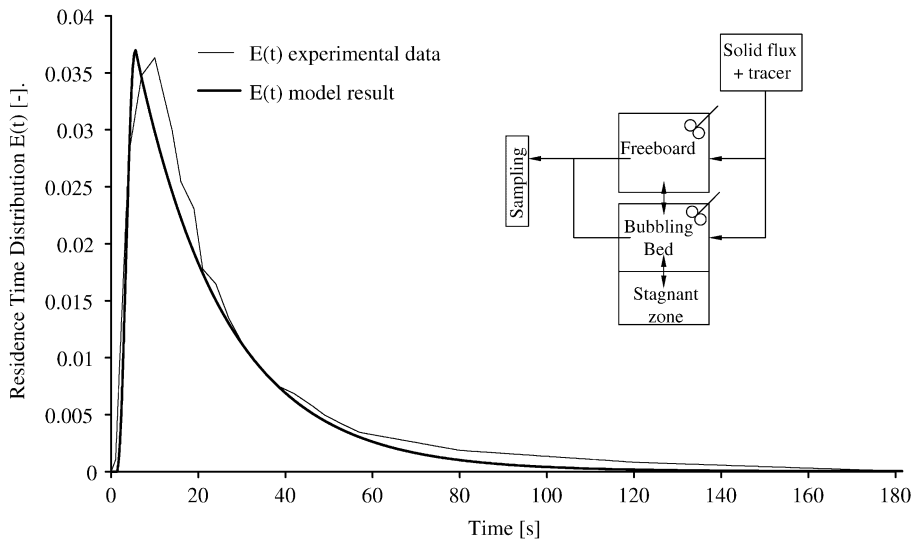
**Figure 7:** RTD for fuel reactor of the prototype CFM vs. variation of solid circulation rate. Oxygen carrier was assumed.

A more detailed analysis shows that the first reduced moments are below unity, indicating dead space in the bed. The conclusions from this are that at low bubbling intensities dead or less active regions in the bed exist. These are probably located close to the distributor plate in between the discharge orifices but dominantly in the annulus of the conical section. In case of increase of the fluidization velocity and decrease of particle diameter the particle mixing improved and the stagnant zones reduced.

A mathematical model was developed to represent the phase flows and reactor zones in the bubbling fluidized bed reactor (Figure 8). The model comprises a dense zone, consisting of a bubbling and a stagnant zone, and a freeboard. Additionally, mass transfer between the different zones is included. Good agreement between model predictions and test results was found for the RTD function (Figure 8). Mass fractions and solid flux in each reaction zone were determined and sensitivities on operating conditions established.

### Gas Leakage

Gas leakage is apart of solids circulation rate the most important hydrodynamic factor determining the  $\text{CO}_2$  capture performance of the CLC process. Very low values of gas leakage between the reactors are required. Any dilution of the exit gas flows complicates the gas analysis and makes it difficult to evaluate the reactor performance in the prototype unit. Parameters varied during experimentation are the total solid inventory, reactor fluidization velocities, loop seal fluidization and the pressure balance between fuel and air reactor. Propane was added into the windboxes of the different fluidizations and at the exits concentrations were detected by a flame-ionization-detector.



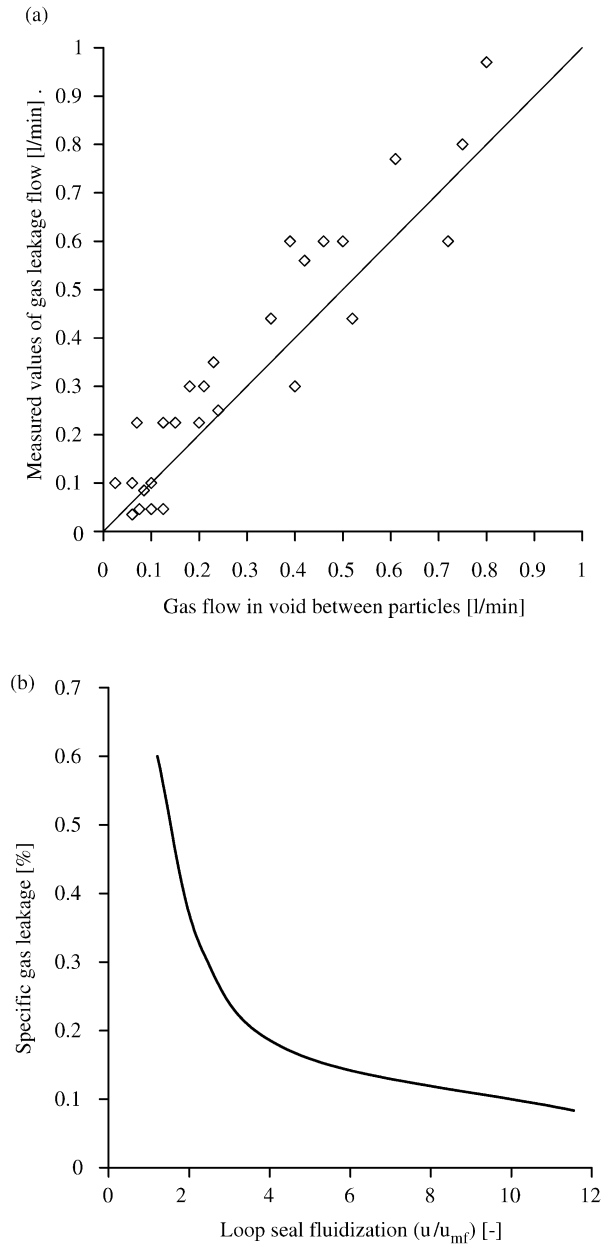
**Figure 8:** Comparison for RTD between measurement and model for fuel reactor of prototype CFM at standard operating conditions.

In Figure 9a correlation of the measured gas leakage flow (the absolute flows are almost identical for both streams) with the gas volume (flow) carried in the void between the particles of the solid flux is presented. Values are representing both loop seals and were measured at the prototype cold flow model. The basic correlation that can be seen in this figure is the proportionality between the gas leakage flows and increasing solids circulation rate. This relationship was confirmed in more detail by the assumption that the gas flow at low loop seal fluidization is equivalent to the inter-particle void fraction of the moving bulk. Thereby, the bed voidage in the loop seal was calculated according to the well known modified Two-Phase Theory [54] for bubbling fluidized bed regimes.

The results are gas leakage flows into the air and the fuel reactor for measurements at different total solid inventories as well as different pressure differences between the fuel reactor exit and the cyclone downcomer. As can be seen the measured gas leakage flows for different solid circulation flow rates correlate very well to the gas flows according to the voidage of the solid flow. As both axes represent measurement data deviations are attributed to inaccuracies. Furthermore, it could be observed that no dependency of gas leakage on the pressure drop across the loop seals and on the total solid inventory exists.

The understanding of the gas leakage mechanism, i.e. the proportionality of the gas leakage and the solids circulation rate, makes possible countermeasure obvious. An increase of the siphon fluidization reduces the gas specific leakage by stripping the gas in between the particles (Figure 9b). Specific leakage data are commonly expressed as gas leakage flow specific to the (inlet) fluidization gas flow of the concerned reactor. In the context of CLC, however, the gas stream of interest is the fuel reactor outlet flow, i.e. the  $\text{CO}_2/\text{H}_2\text{O}$  mixture and this was used for the representation in this figure. It can be seen that increasing the velocity in the loop seals causes a significant decrease of the gas leakage, which theoretically gives the possibility to totally prevent gas leakage by entirely stripping of the solid flow.

From the measurements also the flow of the particle lock fluidization gas (steam or inert gas in case of hot CLC process) could be tracked precisely and it was found that for siphon velocities up to about  $3u_{mf}$  almost the entire gas flow (>97%) is following the solid flow. This result is valuable as it allows also the calculation of the dilution of the gas streams with loop seal fluidization agent.



**Figure 9:** (a) Measured gas leakage of loop seal vs. gas flow in the void between particles for CFM of prototype at  $u/u_{mf} = 1.4$ . Variations of TSI and pressure difference across loop seal. (b) Gas leakage of loop seal specific to fuel reactor outlet flow vs. loop seal fluidization (specific solid circulation rate =  $30 \text{ kg m}^{-2} \text{ s}^{-1}$ ).

From these observations it can be concluded that increasing the siphon fluidization velocity is an effective measure to decrease the gas leakage into both reactors. However, it is obvious that this also increases the dilution of the exit flows by the siphon fluidization gas, which on the other hand would reduce the system efficiency and thus an optimum for the overall process shall be determined.

#### ***Development of Scale-up Guidelines of CLC Process***

Apart from assisting the prototype design, the main objective of this study was the derivation of scale-up guidelines for the CLC process. Scale-up of reactors is commonly grouped into three distinct areas, the hydrodynamics, reaction engineering and the heat transfer. Clearly, the dual-fluidized bed reactor concept coupled by the solid flow gives a rather large degree of freedom for each single reactor. However, optimization and secure scale-up requires a detailed analysis of all different aspects. A closer view during this study was given to hydrodynamics and reaction kinetics not only experimentally but also by mathematical modelling. New models were set up and existing simulations adapted for fluid-dynamic scaling, the mass and energy balances of the CLC system and the reaction kinetics of the prototype fuel reactor. The models were validated and are to be used as scale-up tools to support the design of a large-scale CLC system.

#### ***CLC scale-up criteria***

The *hydrodynamic scale-up* is primarily determined by the fluidization regime of the reactors, in particular the CFB riser. The hydrodynamic behaviour of the transport reactor as driving force of the CFB system determines the solid circulation rate. This, 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 optimise 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.

Following Glicksmans laws the scale-up of the hydrodynamics is primarily pursued by keeping the operating regimes of the fluidized bed systems constant. Various tests in all cold flow models were carried out and the effect of height on solids elutriation and specific solid flux was studied intensively. A difficulty appears when the riser height of the cold flow models is below the transport disengaging height (TDH), which introduces a solid flow dependency on the reactor height. The scale-up of the height of the reactors, in particular the riser of the CLC system, by the same factor as the diameter without changing the operating conditions is an inappropriate scaling criteria. The decrease in the solid circulation rates is therefore to be compensated by an increase of the total solid inventory or the riser velocity. Large-scale units in general are being operated such that the riser height is larger than the TDH. This was confirmed from the cold flow model measurements in this study as the TDH could be approximated by the estimation of Wen [55]. In this case the solid flux is considered independent on the reactor height and as basic scale-up criteria a constant ratio of specific solid circulation rate and specific fuel mass flow rate is suggested.

*Scale-up problems of fluidized bed reactors* are well known although a number of models that can be found in literature have gained general acceptance. The scale-up of the two reactors of a CLC unit is considered separately for each reactor.

The oxidation 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 can be determined straight forward. For scale-up constant mean particle residence time is required. The design with a separate air reactor as realised for large-scale units this can be achieved by variation of the air reactor bed mass. The decoupling allows an independent adjustment in the design process. Constant ratio of the fuel mass flow rate to the air reactor bed mass is recommended as scale-up factor. The gas residence time is not crucial for the air reactor because the excess air compensates for the potentially larger riser gas velocities and lower gas residence times.

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 in the different scales. Similar to the oxidation reactor, reactivity and thermodynamics determine the required solid flow through the fuel



reactor. Further, rate constant and order of reaction are determined at reactivity tests. As a consequence of the required gas residence time the reactor mass is given for a certain thermal power and fuel type. However, because the reactor geometry is not fixed from these requirements an increased reactor height will cause larger bubbles affecting the fuel gas conversion negatively. Grace [56] has presented a model that allows the calculation for the conversion of the reactant based on the Davidson and Harrison model [57]. The model uses dimensionless parameters, i.e. the dimensionless rate constant  $k^*$  and the transfer coefficient  $X$ .  $X$  includes the interphase mass transfer coefficient, the interphase surface area per unit bed volume and the bed geometry. The dimensionless rate constant group  $k^*$  is formed by the rate constant of the fuel reduction, the bed height and the gas velocity. The bed height, on the other hand is calculated with the Two-Phase Theory from the required solid mass in the fuel reactor. The combination of all these parameter allows the calculation of the reactor geometry at a certain power load and fuel gas/bed material combination for an optimum gas conversion.

It is apparent that for low dimensionless reaction rates or for high interphase mass transfer coefficients the difference between the two reactor models becomes small. In these two cases, the mass transfer between both phases is not the rate limiting factor and the concentrations in both phases are almost equal. Thus, the two-phase model converges against the single-phase model and consideration of constant gas residence time as scale-up criteria is appropriate. For the general case, however, the transfer coefficient  $X$  is proposed.

A summary of the scale-up guidelines for the CLC following the abovementioned considerations is given in Table 3.

TABLE 3  
SCALING CRITERIA FOR CHEMICAL-LOOPING COMBUSTION

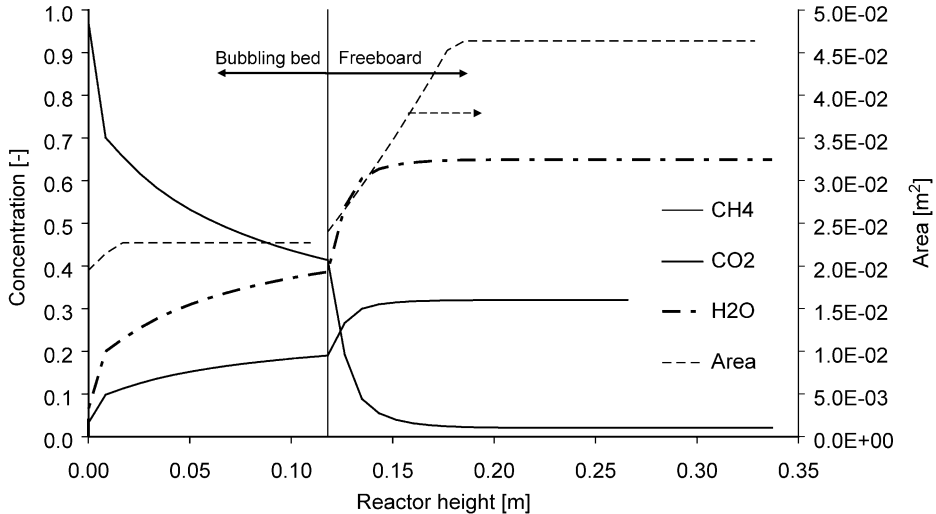
Scaling criteria for CLC reactor systems	
CFB reactor system	$\frac{\text{Specific solid flow rate}}{\text{Specific fuel mass flow rate}} = \text{const.}$
Air reactor	$\frac{\text{Fuel mass flow rate}}{\text{Air reactor bed mass}} = \text{const.}$
Fuel reactor	$\frac{\text{Fuel mass flow rate}}{\text{Air reactor bed mass}} = \text{const.}$
	Transfer coefficient $X = \text{const.}$

#### *Simulation of the fuel reactor*

The reaction kinetics of the fuel reactor were implemented into a mathematical model with the purpose to obtain a design and scale-up tool for a chemical-looping combustor. The model of the fuel reactor incorporates the fluid dynamics of the fluidized bed by the modified Two-Phase Theory [54], mass transfer between bubble and emulsion phase [58], and RTD of the solid material from experimental findings. The heterogeneous gas–solid reaction is described by the Shrinking Core Model and the kinetic parameters were obtained from results of the Instituto de Carboquímica (CSIC) within the GRACE project.

As the reaction kinetics is not of first order with regard to the solid conversion, the solids cannot be represented by the mean conversion, but are divided into several conversion classes. With this model the effect of particle properties, operating conditions and bed dimensions on the gas conversion can be studied. In order to simulate batch tests as well as continuous operating modes the model is developed dynamically. Figure 10 shows the gas conversion of gas species during methane oxidation by iron oxide at a fluidization velocity of  $5u_{mf}$ . The conversion in the bubbling bed is limited by mass transfer between the bubble and

emulsion phase. Further, significant gas fuel conversion occurs in the freeboard of the reactor. From comparison and validating of modelling and experimental results of the GRACE prototype it is concluded that the model can be used for studying parameter variations.



**Figure 10:** Volumetric fractions of species for fuel oxidation in the fuel reactor. Prototype standard operating parameters and iron oxide as oxygen carrier assumed.

## CONCLUSIONS

Three conceptual designs of atmospheric CLC systems were investigated and evaluated on their suitability. From the research findings of this study the following conclusions are drawn:

- The design of the GRACE prototype was examined in a cold flow model and found to be flexible enough for operating conditions dependent on the reaction properties of the oxygen carriers. This is confirmed by experimental work within the GRACE project by Chalmers University at the GRACE prototype.
- The design concept of a large-scale demonstration was explored in order to map suitable conditions for a CLC plant. The concept is assessed as very well suitable for a 0.5 MW CLC demonstration plant but also forms a proper basis for larger units such as the 200 MW considered in the GRACE Grangemouth scenario.
- The findings of the experimental part of this work package together with mathematical description provide a reliable foundation for the definition of scale-up guidelines. Suitable scale-up criteria were developed and form a basis for further development of this novel combustion technology.

## RECOMMENDATIONS

The findings of the experimental part of this work package together with mathematical description provide a reliable foundation for CLC reactor design. The derived scale-up guidelines enable the demonstration of CLC as next step in the development of this technology. Further, the results encourage the application of CLC in the mid-term also on solid fuels with an integrated gasification process. Due to prospectively higher cycle efficiencies, however, in the long term the potential of pressurized CLC system must be exploited.

## NOMENCLATURE

CFM	cold flow model
CLC	chemical-looping combustion
$G_S$	specific solid circulation rate ( $\text{kg m}^{-2} \text{s}^{-1}$ )
$G_{s,\text{crit}}$	critical (maximum) solid circulation rate for CFB ( $\text{kg m}^{-2} \text{s}^{-1}$ )
$E(t)$	residence time distribution function (—)
$H$	expanded bed height (m)
$k$	reaction rate constant
$k_{12}$	interphase mass transfer coefficient ( $\text{m s}^{-1}$ )
MeO	metal oxide
$m_{\text{FR}}$	bed mass in fuel reactor (kg)
RTD	residence time distribution
$S/T$	ratio of secondary air to total air into riser (%)
TDH	transport disengaging height (m)
TSI	total solid inventory of bed material (kg)
$u$	velocity ( $\text{m s}^{-1}$ )
$u_T$	terminal velocity ( $\text{m s}^{-1}$ )
$u_{\text{mf}}$	terminal velocity ( $\text{m s}^{-1}$ )
$u_{\text{Ris}}$	superficial riser velocity ( $\text{m s}^{-1}$ )
$u$	superficial gas velocity ( $\text{m s}^{-1}$ )

### Greek letters

$\Delta p$	pressure drop (Pa)
$\rho_p$	particle density ( $\text{kg m}^{-3}$ )
$\Delta H$	enthalpy of reaction ( $\text{kg m}^{-3}$ )
$\delta_b$	volume fraction occupied by the bubbles (—)

### Indices

b	bubble phase
e	emulsion phase
ox	oxidation reaction
red	reduction reaction

## ACKNOWLEDGEMENTS

This work was performed in the framework of the EU funded research project GRangemouth Advanced CO<sub>2</sub> CapturE Project (GRACE), ENK5-CT-2001-00571.

## REFERENCES

1. B. Kronberger, G. Löffler, H. Hofbauer, Simulation of Mass and Energy Balances of a Chemical-Looping Combustion System. *Int. J. Energy Clean Environ.* (2004) (in press).
2. K.F. Knoche, H. Richter, Verbesserung der Reversibilität von Verbrennungsprozessen, *Brennstoff-Wärme-Kraft* **20** (1968) 205–211.
3. H. Richter, K.F. Knoche, Reversibility of combustion processes, *Efficiency Costing ACS Symp. Ser.* **235** (1983) 71–86.
4. T.H.J. Herzog, The Economics of CO<sub>2</sub> Capture, *Proceedings of Fourth International Conference on Greenhouse Gas Control Technologies*, Pergamon Press, London, 1999, pp. 101–106.
5. M. Anheden, G. Svedberg, Exergy analysis of chemical-looping combustion systems, *Energy Conversion Manag.* **39** (16–18) (1998) 1967–1980.
6. Ø. Brandvoll, O. Bolland, Inherent CO<sub>2</sub> capture using Chemical-Looping Combustion in a natural gas fired cycle, *Proceedings of the ASME TURBO EXPO 2002*, Amsterdam, Netherlands, 2002.

7. R.J. Copeland, G. Alptekin, M. Cessario, Y. Gerhanovich, A Novel CO<sub>2</sub> Separation System. *First National Conference on Carbon Sequestration*, National Energy Technology Laboratory (NETL), Washington, 2001.
8. R.J. Copeland, G. Alptekin, M. Cessario, Y. Gerhanovich, Sorbent Energy Transfer System (SETS) for CO<sub>2</sub> Separation with High Efficiency, *The 27th International Technical Conference on Coal Utilization & Fuel Systems*, Clearwater, Florida, USA, 2002.
9. J. Wolf, M. Anheden, J. Yan, Performance Analysis of Combined Cycles with Chemical Looping Combustion for CO<sub>2</sub> Capture Requirements for the Oxidation and Reduction Reactors, *International Pittsburgh Coal Conference*, Newcastle, New South Wales, Australia, December 3–7, 2001.
10. 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.
11. P. Cho, T. Mattisson, A. Lyngfelt, Reactivity of iron oxide with methane in a laboratory fluidized bed - application of chemical-looping combustion. *Seventh International Conference on Circulating Fluidized Beds*, Niagara Falls, Ontario, 2002, pp. 599–606.
12. P. Cho, T. Mattisson, A. Lyngfelt, Comparison of iron-, nickel-, copper- and manganese-based oxygen carriers for chemical-looping combustion, *Fuel* **83** (2004) 1215–1225.
13. M. Ishida, H. Jin, A novel chemical-looping combustor without NO<sub>x</sub> formation, *Ind. Engng Chem. Res.* **35** (1996) 2469–2472.
14. M. Ishida, H. Jin, T.A. Okamoto, Fundamental study of a new kind of medium material for chemical-looping combustion, *Energy Fuels* **10** (1996) 958–963.
15. M. Ishida, H. Jin, CO<sub>2</sub> recovery in a power plant with chemical looping combustion, *Energy Conversion Manag.* **38** (1997) 187–192.
16. M. Ishida, H. Jin, T. Okamoto, Kinetic behaviour of solid particles in chemical-looping combustion: suppressing carbon deposition in reduction, *Energy Fuels* **12** (1998) 223–229.
17. M. Ishida, M. Yamamoto, T. Ohba, Experimental results of chemical-looping combustion with NiO/NiAl<sub>2</sub>O<sub>4</sub> particle circulation at 1200°C, *Energy Conversion Manag.* **43** (2002) 1469–1478.
18. H. Jin, T. Okamoto, M. Ishida, Development of a novel chemical-looping combustion: synthesis of a looping material with a double metal oxide of CoO-NiO, *Energy Fuels* **12** (1998) 1272–1277.
19. H. Jin, T. Okamoto, M. Ishida, Development of a novel chemical-looping combustion: synthesis of a solid looping material of NiO/NiAl<sub>2</sub>O<sub>4</sub>, *Ind. Engng Chem. Res.* **38** (1999) 126–132.
20. H. Jin, M. Ishida, Reactivity study on novel hydrogen fueled chemical-looping combustion, *Int. J. Hydrogen Energy* **26** (2001) 889–894.
21. H. Jin, M. Ishida, Reactivity study on natural-gas-fueled chemical looping combustion by a fixed-bed reactor, *Ind. Engng Chem. Res.* **41** (2002) 4004–4007.
22. T. Mattisson, A. Lyngfelt, P. Cho, Possibility of using iron oxide as an oxygen carrier for combustion of methane with removal of CO<sub>2</sub>—application of chemical-looping combustion, *Fifth International Conference on Greenhouse Gas Control Technologies*, Cairns, Australia, pp. 205–210, 2000.
23. T. Mattisson, A. Lyngfelt, P. Cho, The use of iron oxide as oxygen carrier in chemical-looping combustion of methane with inherent separation of CO<sub>2</sub>, *Fuel* **80** (2001) 1953–1962.
24. T. Mattisson, A. Lyngfelt, Capture of CO<sub>2</sub> using chemical-looping combustion. *First Biennial Meeting of Scandinavian-Nordic Section of the Combustion Institute*, G—teborg, 2001 pp. 163–168.
25. T. Mattisson, M. Johansson, A. Lyngfelt, Multi-cycle reduction and oxidation of different types of iron oxide particles—application to chemical-looping combustion, *Energy Fuels* **18** (2004) 628–637.
26. H.-J. Ryu, D.-H. Bae, K.-H. Han, S.-Y. Lee, G.-T. Jin, J.-H. Choi, Oxidation and reduction characteristics of oxygen carrier particles and reaction kinetics by unreacted core model, *Korean J. Chem. Engng* **18** (6) (2001) 831–837.
27. H.-J. Ryu, N.-Y. Lim, D.-H. Bae, G.-T. Jin, Carbon deposition characteristics and regenerative ability of oxygen carrier particles for chemical-looping combustion, *Korean J. Chem. Engng* **20** (1) (2003) 157–162.
28. H.-J. Ryu, G.-T. Bae, Effect of temperature on reduction reactivity oxygen carrier particle for chemical-looping combustor in a fixed bed reactor, *Korean J. Chem. Engng* **20** (5) (2003) 960–966.
29. K.S. Song, Y.S. Seo, H.K. Yoon, S.J. Cho, Characteristics of the NiO/hexaaluminate for chemical looping combustion, *Korean J. Chem. Engng* **20** (2003) 471–475.
30. A. Lyngfelt, B. Leckner, T. Mattisson, A fluidized-bed combustor process with inherent CO<sub>2</sub> separation; application of chemical-looping combustion, *Chem. Eng. Sci.* **56** (2001) 3101–3113.

31. E. Johansson, A. Lyngfelt, T. Mattisson, F. Johnsson, A circulating fluidized bed system with Inherent CO<sub>2</sub> separation - application of chemical-looping combustion, in: J.R. Grace, J. Zhu, H.d. Lasa (Eds.), *Proceedings of the Seventh International Conference of Circulating Fluidized Beds*, Canada, 2002, pp. 717–724.
32. E. Johansson, B. Kronberger, G. Löffler, T. Mattisson, A. Lyngfelt, H. Hofbauer, A two-compartment fluidized bed for chemical-looping combustion—design and experiments. *Proceedings of the Clean Air 2003, Seventh International Conference on Energy for a Clean Environment*, Lisbon, Portugal, 2003.
33. H.-J. Ryu, D.-H. Bae, S.-Y. Lee, G.-T. Jin, 50 kWth Conceptual design of a 50 kWth, *Theories Appl. Chem. Engng.* **8** (2002) 3792–3798.
34. H.-J. Ryu, D.-H. Bae, G.-T. Jin, Chemical-Looping Combustion Process with Inherent CO<sub>2</sub> Separation; Reaction Kinetics of Oxygen Carrier Particles and 50 kWth Reactor Design, *The World Congress of Korean and Korean Ethnic Scientists and Engineers*, Seoul, Korea, 2002, pp. 738–743.
35. W. Haslinger, H. Hofbauer, L. Gavriil, I. Boukis, Scale-up guidelines for a circulating fluidized bed biomass pyrolyser, in: J. Werther (Ed.), *Circulating Fluidized Bed Technology VI*, DECHEMA, Frankfurt am Main, 1999, pp. 899–905.
36. H. Hofbauer, Internally Circulating Fluidized Beds, Fundamental and Applications, *Proceedings of the First SCEJ Symposium on Fluidization*, Tokyo, 1995, 275.
37. E. Hugi, Auslegung hochbelasteter Zyklonabscheider für zirkulierende Gas/Feststoff-Wirbelschicht-Reaktorsysteme, *Diss. ETH 12171* (1997).
38. E.G. Gottung, S.L. Darling, Design considerations for circulating fluidized bed steam generation, in: A. Manaker (Ed.), *Proceeding of the 11th International Conference on Fluidized Bed Combustion*, ASME, 1989, pp. 617–624.
39. CO<sub>2</sub> Capture Project (CCP). [www.co2captureproject.org](http://www.co2captureproject.org).
40. G. Goldbach, 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.
41. L.R. Glicksman, Scaling relationships for fluidized beds, *Chem. Engng Sci.* **39** (1984) 1373–1379.
42. L.R. Glicksman, M. Hyre, K. Woloshun, Simplified scaling relationships for fluidized beds, *Powder Technol.* **77** (1993) 177–199.
43. B. Kronberger, A. Lyngfelt, G. Löffler, H. Hofbauer, Design and hydrodynamic testing of a 10 kWth prototype for continuous chemical-looping combustion (submitted for publication).
44. M. Rhodes, S. Zhou, T. Hiram, H. Cheng, Effects of operating conditions on longitudinal solids mixing in a circulating fluidized bed riser, *AIChE J.* **37** (10) (1991) 1450–1458.
45. B. Kronberger, G. Löffler, H. Hofbauer, Residence time distribution of solids in a chemical-looping fluidized bed fuel reactor, *Proceedings of the 16th International Congress of Chemical and Process Engineering*, Prague, Czech Republic, 2004.
46. T.S. Pugsley, F. Berruti, Core-annulus solids interchange model for circulating fluidized bed and FCC risers, *Fluidization VIII* (1995) 379–388.
47. F.A. Zenz, N.A. Weil, A theoretical-empirical approach to the mechanism of particle entrainment from fluidized beds, *AIChE J.* **4** (1958) 472–479.
48. R.H. Venderbosch, W. Prins, J.H.A. Kiel, W.P.M. Swaaij, Solids Hold-Up and Pressure Gradient in a Small Laboratory Riser, *Proceedings of Circulating Fluidized Bed Technology V*, Beijing, 1996.
49. H. Hofbauer, Experimentelle Untersuchungen an einer zirkulierenden Wirbelschicht mit Zentralrohr, PhD Thesis, Vienna University of Technology, 1982.
50. E.-U. Hartge, Y. Li, J. Werther, Analysis of the local flow structure of the two phase flow in a fast fluidized bed, in: P. Basu (Ed.), *Circulating Fluidized Bed Technology*, Pergamon Press, Oxford, 1986, pp. 153–160.
51. G.S. Patience, J. Chaouki, F. Berruti, R. Wong, Scaling considerations for circulating fluidized bed risers, *Powder Technol.* **72** (1992) 31–37.
52. S.K. Gupta, F. Berruti, Evaluation of the gas-solid density in a FB riser with exit effects, *Powder Technol.* **108** (2000) 21–31.
53. K.Y. Krishnaiah, P. Setty, Residence time distribution of solids in multistage fluidisation, *Chem. Eng. Sci.* **37** (1982) 1371–1377.
54. F. Johnsson, S. Andersson, B. Leckner, Expansion of a freely bubbling fluidized bed, *Powder Technol.* **68** (1991) 117–123.

55. C.Y. Wen, L.H. Chen, Fluidized bed freeboard phenomena: entrainment and elutriation, *AIChE J.* **28** (1982) 117–128.
56. J.R. Grace, Fluidized beds as chemical reactors, in: D. Geldart (Ed.), *Gas Fluidization Technology*, Wiley, Chichester, New York, Brisbane, Toronto, Singapore, 1986.
57. J.F. Davidson, D. Harrison, *Fluidised Particles*, Cambridge University Press, Cambridge, UK, 1963.
58. S.P. Sit, J.R. Grace, Interphase mass transfer in an aggregative fluidized bed, *Chem. Eng. Sci.* **33** (1978) 1115–1122.