Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

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Volume 1

ELSEVIER
2005

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

ELSEVIER B.V.
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Kidlington, Oxford OX5 1GB
UK

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84 Theobalds Road
London WC1X 8RR
UK

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.

Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1
D.C. Thomas and S.M. Benson (Eds.)

Chapter 33

CHEMICAL LOOPING COMBUSTION (CLC) OXYFUEL TECHNOLOGY SUMMARY

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ABSTRACT

This chapter provides a general overview of the Chemical Looping Combustion Technology Research and Development Program, carried out with EU and CCP funding by a Partnership composed by BP, Alstom Power, Chalmers University of Technology, Instituto de Carboquimica (CSIC) and Vienna University of Technology. The contribution of the Partners will be discussed in detail in the following chapters.

INTRODUCTION

The chemical looping combustion concept is based on the transfer of oxygen from the combustion air to the fuel by means of an oxygen carrier in the form of a metal oxide. Central to the system are an air reactor and a fuel reactor. The gaseous fuel is introduced to the fuel reactor, where it is oxidized by the oxygen carrier, i.e. the metal oxide, MeO. E.g. for methane fuel:

$$MeO + CH_4 \rightarrow Me + 2H_2O + CO_2 \quad (1)$$

The exit gas stream from the fuel reactor contains CO_2 and H_2O, and almost pure CO_2 is obtained when H_2O is condensed. The particles of the oxygen carrier are transferred to the air reactor where they are regenerated by taking up oxygen from the air:

$$Me + \frac{1}{2}O_2 \rightarrow MeO \quad (2)$$

The air reactor gives a flue gas containing only N_2 and some unused O_2. The total amount of heat evolved from reactions (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The significant advantage compared to normal combustion is that the CO_2 is not diluted with N_2. As opposed to other technologies proposed for carbon dioxide separation, this process has no significant energy penalty for the capture process, and external capture devices are avoided. Thus, the process is expected to be less costly than available technologies for carbon dioxide separation. It is also free of certain other emissions such as NO_x and should be suitable for any gaseous fuel. A conceptual process scheme is shown in Figure 1.

THE RESEARCH AND DEVELOPMENT PROJECT

The Chemical Looping R&D activity was part of the GRACE Project (Grangemouth Refinery Advanced CO_2 Capture Project) aimed to develop novel technologies able to reduce the cost of CO_2 capture with possible application to revamping of the boilers and heaters network in an existing refinery.

Abbreviations: CCP, CO_2 Capture Project; CEM, common economic model; CFB, circulating fluidized boiler; EU, European Union.

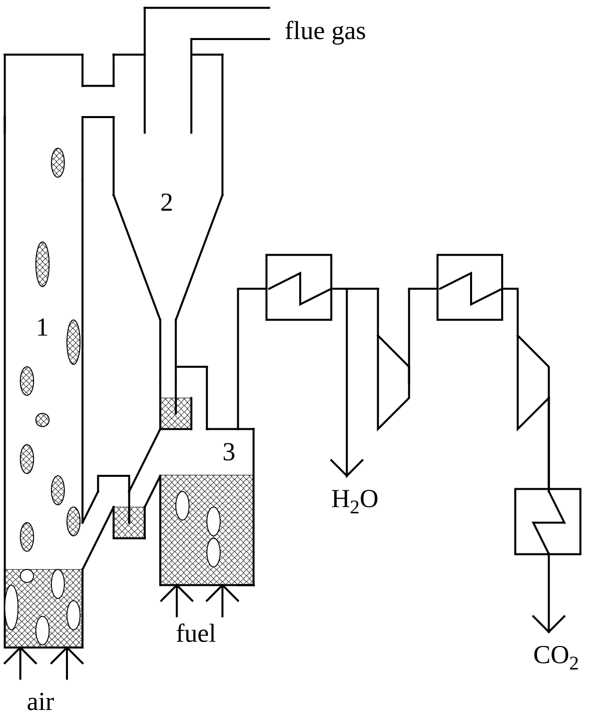

Figure 1: Chemical looping conceptual scheme.

The Grangemouth refinery (UK) was selected as the site for potential application of the technologies under development, to align technical/economical evaluations on a comparable basis. This refinery is also the selected site for one of the CCP Scenarios, so that GRACE evaluations have been easily inserted in the wider range of the CCP evaluations.

The concept of the chemical looping may in principle be applied to other Scenarios (e.g. power generation in a combined cycle) or other fuels (e.g. liquid or solid fuels), but these possible applications were not investigated in the context of the GRACE Project.

The Chemical Looping Partnership was composed by BP (Project Coordinator), Alstom Power Boilers, Chalmers University of Technology, Consejo Superior de Investigaciones Cientificas (CSIC) and Vienna University of Technology. The Project had a duration of 2 years (01/01/2002–31/12/2003) and the main target was to achieve the Proof-of-Feasibility of the technology through operation of a hot pilot unit with continuous solid circulation at Chalmers University. Due to the complexity of the Project, the activities were split into five technical Work Packages (WP), with different Partners in charge of each WP, with WP1 specifically devoted to the whole Project Coordination by BP:

- Work Package 2: particle development and screening tests (CSIC and Chalmers);
- Work Package 3: comprehensive testing of materials (CSIC and Chalmers);
- Work Package 4: fluidization conditions (Vienna University);
- Work Package 5: construction and test of chemical looping combustor unit (Chalmers)
- Work Package 6: design Criteria (Alstom).

Activity and main results for each WP are briefly summarized here below.

Particle Development and Screening Tests
The screening activity was performed by Chalmers and CSIC on a total of about 240 different materials. The base for the screening was the combination of four active oxides, and five supports, investigating different active material/support ratios, calcination temperatures, and preparation methods (extrusion, impregnation, freeze granulation).

Experimentation was carried out in fixed (first screening) and fluidized bed (second screening) reactors, using the following criteria for selection:

- Chemical reactivity;
- Attrition resistance and crushing strength.

This activity allowed to assess a number of possible materials for further testing. Four of them were initially selected for further work in the Project, in the frame of Work Package 3 and Work Package 5.

Comprehensive Testing of Materials
The materials selected in Work Package 2 have been subjected to intensive experimentation aiming to define optimal operating conditions and kinetic parameters to be introduced in the mathematical model for simulation. This experimentation also allowed assessment of NiO/Al_2O_3 as the most promising material with highest priority for pilot plant testing in Work Package 5, due to its high reactivity both in the oxidation and the reduction phases. This material also produces small amounts of H_2 and CO in the combustion (reduction) phase.

A Fe-based material was selected as second best for pilot testing, since it shows lower reactivity, leading to higher inventory for commercial units, but higher environmental acceptability than Ni-based materials.

Fluidization Studies
Vienna University performed the activities of Work Package 4 through construction and operation of three cold flow units, simulating the circulating fluidized bed (CFB) process scheme foreseen for pilot and commercial units:

- CFM1 was the cold twin (slightly scaled down) of the pilot unit at Chalmers University (Work Package 5).
- CFM2 was twin of CFM1 providing alternative options to control the solid circulation flow rate.
- CFM3 was the scaled down version (from 200 to 0.5 MW) of the commercial design proposed by Alstom (Work Package 6).

CFM1 and CFM2 confirmed the operability of the pilot unit in the desired range of conditions and allowed optimization of the circulating loop and loop seals. CFM3 confirmed the design criteria for the commercial unit. The results of the experimentation were used to define the scale-up guidelines for chemical looping units. The correlations thus developed were implemented in a mathematical model to be combined with the kinetics developed in Work Package 3 for design and simulation of commercial units.

Construction and Test of Pilot Unit
A 10 kW pilot unit was designed, built and operated by Chalmers University with the target to supply Proof-of-Feasibility for the technology. The unit was operated with a solid inventory of 10–15 kg. Tests were performed with Ni-based particles in the following conditions:

- Oxidation reactor: 900–1000 °C
- Reduction reactor: 750–900 °C

The oxidation reactor worked positively leaving a concentration of oxygen in the gaseous effluent in the 6–7% range. Methane combustion in the reduction reactor was almost complete. Methane concentration in the flue gas ranged from 500 ppm (at 750 °C) to 1% (at 900 °C). Concentration of both H_2 and CO in the flue gas was close to equilibrium (total lower than 1% volume). No significant particle attrition or catalyst aging were detected during operation (total of about 300 h in temperature and 100 h in reaction.

Design Criteria
Applying internal knowledge on CFB units, together with results from the pilot unit and the cold model units, Alstom designed a 200 MW chemical looping system, to replace an existing boiler in the Grangemouth refinery (CCP European refinery Scenario). The technical package was supplied by Alstom to the CCP. A preliminary evaluation performed in 2002 resulted in $>40\%$ saving compared to the post-combustion baseline.

CONCLUSIONS

The Chemical Looping Project was a technical success, supplying the target result of Proof-of-Feasibility for the technology through operation of the pilot unit at Chalmers University. The main technical achievements are summarized here.

- Proven reversible oxidation/reduction of the solid material with oxygen transfer between the two reactors.
- Achievement of almost complete combustion of oxygen ($>99\%$).
- No gas leakage between reactors detected in pilot unit operation.
- CO_2 purity in the dry flue gas $>98\%$.
- Achieved solid circulation rate and reaction rate assumed for commercial scale design and utilized for the economic evaluation.
- No significant particle attrition or chemical decay were observed.

The major concerns still to be addressed by further research activity are related to the development of the solid material, namely:

- Chemical and mechanical aging;
- Scale-up of manufacturing procedure.

Once these issues are solved, scale-up risk should be considered as moderate, due to similarity with the existing commercial technology for CFB boilers for coal combustion. According to Alstom, a 1 MW demo-unit would be sufficient for scale-up to commercial size.

ACKNOWLEDGEMENTS

The contribution of Francesco Saviano, former Oxyfuel Team member, in the development of chemical looping process schemes for the evaluation by the CCP is acknowledged.