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CALCIUM CYCLE FOR EFFICIENT AND LOW COST CO2 CAPTURE IN FLUIDIZED BED SYSTEMS

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Final

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1 Project execution

1.1 Project objectives

The project aims to develop an advanced dry CO₂ capture system applicable for both PF and CFB boiler systems. Two options for CO₂ capture from boiler systems are investigated: an integrated atmospheric fluidized bed system for post-combustion capture from PF or CFB boilers and an in-situ capture system for PFBC boilers. The atmospheric option will be directed to the development of a pilot plant application. For the pressurized option, the project will seek a proof of principle to determine if the expected benefits of a pressurized capture system can balance the known limitations of PFBC systems. The quantifiable objectives of the development are:

- Low CO₂ capture costs (<20€/ton for atmospheric, <12€/ton for pressurized systems)
- Low efficiency penalty for CO₂ capture ($\leq 6\% \eta_{el}$ including CO₂ compression to 100 bar). The efficiency penalty is even lower ($\leq 4\%$) when considering the integration with a cement plant where pre-calcined feed reduces energy consumption and CO₂ release
- >90% carbon capture for new power plants and >60% for retrofitted existing plants
- A calciner gas stream containing >95% CO₂ (dry base)
- A solid product usable for cement production
- Simultaneous sulphur and CO₂ removal with sulphur recovery option

By integrating a closed carbonation-calcination loop in the flue gas of a conventional CFB-boiler, the CO₂ in the flue gas can be removed. The heat required for calcination is released during carbonation and can be utilised efficiently (i.e. at high temperature) in the steam cycle of the boiler. Highly concentrated CO₂ can be generated when using oxygen blown calcination. Because the fuel required for supplying sufficient heat for calcination is only a fraction of the total fuel requirements, the required oxygen is only about 1/3 to 1/2 of the oxygen required for oxyfuel processes. This CO₂ capture technology can be compared to wet scrubbers using amines for CO₂ absorption. These scrubbers need as well a regenerator operating at higher temperatures than the absorber, but at a considerably lower temperature level compared to the lime loop. The lime based “dry scrubber” operates at typical steam cycle temperatures, so the energy can be directly reused. Therefore, the efficiency penalty of such a capture system is typically very low (< 6%) compared to other capture technologies. Since limestone is a low cost material with good geographical distribution, it allows the use of local limestone resources from power plants for CO₂ capture with minimal limestone-related infrastructure investment.

1.2 Contractors involved

Contractors involved in this project are: the University of Stuttgart- Institute for Process Engineering and Power Plant Technology (USTUTT) which is the project coordinator, ENDESA Generación, S.A (ENDESA), University of Mulhouse (UHA), Alstom Power Boilers (APBFR), IVE Weimer (SME) (IVE), Główny Instytut Górnictwa-Central Mining Institute (GIG), The Southern Power Generation Concern (PKE), The All-Russian Thermal Engineering Institute (VTI), CEMEX Trademarks Worldwide Ltd. (CEMEX), Cranfield University - Power Generation Technology Centre (Cranfield), Consejo Superior de Investigaciones Científicas (CSIC), CANMET Energy Technology Centre-Ottawa

(CANMET). Therefore, the project consortium is an ideal mix from universities, industries and research institutes that brings together experience from EU and non EU countries.

1.3 Work performed and end results

1.3.1 Process definition and boundary conditions (WP 1)

The project started with intense activity in this WP, as it was necessary to define in sufficient detail the three base cases of full power plant concepts to be investigated in the project (new atmospheric, retrofitted atmospheric and new pressurized power plant) and clarify and prioritize the experimental work at particle level (WP2), at reactor level (WP3) and the boundary conditions for the economic analysis (WP4). The definition of these base cases was site dependent and required specific site data of existing power plants. **APBFR** led the work to define the key **process requirements** and the status of enabling technologies for the key components of the process. **CSIC** contributed to this work by reviewing issues of sorbent requirements and main operating windows for carbonator and calciner for the atmospheric and pressurized options (a scientific publication on the sensitivity of the heat requirements in the calciner as a function of process conditions and sorbent, fuel characteristics resulted from this work, see [9]). **CEMEX** developed a model that allowed for the calculation of the requirements of the purge material as input for a cement kiln under different, user-defined conditions.

The **three representative cases for the application of the three capture concepts** considered in this project were also defined: **APBFR** provided a detail definition of the project specification for a new 445 MWe atmospheric CFB boiler island-design case, where capture of CO₂ with the proposed process could be applied. **ENDESA** defined the project specification for a 3x350 MWe existing atmospheric PF boiler. **CSIC** defined, with background information from **CANMET**, the base case for CO₂ capture in a pressurized fluidized bed combustor-carbonator (a joint journal publication by these two partners on this process was produced, see [6]). Concerning **fuel, sorbent supply to partners** for investigations at particle, reactor level and site selection, **ENDESA**, **PKE** and **CEMEX** selected and supplied samples for investigation in the experimental WPs. **ENDESA** selected its Teruel Power Plant as a possible location for the pilot plant for postcombustion capture with CaO. Moreover, several limestones were studied to be used and tested in this project. **GIG** identified the majority of power plants of **PKE** as potential locations for CC technologies, consuming the bituminous coal of energetic quality. Examples are the Halemba, the Blachownia, the Siersza, the Jaworzno III, the Katowice and the Bielsko-Biala power plants. The portfolio of the power installations owned by **PKE** represents the broad window of opportunities for further analysis of CO₂ Capture demo location: from low moisture content gases of Halemba to potentially wet flue gases from Bielsko Biala CHP installations assuming optionally pure natural gas.

1.3.2 Selection and improvement of sorbent materials (WP 2)

Under WP2, extensive work was performed to better understand the behaviour of the sorbent. The reactivity of CaO towards CO₂ (carbonation) and the deactivation by sintering were investigated, both experimentally and theoretically. Kinetic parameters have been determined in order to be used as inputs in a model of the complete process.

The **CO₂ absorption capacity** of the sorbent is naturally one of the most important parameters of the process. Therefore, **CSIC** was in charge of an extensive screening testing programme of a wide variety of limestones and other sources of carbonate that could be sorbent precursors (like mussel shells, used for desulfurization in some power plants of **ENDESA**). Multi-cycle tests (up 100 thermograms for each sample) have been carried in a new thermogravimetric device specially designed for these type of test, with two moving ovens that rapidly change the temperature around the sample between carbonation and calcination conditions. All limestones followed a similar general trend (in carbonation capacity along cycling measured as Ca conversion). The series of experiments with mussel shells gave very different decay curves and different texture after calcination as observed by Scanning Electron Microscopy. A sintering equation based on the model published by **CANMET**, but with a residual activity at long cycle numbers, has been found to best fit the available experimental results. Extended experiments of up to 500 cycles confirmed the general validity of the model and a publication in a scientific journal was the result of this work, as shown in [5].

Furthermore, **VTI** developed a technique for definition of the CO₂ carrying capacity of lime during removal of CO₂ from flue gases and investigated the influence of SO₂ on this process. A technique has been developed with the purpose of standardization of the estimation of the CO₂ carrying capacity of lime.

CSIC also conducted a review of synthetic sorbents and conducted tests to replicate some of the results claimed in the literature with some synthetic CaO precursors. Our results confirm the good performance of some of these synthetic sorbents under mild calcination conditions and/or long carbonation times used in the original references. However, it has been shown that these sorbents deactivate very quickly when realistic regeneration conditions (high temperatures for calcination at high partial pressures of CO₂) are used in the laboratory test. In conclusion, none of the reviewed sorbents have a chance to compete with the performance of natural limestones, of much lower cost. A publication was made summarizing this work [8].

Being able to **model the different aspects of the sorbent behaviour** is crucial so as to develop tools which allowed the proper reactor design in WP3, are needed for process scale up and economic evaluation (WP4). **CSIC** has investigated the effect of higher calcination temperatures (up to 1200 °C) in the deactivation trends of a typical sorbent (limestone from Katowice-Poland). This work is relevant for the high pressure process considered in this project that involves very high temperatures in the calciner to overcome the high partial pressures of CO₂ inherent in the high pressure operation. The equations proposed in previous works and in the open literature to describe the decay in sorbent capture capacity along cycling are limited to moderate calcination temperatures (typically well below 950 °C). At higher calcination temperatures (over 950 °C) the decay in carbonation capacity with the number of cycles is more pronounced and increases with the cumulative number calcination cycles. At the highest temperatures tested in this work (up to 1200 °C), the residual carbonation conversion is almost non-existent. This additional decay in carbonation conversion over cycling for very high calcination temperatures and times has been modelled by adding a time-dependent sintering mechanism (modelled with the German-Munir equation) to the sintering due to the increase in the number of cycles reported in previous reporting periods. The resulting equation fits the available data reasonably well, there being good agreement between the experimental data and those calculated by applying the proposed equation over a wide range of calcination temperatures, calcination times and numbers of cycles. A publication to the journal Energy and Fuels [1] has been made with these results. Moreover, **CSIC** has also conducted extensive experimental and modelling work on the carbonation reaction rates of highly cycled sample at typical low partial pressures of CO₂ expected in the carbonator reactor, in the main postcombustion options considered in this

project. First, a basic reaction model was used to interpret the reactivity data corresponding to the fast carbonation period of these particles. Kinetic constants were in agreement with other values reported in the literature. A publication in an international journal was derived from this work [3]. Later on and due to the importance of having available more detailed and realistic reaction rate models to describe the behaviour of CaO particles with respect to the carbonation reaction, this model was expanded and redefined using the more general Random Pore Model. Extensive experimental work involving hundreds of tests with samples of different cycle numbers and calcination conditions was completed and a database of kinetic data was built. Selected samples were texturally analyzed to derive structural parameters for the model when needed. It was shown that with the Random Pore Model it was possible to describe the carbonation reaction as a two stage reaction. In the first stage, the carbonation is controlled by chemical reaction and in the second period there is a combined control by chemical reaction and CO₂ diffusion through the product layer. This new version of the RPM model for the carbonation reaction of highly cycled particles integrated knowledge obtained in previous works on intrinsic carbonation rates, critical product layer thickness and pore structure evolution in highly cycled particles. A paper in AIChE Journal has been accepted for publication of these results [2].

UHA studied the decrease of the extent of carbonation along cycles in a fixed bed reactor. This phenomenon was interpreted by sintering of CaO micrograins during calcination at 850°C. Sintering was successfully modelled by the decrease of the specific surface area during calcination, according to the law:

$$\frac{dA_i}{dt_{\text{calcination}}} = -k(A_i - A_\infty)$$

A_i is the specific area of CaO at the end of calcination i and A_∞ is the asymptotic surface area after a large number of cycles. The constant k for sintering was estimated at three temperatures. It ranges from 2.9x10⁻⁵ s⁻¹ at 750 °C to 5.5x10⁻⁴ s⁻¹ at 950 °C.

The carbonation process was studied at a microscopic level. Reaction was supposed to occur at the surface of micrograins of CaO. A shrinking core model was used. The reaction is very fast and under kinetic control in the early stage when the thickness of the carbonate layer is very small. This reaction moves towards a mixed regime (diffusion and kinetics) when the carbonate layer increases. When the available voids between micrograins is filled by carbonate, reaction moves towards a diffusion control at the scale of the whole grain. Intrinsic kinetic constants for carbonation and a realistic diffusion coefficient of CO₂ through the carbonate layer have been proposed, as shown in [10]. These data are necessary for the prediction of the sorbent behaviour along the successive carbonation/calcination cycles.

USTUTT created a predictive CFB carbonator reactor model that couples CFB fluid dynamics with the carbonation reaction in order to define the CFB process parameter settings that result in high CO₂ capture. The CFB carbonator has been divided into three different zones each with its unique hydrodynamic and reaction model: (1) a dense bed zone; (2) an acceleration zone; (3) and a fully-developed flow zone with a core-annulus flow structure. The developed model has the following inputs: reactor dimensions, particle properties (e.g. d_p, density), bed inventory, temperature, inlet velocity, inlet CO₂ concentration, and the fraction of free active CaO (f_a) available for reaction. The main outputs of the model are: CO₂ capture efficiency (Ec), solid fluxes and voidage (both axial and radial in zone 3). The rate of carbonation used in this model is a modified version of the rate given by Bhatia and Perlmutter (1983) who used the random pore model to determine the surface reaction rate, with k_s = 5.95e-10 m⁴/s-mol and zero activation energy (between 550-725 °C). Since in the CO₂ looping cycle, the maximum carrying capacity can be very low a modification to the original equation was considered necessary. This model has been published in [12].

Sorbent Attrition is a very important aspect of the process since it is related to the need of fresh limestone supply to a C3 Capture technology plant. **UHA** intended to investigate the sorbent attrition within a fully integrated high velocity rig supplied by **APBFR**. This device, electrically heated, was designed in order that the solids undergo a large number of cycles between carbonator and calciner. Unfortunately, it was impossible to keep the circulating solids within the system during heating, preventing further study. The very compact system made impossible necessary modifications so that a completely redesigned device would be necessary for the study. From continuous testing of carbonation-calcination conducted from **USTUTT** with use of its 10 kWth Dual Fluidized Bed facility, the rate of sorbent attrition was found to be 2 wt-%/h. This is below the required sorbent make-up flow rate required in order to maintain high sorbent activity. However, **CANMET** has shown from experiments in their 75 kWth Dual Fluidized Bed facility that attrition is significant and does not only occur as a result of the first calcination but evolves during operation.

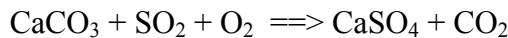
The **impact of SO₂ present on the carbonation efficiency and the separation of SO₂ from the sorbent** are significant issues also affecting the limestone needs of a C3 technology plant. **CANMET** conducted experiments in an ATGA (Atmospheric Thermo-Gravimetric Analyzer) in order to study the effect of SO₂ during carbonation and concluded that sorbent conversions decayed more quickly when SO₂ was present for all sorbents. SEM, EDX, and pore-size distributions revealed that direct sulphation becomes dominant after completion of an initial fast stage of carbonation, filling larger pores by sulphation from the outside, enveloping the sorbents with an impermeable shell, and thus inhibiting further carbonation and impeding subsequent calcination. Furthermore, **Cranfield** conducted experiments in a BFB (Bubbling Fluidized Bed) so as to study the effect of SO₂ during calcination on subsequent carbonation. It can be clearly seen that the sorbent prepared by calcination in an atmosphere containing low concentrations of SO₂ performed significantly better in subsequent carbonation experiments than the sorbents prepared in atmospheres with high concentrations of SO₂. Similarly to **CANMET**, **Cranfield** concluded that this is due to the sulphation reaction occurring simultaneously with the calcination reaction, forming a layer of sulphate that impedes the access of CO₂ to smaller pores and thus to the active CaO surface. **CSIC** also started to carry out experimental testing of SO₂ effects on carbonation-calcination performance. During this project, work was completed investigating the effect of partial sorbent sulphation on total CaO utilisation in systems where both carbonation and sulphation reactions will take place. This work has confirmed that changes in sorbent texture due to repetitive carbonation-calcination cycles increase sorbent sulphation capacity for all sorbents tested (i.e. particles of lime with low carbonation capacity because extensive sintering and large pore network, tend to show substantially better performance as SO₂ sorbents). Also, it has been found that SO₂ is able to react with non-active CaO towards CO₂ carbonation and is therefore less active than expected in the deactivation of the sorbent used in the CO₂ capture system. Results of this work were also published in a scientific journal [5]. However, it has been proved from **UHA** that this inhibition process is not irreversible and that alternatively reducing and oxidizing conditions are able to completely decompose sulphates, contained in the used sorbent, into SO₂ without CaS accumulation within the particles. During the oxidizing step, CaS formed during the reducing step is oxidized into SO₂. This can thus provide a procedure for separation of sulphur from calcium in a used sorbent.

GIG has investigated **technologies for the use and recycling of fines** since in any case fines are generated in the process due to limestone attrition. The most important scientific conclusion regarding the attrition phenomena, completed by **GIG**, is that the resistance of the CaO based sorbent particles produced from the milled mineral calcium carbonate (Czatkowice limestone) to the attrition and cracks evaluated **under the fluidized bed regime at room**

temperature (as it is the common practice in the standard attrition studies), **are not relevant** for their mechanical integrity during exploitation at high temperatures at real process conditions. It is important to notice, that the damage to the particles caused by the thermal or chemical mechanisms of attrition is several times more intensive than the attrition observed during experiments at room temperatures. Such findings are especially appropriate for the sorbent grains (with average diameter 50-70 micrometers) produced from waste of solid CaCO_3 separated as fines from the outlet gas during the calcination-carbonation cyclic processes in the fluidized bed. Such recycled particles of high reactivity but low attrition resistance were produced by the physical agglomeration and calcination of fines captured inside the filter bag introduced into the outlet stream of fluidizing carrier contaminated by dust. The relevant conclusions were derived for prognosis of the mechanical stability of the highly active, high internal surface area solid materials produced from the synthetic PCC (Precipitated Calcium Carbonates) of diverse origin. Moreover, it was documented that recycled CaO sorbents, participating in the carbonation stage of the processing cycles at low temperature with wet and hot flue gases (containing water close to the condensation point), agglomerate fast and cause problems by sticking to the surfaces of the processing columns. Much higher mechanical stability of the sorbent was observed for agglomerates produced from fines employing the chemical agglomeration, i.e. using the solution of potassium/sodium silicates in water as cementing additive. Higher product resistance to attrition was however compromised by the lower reactivity of the product in carbonation process (higher internal resistance to mass transfer). The chemically bound fines have exposed an interestingly high activity regarding the process of SO_x removal from synthetic flue gas containing sulphur oxides. In the final part of the work the possibility of applying the fines as the low-cost micro and nano-porous solid support/carrier for production of the novel type "dry sorbents", that could be effectively used for CO_2 removal at low temperature from humid flue gases, was explored. This is interesting especially for retrofitting power plants combusting natural gas as energy carrier. The attrition tests were performed in more than hundred experimental calcination-carbonation runs accompanied by determination of the changes in sorbents particle size distribution, screened out at various times of fluidized bed operation (start of the process, 20 min, 60 min and 180 min). The runs have been carried out at several ranges of temperatures, i.e. at the room temperature, at 200 °C and at 850 °C, employing the inert gas (nitrogen), the synthetic dry flue gas (15 % of CO_2 in nitrogen) and the humid flue gas as the carrier fluids. The opportunities to carry out the complex, physical and chemical studies of attrition in the realistic "industrial" conditions was possible due to the design, construction and commissioning of the special, high temperature rig able to work in broad range of temperatures, furnished with the system of generation of fluidized gas stream of precisely controlled flow rate and composition. The differential capacities of the sorbents to capture CO_2 from flue gases, as a function of the time on stream, processing conditions and/or number of reaction cycles was measured by chemical volumetric methods. At the practical level, the major achievement of the GIG's team consists in elaboration of the recommendations for the rational choice of the attrition resistant sorbents to be used effectively in the frame of C3 Capture technology and the development of feasible concepts for effective reuse of the fines produced during the fluidized bed operations. This could be concluded in the following statements:

1. Taking into account the costs and the scale of the processes of carbon dioxide recovery from flue gas and recognizing experimentally the highest attrition resistance of the sorbents obtained by calcination of CaCO_3 of mineral origin, it is recommended to use this type of sorbent in the post combustion carbon capture process.

2. There is the common property of sorbents produced from the fines- they must be reprocessed back to the required powder form before reuse. It was found that the sophisticated but expensive process of physico-chemical agglomeration of fines combined with thermal reactivation is needed so as to produce the necessary powders.
3. The low cost process of physical agglomeration of fines, which uses only water and inexpensive reagents (surfactants), produces porous sorbent of high reactivity, which could be utilized in desulfurization of flue gases without the necessity of activation of the granules by calcination. This product could be used for preliminary removal of SO₂ in the combustors according to the reaction (simplified form):



4. The fines collected from the “dusty” outlet gases, after calcination produce the fine porous particles, which could be used as the effective support in preparation the dry sorbents of high activity. Those are of increasing interest in CO₂ capture from humid flue gases at low temperatures.

Sorbent pre-treatment and post-treatment are approaches so as to solve the biggest weakness of the C3 technology which is the decay of the CO₂ carrying capacity with increasing carbonation-calcination cycles. **CANMET** investigated the methodologies of steam hydration, pelletization and thermal activation of limestone/lime to improve sorbent utilization for in-situ CO₂ capture under operating conditions typical of fluidized bed combustion (FBC). A pressurized thermogravimetric analyzer (PTGA) was used to evaluate the performance of modified sorbents from several domestic limestones. Steam hydration itself was done under atmospheric pressure in saturated steam at 100°C for periods of 15, 30 and 60 min. It revealed that steam hydration of CaO improved the carbonation capacity as much as 3-5 times after multiple cycles since both pore area and pore volume are enhanced for long-term lime reactivity for carbonation [14]. Steam hydration was performed on spent sorbents obtained from a 75 kWth pilot-scale dual fluidized bed combustion pilot unit operating in a CO₂ looping cycle mode. The samples were collected from the system under various conditions, which included pure air calcination with electric heating, as well as firing with coal, biomass under air and oxy-fuel combustion conditions [15]. In addition, different operating times, i.e. number of cycles (1–25 cycles) were examined, with the carbonator operating at temperatures of 600–700°C and the calciner at 850–900°C. All samples were characterized for their hydration and carbonation levels, their unreacted CaO content, pore distribution with nitrogen adsorption/desorption (BET and BJH), skeleton characterization with density by He pycnometry and particle surface area morphology (SEM/EDX), as well as changes in sample volume during hydration (sample swelling). The results obtained showed successful hydration (typically only ~10% unreacted CaO) even for hydration periods as short as 15 min, and very favorable sample properties. Their pore surface area, pore volume distribution and swelling during hydration are promising with regard to their use in additional CO₂ capture cycles or SO₂ retention. However, the hydrated sorbent was very fragile and its application could be limited in FBC applications for CO₂ capture technology due to intensified attrition and consequent elutriation from the reactor. Similar sorbent improvements in terms of reactivity maintenance were observed by sorbent fine grinding and pelletization, which has proven to be an excellent solution for using the hydrated sorbent in fluidized bed systems [14]. Hydrated and pelletized limestone derived sorbents have been developed and tested by thermogravimetric analysis that have shown excellent activity for carbon dioxide capture. The pelletized sorbents that have been developed appear to have reduced resistance to mass transfer as a result of their open pore structure. This has increased the rate of reaction

during both calcination and carbonation for pellets of suitable size for fluidized bed combustors as compared to crushed limestone. The calcination and carbonation process conditions for CO₂ capture were optimized for the modified sorbents and compared to their original sorbent forms. Another pretreatment method investigated is thermal activation for different types of CaO-based sorbents [16]. Pretreatments were performed at different temperatures (800-1300 °C) and different durations (6-48 h) using four Canadian limestones, Kelly Rock, Cadomin, Graymont and Havelock. Pretreated samples were evaluated using a thermogravimetric analyzer and a tube furnace. The most important result was that thermal pretreatment could improve long-term sorbent performance. In comparison to the untreated limestone, pretreated sorbents showed better CaO conversions over a long series of CO₂ cycles. Moreover, in some cases sorbent activity actually increased with cycle number, and this effect was especially pronounced for powdered samples pretreated at 1000°C. In these experiments, the increase of conversion with cycle number (designated as self-reactivation) after 30 cycles produced samples that were ~50% carbonated for the four sorbents examined here, and there appeared to be the potential for additional increase. These results were explained with the newly proposed pore-skeleton model. This suggests, in addition to changes in the porous structure of the sorbent, that changes in the pore-skeleton produced during pretreatment strongly influences subsequent carbonation/calcination cycles.

1.3.3 Experimental testing of the process (WP 3)

The main objective of WP3, carried out successfully, was to prove the feasibility of the process with use of 10-75 kWth atmospheric Dual Fluidized Bed facilities by achieving high CO₂ capture efficiencies. Since a pressurized C3 Capture system is also of great interest due to the ability of combining the CFB combustor and carbonator in one reactor, pressurized carbonation and calcination experiments were carried out at pressures up to 1.6 MPa in batch FBs. Moreover, by increasing the partial pressure of CO₂ in the inlet flue gas of a carbonator of an atmospheric Dual Fluidized Bed system, the feasibility of the pressurized C3 technology was also evaluated at continuous mode of operation.

Therefore, the **design and modification of suitable Dual Fluidized Bed facilities** was of great concern at the start of this project. **CANMET**, **USTUTT**, **UHA** and **Cranfield** have completed rigs of 10-75kWth within this project. The facilities varied widely from a design point of view in regard to the gas solid contacting in carbonator and regenerator (Bubbling Fluidized Bed mode, Circulating Fluidized Bed mode) and in regard to the solid circulation system between the carbonator and the regenerator. However, information coming from **WP2**, regarding the sorbent reaction rate and decay of the sorbent activity with increasing number of carbonation-calcination cycles, has been crucial in determining reactor size-inventory and circulation rates between the beds. **CANMET** dual fluidized bed system (75 kWth) was constructed and commissioned in spring 2007 to implement the tasks involved in the C3 Capture project. The system consists of two fluidized bed reactors: a sorbent calciner/regenerator, which is a circulating fluidized bed combustor upgraded for operation with oxy-fuel firing using flue gas recycle to burn solid fuels and a combustor/carbonator, which is divided into two stages and designed to separate combustion/sulphation from carbonation. Both reactors have an ID of 100 mm and can be operated at up to 1000°C at atmospheric pressure. At the bottom of the reactors, a 45-degree "T" lines allow the solids to go from reactor to the other to create and maintain sorbent (limestone) looping [17]. **USTUTT** has built a 12.4 m high and 7 cm wide CFB and has modified an 11.4 cm wide existing BFB. During this project the BFB has been operated as a carbonator, while the CFB served as the regenerator, although the opposite is also possible. The circulation rate between

the beds is controlled through a cone valve placed in the CFB loop seal. The regenerator is fired with natural gas and air or under oxy-combustion conditions. **UHA** coupled two CFBs, one devoted to carbonation of lime and the other devoted to limestone calcination. The diameter of the carbonator is 10.4 cm while the diameter of the regenerator is 5.3 cm in the lower part and 8.1 cm in the upper part. Oxy- combustion of coal is possible. The circulation rate between the two CFBs was controlled through two double exit loop seals by varying the aeration between the different loop seal exits. **APBFR** has contributed by recommendations to **UHA** for the design of this coupled rig. **Cranfield** built a 4.5 m high and 10 cm wide CFB carbonator and a 16.5 cm wide BFB calciner. The two rigs are coupled via loop seals. Solids are fed from the top of the vessels with using screw feeders. The carbonator is fluidised with real flue gases coming from a 25 kW natural gas burner and synthetic gases. The calciner is oxy-fired with natural gas.

The issue of **solid circulation behaviour of CaO between the beds** was investigated due to its significance through the continuous operation of the DFB systems of the partners. **USTUTT** operated with a coarse PSD having a median particle size of above 300 μm and experienced no problems regarding the circulation of material between the carbonator and the calciner. Moreover, **CANMET** from the second year of the project had also shown that solid circulation between the carbonator and the calciner is not a problem. More detailed discussion on the issue of solid circulation can be found in corresponding publications [11] and [17]. **UHA** experienced plugging during limestone circulation. A solid mixture of 70 % CaCO_3 and 30 % alumina with an optimized particle size distribution, allowed obtaining a satisfactory solid circulation. **USTUTT** and **APBFR** had conducted detailed cold model testing that led to significant improvements of the hydrodynamics and solid circulation system of their Dual Fluidized Bed facilities. **USTUTT** used the Glicksman criteria to achieve hydrodynamic similarity between the 2.33 times scaled cold model and the actual facility, as is found in [13]. Concepts of controlling the circulation rates between the two beds by using a loop seal with cone valve (**USTUTT**), or a double exit loop seal with aeration variation between the exits (**UHA**) and 45-degree T lines at the bottom of the beds (**CANMET**) have been validated.

The C3 Capture technology has been realized with great success with use of the Dual Fluidized Bed systems operated within this project. **CANMET** has demonstrated this technology with more than 500 hours of operation completed. The facility achieves high (>95%) removal of CO_2 from a synthetic flue gas stream at temperatures above 500°C [17]. A gas mixture of air and CO_2 (15%) was employed to simulate combustion flue gas. A variety of operating conditions, including sorbent looping rate, flue gas stream volume, CaO/CO_2 ratio and combustion mode for supplying heat, were investigated. Oxy-fuel combustion of biomass and/or coal was employed in the sorbent regeneration step, creating a high- CO_2 off-gas stream of 85% CO_2 . Greater than 97% CO_2 removal from synthetic flue gas has been achieved, with the highest captures seen over the first several looping cycles. Multi-cycle tests dropped the CO_2 capture but to a still acceptable level (>75%) even after more than 25 cycles. Besides the decay of sorbent reactivity, sorbent attrition was found to be another significant factor to be limiting sorbent performance with increasing number of looping cycles. It is interesting to note that the optimized temperature window associated with CO_2 capture in the carbonator became higher with the number of sorbent cycles. Better CO_2 capture was obtained at carbonator temperatures of ~700°C after more than 20 cycles, compared to 600°C for the initial cycles with fresh sorbent. This suggests that particle sintering and pore plugging experienced after a number of cycles needs driving force from higher temperature to enhance the CO_2 ability to penetrate into the deep pores available inside the particles. Changes in the sorbent morphology during the tests at pilot-scale system have been identified by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDX). Changes in

pore size distribution and sorbent surface area that occurred during reaction have been determined by N₂ BET porosimetry. TGA has been used to determine the activity of the sorbent after processing in the dual fluidized bed combustion system. It has been found that oxygen-fired calcination with high CO₂ partial pressure reduced the effectiveness of two limestone sorbents for CO₂ capture when compared to material calcined under oxygen-enhanced air combustion [18]. A shell 1-2 μm thick, with reduced porosity, has been formed around the sorbent particle and is believed to be responsible for reduced conversion of CaO to CaCO₃. It is believed that ash deposition is contributing to the formation of the shell.

USTUTT achieved CO₂ capture efficiencies higher than 90% for a range of experimental conditions, as shown in [11]. The limestone that was used originated from the region of Schwabian Alb in Germany. Long and stable steady states can be achieved with great ease. Optimum temperatures for such capture efficiencies are 630-660°C. Molar circulation rates of CaO between the beds that are 15 times higher than the molar flow of incoming CO₂ in the carbonator lead to equilibrium CO₂ capture efficiencies higher than 90% almost irrespective of the solid inventory in the carbonator. CO₂ capture efficiency can be kept higher than 80% even if the molar rate of CaO between the beds is 5 to 8 times greater than the incoming molar flow of CO₂, if the carbonator inventory is sufficient. It is shown from the experimental results that a CFB carbonator operating with an inventory of 100 mbar can lead to CO₂ capture efficiencies higher than 90%. Both the circulation rates required between the beds as well as the required inventory can be realized in Dual Fluidized Bed Systems. Solid samples from the experimental runs of **USTUTT** were analyzed from **CEMEX** so as to better understand obtained results. **CEMEX** analyses involved: chemical composition by XRF, mineralogical phase quantification by XRD Rietveld, BET and small pore distribution, grindability index and SEM photos. **UHA** during their experimentation found that the key problem was the solid circulation between the two rigs. The main problem came from the use of limestone which blocks within the pipes. Using an inlet gas mixture containing 15% CO₂ entering the carbonator, a 20% capture efficiency was obtained at steady state in the presence of aged sorbent material. This efficiency is low due to the small gas residence time in the presence of lime within the carbonator. This efficiency could be improved by using a bigger mass of circulating solid.

The investigation of the **feasibility of the pressurized C3 Capture technology option** is significant due to the much lower cost that results due to the combination of the combustor with the carbonator. **USTUTT** with use of its atmospheric Dual Fluidized Bed (DFB) system has simulated 4 bar carbonation by using gas with 60 vol.-% CO₂ for fluidizing the carbonator. The DFB system was operated under continuous carbonation-calcination conditions. The CO₂ capture efficiency, for the simulated 4 bar carbonation, was above 80% at a temperature of 800 °C. Hence, it can be concluded that combustion and CO₂ capture can be combined in one pressurized fluidized bed reactor since 800 °C is a typical fluidized bed combustion temperature. **VTI** has carried out CO₂ absorption tests in a batch fluidized bed with use of calcareous sorbents, namely dolomite, fossil rock, chalk. Experimentation was carried out at temperatures 600-850 °C and pressures of 0.1-1.6 MPa. The concentration of CO₂ was 5-20 % and of SO₂ was 600-3000 mg/m³. Results indicate that a decrease of the specific surface of the calcareous sorbents during experimentation in the range of 1.5-5 times takes place. Furthermore, the mass-transfer coefficient does not depend on initial volumetric concentration CO₂ within the limits of 5-18 %. Empirical equations present a dependence of the mass-transfer coefficient from time, temperature and superficial velocity of the reactor. Calcination experiments were conducted using chalk from the region of Beograd at temperatures of 800-1050 °C. For fluidization of the calciner pure air and a synthetic gas mixture of 90% CO₂ and steam were used. The particle size distribution of the chalk used was 0.09-0.35 mm. The superficial velocity of the calciner, in the range of 0.28-0.7 m/s, does not

affect the reaction rate of calcination. In the temperature range of 800-900 °C the logarithm of the calcination reaction rate is a linear function of extent of calcination and the diameter of the particles. Calcination reaction rate reduces when the extent of calcination increases. Empirical equations presenting the dependence of calcination reaction rate on temperature and extent of calcination are shown. **Cranfield** finished building a pressurized BFB facility during this period. Calcination with the addition of steam significantly enhanced the calcination reaction rate. Calcination at 950 °C and a pressure of 4 bar resulted in reducing the capture capacity of the sorbent, in comparison to atmospheric calcination, most likely caused by insufficient calcination at higher pressure. Higher calcination temperatures (1050 °C) did not improve results most likely due to particle sintering.

An important point of this WP was also to determine the **residence time in the CFB solids loop** in order to provide data for the design of industrial plants. **APBFR** has subcontracted to Compiegne University a study to develop a method to evaluate gas and solids residence time in a Circulating Fluidized Bed. The method has been defined after a bibliographical study. Helium was selected as a tracer for gas residence time determination and phosphorescent tracers for solids residence time determination. Tests were carried out, with success, on a tubular bench reactor, set up to develop the method. On the CFB cold flow model (10 meters high – 0.45 m² section), some difficulties mainly due to the size of the installation have been faced. Feasibility of the method has been proven but some modifications have to be brought to the protocol to improve reliability of the results.

CSIC work related to WP3 and not carried out in the framework of WP3

When the project proposal was written, **CSIC** did not commit work for this workpackage while **ENDESA** planned some small pilot testing of the concept with in a side flue gas stream. However, because new parallel national projects in the field, **CSIC** has been able to built and operate, with partial financial support from **ENDESA**, a 30 kW test facility involving two interconnected circulating fluidized bed reactors of 10 mm ID and 6.5 m height to test the process. Although the results obtained in this facility have not been obtained under the C3-Capture project, and the cost of this test-rig and associated work are not included in this project, it has been possible to present and disseminate some of the main findings in the national project to the C3-Capture project partners in three project coordination meetings during 2007 and 2008. Furthermore, the main results have been recently published at the GHGT-9 conference in Washington and they clearly support and fullfil some of the key objectives of the C3-Capture project and WP 3. Capture efficiencies between 70 and 97% have been obtained under realistic flue gas conditions in the carbonator reactor (circulating fluidized bed). Attrition of the limestone used in **CSIC** experiments was unusually intense in the first calcinations but the remaining attrited solids showed little tendency to further attrition afterwards. In general, the CFB carbonator works as an effective CO₂ absorber when supplied with a sufficient flow of CaO (even if this is deactivated) and the fluid-dynamics of the CFB riser allow for a sufficient bed inventory of the fine material that remains in the system after the first few calcination carbonation cycles. These are both necessary conditions but their quantitative values are within the range of what can be considered normal solid circulation rates and bed inventory in large scale CFB combustors. Therefore, these results provide strong confidence about the need to scale up and further development of this technology.

1.3.4 Technical and economic process evaluation (WP4)

ENDESA has developed a **complete technical and economical model** for a retrofitting case of a pulverised coal with C3 Capture technology CO₂ capture system. The main hypothesis considered in the development of these models, came from the experiences and results obtained in the WP2 and WP3 by other partners of the consortium concerning limestone and system performance.

The main results and conclusions of these models show:

- It is possible to establish a commercial system with both fluidized beds working under parameters close to standard fluidized circulating beds.
- It is possible to recover most of the heat available in this capture system in a new supercritical water-steam power cycle with very high efficiency. This extra power generated reduces considerably the costs of the CO₂ captured. Different configurations were analysed, by ENDESA, for the power cycle. Due to the high power required by the CO₂ compression (this flow includes the CO₂ captured from the existing power plant and the CO₂ generated from calciner combustion) significant benefits could be obtained in a compressor steam-driven design. Moreover, most of the heat available in the intercoolers of the compressor could be also integrated in the water-steam cycle increasing the power output of the plant. An efficiency of more than 36% is possible for a configuration with steam-driven compressors and steam feeding water pump.
- The integrated system, consisting of the existing power plant and the C3 Capture technology plant, could reduce the costs of the CO₂ avoided in the range of 20-25 €/t CO₂ which is very low when comparing with other systems like MEA or oxy-fuel combustion which exhibits values over 30 €/t CO₂.
- One of the parameters with most influence in the final cost of the CO₂ captured and in the cost of electricity is the annual equivalent operation ratio. The goodness of this system came from the extra electricity produced in the plant. The income of this electricity covers the high investment cost of the system. So, it is necessary to guarantee a minimum value of operation hours. On the other hand, the possibility of selling the deactivated material purged from the system to a cement industry could reduce the final economical balance notably.
- The three main inconveniences of this capture system are the high area needed for the erection, (normally this is a critical issue in existing sites), the necessity of a limestone provider and an own infrastructure for limestone storage and pre-treatment, and the high investment cost needed for carrying out the project. Nevertheless, new extra power is installed with integrated CO₂ capture systems. That new power compensates the extra space and investment cost needed, and reduces considerably the cost of the electricity of the integrated system.

PKE performed a detailed economic analysis. Two options are analyzed. In the first option the C3 Capture technology plant is located upstream the FGD while in the second it is located downstream the FGD of a power plant. Assumptions regarding the analysis involved fuel and flue gas compositions as well as aspects of the power unit and the CO₂ capture unit. Flow and energy streams as well as reasons resulting in power need for the CO₂ capture system are also taken into account. Assumptions for the conducted analysis were same as ENDESA. A

balance was made between the factors that change the income and the cost of the power unit utilizing a CO₂ capture system. Factors like the price of limestone, price of CO₂ bonds, price of byproduct to the cement industry etc. are taken into account. Preliminary results show that the efficiency of the power unit is lowered by approximately 10 %. The two options are similar from a cost point of view. Crucial subjects open are the quality, quantity and price of the sorbent byproduct needed for the cement industry, the quality of gas suitable for transportation and storage and the cost of this process, optimization of the process and selection of suitable power plants.

CSIC and **CANMET** have contributed to the general understanding of the cost structure of the main processes considered in this project, conducting an analysis of the main cost components of both the atmospheric and pressurized process routes considered in this project [7, 6]. In the second case, **CANMET** developed an Excel-based economic model, to estimate the 30-year levelized cost of CO₂ capture per ton for a utility-scale power plant. An order of magnitude capital and operating estimate for a 360 MW pressurized fluidized bed combustor (PFBC) was presented, assuming a western Canadian location. Additional costs for calciners, O₂ plant, and related equipment necessary to create a Ca-based CO₂ chemical capture loop was presented separately. These costs are evaluated in a series of spreadsheets, and the impact of process flows, as well as capital, operating/maintenance and feedstock costs (in particular the requirement for a large purge of sorbent from the CaO loop, estimated from **CSIC** sorbent performance data and particle distribution model) are determined in a sensitivity analysis. The financial results for CO₂ capture are found to compare favourably with amine-based capture systems. A simpler approach is adopted in the work to analyse the cost structure of the post-combustion atmospheric system, taking benefit of the information already available in the literature on the cost of the main technology blocks. The complete capture system includes three key cost components: a full combustion power plant, a second power plant working as an oxyfired fluidized bed calciner and a fluidized bed carbonator interconnected with the calciner and capturing CO₂ from the combustion power plant. The simplicity of the economic analysis is possible because the key cost data for the two major first components is well established in the open literature. It is shown that there is a clear scope for a breakthrough in capture cost to around 70% of the CO₂ avoided cost of the equivalent stand alone oxyfired system. This is mainly because the capture system is generating additional power (from the additional coal fed to the calciner) and because the avoided CO₂ comes from the capture of the CO₂ generated by the coal fed to the calciner and the CO₂ captured (as CaCO₃) from the flue gases of the existing power plant, that is also released in the calciner.

CEMEX made an analysis of the value that the purge (spent sorbent) could potentially have as a raw material in the cement industry, see deliverable 4.3. The analysis also considered preliminary results from an extensive series of laboratory tests that were performed at **CEMEX**'s laboratories in collaboration with **USTUTT** (that provided samples of spent sorbent). The results indicate that the purge is indeed a suitable limestone substitute in the production of Portland clinker, with substitution rates up to 100% possible, and that the value of using spent sorbent in the cement industry, in particular the value of the CO₂ savings, can be quite significant. From this point of view the integration of the CO₂ capture process with a cement kiln appears a very attractive option. However, more work is still required to confirm the suitability of the purge as a raw material for the cement industry; the samples analyzed were produced with natural gas combustion in the regenerator, whereas in industrial applications more impurities from solid fuels such as sulfur, chlorine, alkalis and heavy metals have to be expected.

IVE has compared the C3-Capture technology application in coal fired power plants with alternative approaches for CO₂ capture. The main attractive alternatives taken into account have been Oxyfuel combustion and MEA scrubbing of flue gas. It can be concluded that the C3 Capture technology is for retrofit of existing power plants the better alternative compared to MEA scrubbing because of significant reduced cost for power production. For green field new power plants the total cost of application of the C3 Capture technology and Oxyfuel combustion are in the same range. On the other hand there is the possibility to integrate cement production combined with C3 Capture technology application in a power plant. This will lead to additional advantages from an economical (power cost reduction greater 10 %) and an ecological point of view because CO₂ emissions and fuel demand of cement production can be minimized leading to a green cement production. Further, **industrial applications for the C3-Capture technology are investigated by IVE.** There are two basic conditions for promising industrial C3-Capture technology applications – Large CO₂ flue gas streams and the use of lime. Based on these assumptions possible industrial applications for the C3-Capture technology are identified. The most promising application is the cement industry which was investigated in detail. Beside cement production iron and steel production looks promising, but for a green iron and steel industry hydrogen production using lime is even more attractive than CO₂ capture from flue gas. The remaining very interesting industrial sector for introducing the C3 Capture technology is pulp production. Here limestone calcination and a power station are already integrated and can be substituted by a more efficient C3-Capture technology plant. Furthermore, C3 Capture technology integration in pulp production leads to a CO₂ sink which counterbalances emissions from other sectors. A further improvement is possible with the integration of the bark boiler in the C3 Capture technology plant. This bark boiler can be used for the energetic utilisation of other organic materials than the bark from the pulp process as well.

In WP4, a **conceptual design of a CO₂ capture by calcium cycle** has been developed by **APBFR**. Preliminary design of a CO₂ capture for the two atmospheric base cases defined in WP1 has been performed: a greenfield 445 MWe Circulating Fluidized Bed and a retrofit 350 MWe pulverized Fuel Boiler. Heat and mass balance, process flow diagram and main equipment sizing have been determined. The investment and operating costs has been evaluated and a CO₂ mitigation cost has been determined. The value obtained is similar to the figures published for oxy-technologies. Some improvement in the cost evaluation of the technology could be obtained by integration of the unit to a cement plant. The end products of the CO₂ capture unit could be reused by the cement plant and the CO₂ capture unit will allow to save energy in the cement plant by precalcining the raw material upstream the rotary kiln.

VTI analysed the performance of the design for two types of coals: bituminous coal and brown coal from a heat balance analyse for the cycle, and for two different pressures in the carbonator: atmospheric pressure and 1.6 MPa.

Next results were achieved:

- In case of bituminous coal when reactor-carbonator works at the atmospheric pressure for own needs 72 % of heat are spent.
- In case of bituminous coal when reactor-carbonator works at pressure 1.6 MPa for own needs 37 % of heat are spent.
- In case of a brown coal when reactor-carbonator works at the atmospheric pressure for own needs 83 % of heat are spent.
- In case of a brown coal when reactor-carbonator works at pressure 1.6 MPa for own needs 37 % of heat are spent.

VTI has also carried out analysis of a system for flue gases CO₂ removal by the soda method with absorption of CO₂ by solutions of soda and calcium bicarbonate.

1.3.5 Pilot Plant Design (WP 5)

The experimental tests carried out in the C3 Capture project have demonstrated the viability of the process in a basic research size. Nevertheless, it is necessary that a new experimental facility of bigger scale is built, where hydrodynamics of the process could be analysed in detail. Large pilot testing will provide an intermediate validation step between the lab and the demonstration 20/50 MWe and will allow for preparation of back up plans to produce CO₂ according to specification. A 1 MWth pilot will allow testing of the process in conditions closed to an industrial unit. **APBFR** has performed a preliminary design and costing of a 1 MWth unit. **ENDESA** jointly with **CSIC** and other industrial companies prepared a business plan for developing the technology to a demo plant size. The plan is scheduled in 3 phases, where C3 Capture and a parallel national project carried out by **CSIC** and **ENDESA** during 2008 represents the first stage. The second step is the design and construction of a pre-industrial plant of 1 MWt in Spain integrated in a post-combustion scheme in an existing power plant. The main objective is to demonstrate the technology in real operational conditions. The 1 MWt plant is planned to start the operation in 2010. Depending of the goodness of the results obtained in this pre-industrial plant, the third stage of the development would be started. This third stage consists in the construction of a demo commercial plant to capture the CO₂ from the flue gases of an existing power plant. The design of this plant would start on 2014. **USTUTT** participates in a project in Germany aiming in the construction of a 350 kWth Dual Fluidized Bed facility to demonstrate the project at pilot scale. **IVE** investigated the integration of a cement plant in a power station with C3 Capture technology plant to further increase the process performance.

2 Dissemination and use

During this year of the project the following publications were made by partners.

From CSIC:

[1] Modelling of the deactivation of CaO in a carbonate loop at high temperatures of calcination

Belén González, Gemma S. Grasa, Mónica Alonso, and J. Carlos Abanades Energy and Fuels (in press)

[2] Application of the Random Pore Model to the carbonation cyclic reaction

G. S. Grasa, J. Carlos Abanades, M. Alonso, R. Murillo. AIChE Journal. (in press)

[3] Reactivity of highly cycled particles of limestone in a carbonation/calcination loop

Gemma S. Grasa, J. Carlos Abanades, M. Alonso, B. González. Chem Engng. J. 137, 561-568. 2007

[4] Sulphation of CaO particles in a carbonation/calcination loop to capture CO₂

Gemma S. Grasa, J. Carlos Abanades, Mónica Alonso. Ind. Eng. Chem. Res. 47(5) (2008) 1630–1635

[5] CO₂ capture capacity of CaO in long series of carbonation/calcination cycles; G.

Grasa, J.C. Abanades Ind. Eng. Chem. Res. 45, 8846-8851. 2006

[6] Economics of CO₂ Capture using the Calcium Cycle with a Pressurized Fluidized Bed Combustor; MacKenzie, A.; Granatstein, D.L.; Anthony, E.J., and J.C. Abanades

Energy & Fuels 21, 920-926, 2007

[7] The cost structure of a postcombustion CO₂ capture system using CaO. Abanades, J.C.; Grasa, G.; Alonso, M.; Rodríguez, M.; Anthony, E.J. Environmental Science and Technology 41(15), 5523-5530, 2007

[8] Comparison of CaO-Based Synthetic CO₂ Sorbents under Realistic Calcination Conditions.

Gemma Grasa, Belén González, Mónica Alonso, J. Carlos Abanades Energy and Fuels 21 3560-3563, 2007

[9] Heat requirements in a calciner of CaCO₃ integrated in a CO₂ capture system using CaO.

N. Rodriguez, M. Alonso, G. Grasa, J. Carlos Abanades, Chemical Engineering Journal (138), 148-154, 2008

From UHA:

[10] The decrease of carbonation efficiency of CaO along calcinations-carbonation cycles: experiments and modelling.

Eric Bouquet, Gontrand Leyssens, Cornélius Shönenbeck. Submitted to Chemical Engineering Science (2008).

From USTUTT:**[11] Parametric study on the CO₂ capture efficiency of the Carbonate Looping Process in a 10kW Dual Fluidized Bed.**

A. Charitos, C. Hawthorne, A.R. Bidwe, H. Holz, T. Pfeifer, A. Schulze, D. Schlegel, A. Schuster, G. Scheffknecht. submitted to 20th Int. Conference on Fluidized Bed Combustion, May18-20, 2009, Xi'an, China.

[12] Hydrodynamic and reactor model of a dual fluidised bed system for the post combustion of CO₂ using CaO**Part I: Carbonator Reactor Model**

C. Hawthorne, A. Charitos, C.A. Perez-Pulido, G.Scheffknecht.

[13] Hydrodynamically scaled cold model investigation of a dual fluidised bed system for the post combustion of CO₂ using CaO**Part II: Scaled Cold Model Investigation**

A. Charitos, C. Hawthorne, A. Bidwe, L. He, G.Scheffknecht

From CANMET:**[14] Hydration and Pelletization of CaCO₃ Derived Sorbents for in-situ CO₂ Capture,**

D.Y. Lu, R.W. Hughes, T. Reid and E.J. Anthony, submitted to 20th Int. Conference on Fluidized Bed Combustion, May18-20, 2009, Xi'an, China.

[15] Steam Hydration of Sorbents from a Dual Fluidized Bed CO₂ Looping Cycle Reactor, V. Manovic, D.Y. Lu and E.J. Anthony, Fuel 87 (2008) 3344- 3352.**[16] Thermal Activation of CaO-Based Sorbent and Self-Reactivation during CO₂ Capture Looping Cycle,** V. Manovic and E.J. Anthony, Environ. Sci. Technol. 42 (2008): 4170- 4174**[17] Ca-based Sorbent Looping Combustion for CO₂ Capture in Pilot-Scale Dual Fluidized Beds,** D.Y. Lu, R.W. Hughes and E.J. Anthony, Fuel Process. Technol. 89 (2008): 1386-1395.**[18] Changes in Limestone Sorbent Morphology during CaO-CaCO₃ Looping at Pilot Scale,** R.W. Hughes, A. Macchi, D.Y. Lu and E.J. Anthony, Chem. Eng. & Tech., Jan 2009, published on-line.