IMPROVEMENT OF CaO-BASED SORBENT PERFORMANCE FOR CO₂ LOOPING CYCLES

by

Vasilije MANOVIC and Edward J. ANTHONY

UDC: 662.613.5:666.9.051 BIBLID: 0354-9836, *13* (2009), 1, 89-104 DOI: 10.2298/TSCI0901089M

This paper presents research on CO_2 capture by lime-based looping cycles. This is a new and promising technology that may help in mitigation of global warming and climate change caused primarily by the use of fossil fuels. The intensity of the anticipated changes urgently requires solutions such as the developing technologies for CO_2 capture, especially those based on CaO looping cycles. This technology is at the pilot plant demonstration stage and there are still significant challenges that require solutions. The technology is based on a dual fluidized bed reactor which contains a carbonator – a unit for CO_2 capture, and a calciner – a unit for CaO regeneration. The major technology components are well known from other technologies and easily applicable. However, even though CaO is a very good candidate as a solid CO_2 carrier, its performance in a practical system still has significant limitations. Thus, research on CaO performance is critical and this paper discusses some of the more important problems and potential solutions that are being examined at CETC-O.

Key words: CO₂ capture, CaO-based sorbents, looping cycles, hydration, thermal pretreatment

Introduction

It is widely accepted that climate change is being exacerbated by increasing concentrations of greenhouse gases, and it is a key problem that requires urgent solutions. Fossil fuel combustion power plants represent a major source of anthropogenic CO_2 . About a third of global CO_2 emissions comes from the burning of fossil fuels in power production. Reduction of such emissions may significantly decrease total emissions of greenhouse gases to the atmosphere. One possible approach is the capture of CO_2 from flue gas followed by its sequestration in geological formations or perhaps on the ocean floor [1-3]. Other approaches are energy efficiency, *i. e.*, efficient use of energy, and switching to non-fossil fuels and renewable energy. Since energy efficiency has thermodynamic limits and sources of non-fossil fuels are limited, carbon capture and sequestration (CCS) must be considered as an important option. The purpose of CO_2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage site. Although, in principle, the entire gas stream containing low concentrations of CO_2 could be transported and injected underground, energy and other associated costs generally make this approach impractical. It is, therefore, necessary to produce a nearly pure CO_2 stream for transport and storage.

The capture/separation step for CO_2 from large point sources is a critical one with respect to the technical feasibility and cost of the overall carbon sequestration scenario. The CO_2

separation is the first and most technically challenging and energy intensive step of CCS; thus, much research has been targeted at improving current technologies or developing new approaches of CO_2 separation and capture. For power plants, CO_2 separation and capture processes can be divided into several scenarios: post-combustion processes for a traditional coal-fired power plant, pre-combustion processes for gasification or reforming, and oxy-fuel processes, sometimes referred to as oxy-firing or oxy-combustion [1-4].



Figure 1. Schematic representation of post-combustion CO₂ separation

The post-combustion scheme is presented in fig. 1. Chemical absorption by liquid organic solvents, such as monoethanolamine (MEA) [5, 6], has been widely used in the natural gas industry for over 60 years and it is being considered for separation of CO_2 from flue gas. The advantage of this technique is production of a relatively pure CO_2 stream, but it is very energy intensive, using 1/4-1/3 of the total steam produced by the plant, resulting in higher electricity costs (by 70%).

Important new classes of technologies for CO_2 separation are based on solid looping cycles [7]. These cycles employ a solid carrier to bring oxygen to the fuel, or remove CO_2 from combustion or gasification gases to be released as a pure CO_2 stream, with subsequent regeneration of the O_2 (O_2 cycles) or CO_2 carrier (CO_2 cycles), and they are considered in more detail below.

Pre-combustion CO_2 capture is schematically presented in fig. 2. In this process, fuels are first converted into a mixture of CO_2 and H_2 through a reforming (natural gas) or gasification (coal) process and the subsequent shift reaction. CO_2 can be separated from the conversion product stream and H_2 can then be burned in a gas turbine or be used in a fuel cell. Gasification



Figure 2. Schematic representation of pre-combustion CO₂ separation

partially oxidizes coal to produce a gaseous fuel, which is essentially a hydrogen and carbon monoxide mixture. When syngas is used to fuel a plant similar to a traditional combined-cycle power plant, the process is referred to as integrated gasification combined cycle (IGCC) [8, 9]. Methods that can be used for separation of CO_2 after fuel conversion are absorption processes (for example, by MEA, CaO), and physical processes

(pressure swing adsorption, membrane technology). Pre-combustion capture is potentially less expensive than post-combustion capture. IGCC power plants applying pre-combustion capture are more efficient than pulverized coal-fired plants and would be the choice for new plants. Oxy-fuel combustion is schematically presented in fig. 3. In this process pure O₂ is



Figure 3. Schematic representation of oxy-fuel combustion

separated from air and sent to an energy conversion unit to combine with partially recycled flue gas (concentrated CO_2) to moderate the furnace temperature. Combustion takes place in an environment of O_2/CO_2 . The resulting flue gas is a high-purity CO_2 stream (~90%), and further concentration is not necessary [9-11]. The advantages of this technology are elimination of NO_x control equipment, potentially smaller boiler size and reduced downstream equipment size, such as the SO_2 scrubber, because only oxygen is supplied for combustion. Disadvantages include the corrosion of equipment by increased SO_2 concentration in the exhaust gas stream and the high cost of oxygen separation that would consume about 1/4 to 1/3 of the total plant output.

Solid looping cycles

Two types of solid looping cycles for CO_2 separation are chemical-looping combustion (O_2 cycles) and CaO-based CO_2 looping cycles. The common characteristic is the use of solids that circulate between two different chemical environments with fluidized bed combustion (FBC) systems as an optimal technology.

Chemical-looping combustion [12, 13] involving O_2 cycles, is a combustion technology with inherent CO_2 separation. A chemical-looping combustion system, which is schematically presented in fig. 4, consists of two reactors, a fuel and an air reactor. An oxygen carrier, typically a metal oxide, transferring the oxygen from the air to the fuel, circulates between these

reactors. This means that the combustion air and the fuel are never mixed, and the flue gas from the fuel reactor consists of a concentrated CO_2 stream, ready for sequestration after steam condensation. The fuel is usually syngas from coal gasification or natural gas, but new research has shown that combustion of solids is also feasible [14, 15]. The main reaction in the fuel reactor is:



Figure 4. Schematic representation of chemical looping combustion

$$(2n+m)Me_xO_y + C_nH_{2m} \rightarrow (2n+m)Me_yO_{y-1} + nCO_2 + mH_2O$$
(1)

where Me_xO_y is the oxidized form of the O_2 carrier and Me_xO_{y-1} is the corresponding reduced form. Tested O_2 carriers have active oxides of Fe, Ni, Cu, or Mn combined with some type of inert carrier, such as Al_2O_3 , ZrO_2 , TiO_2 , or MgO. The reduced form of the O_2 carrier is transported to the air reactor where it is oxidized by the oxygen in the incoming air:

$$Me_x O_{v-1} + \frac{1}{2}O_2 \rightarrow Me_x O_v$$
⁽²⁾

The oxidized form of the O_2 carrier is returned to the fuel reactor for a new cycle. Oxidation of the O_2 carrier is exothermic, while the reaction in the fuel reactor could be either endothermic or exothermic, depending on the O_2 carrier and the fuel.

Looping cycles for CO_2 capture which employ a solid CaO-based carrier, represent an important new class of technology that is schematically presented in fig. 5. They may inexpensively and effectively remove CO_2 from combustion (or gasification gases), allowing it to be regenerated as a pure CO_2 stream suitable for sequestration [7, 16]. The use of solids also means that in many again EBC systems will rep

that, in many cases, FBC systems will represent optimal technology for such processes [17-19] since they permit large amounts of solids to be transferred easily from one chemical environment to another [20]. The deployment of such technologies has the added advantage that both large (>350 MWe) atmospheric and



Figure 5. Schematic representation of CaO-based CO₂ looping cycles

pressurized systems also exist [21, 22], and so the technical challenges of developing such systems for a number of possible looping cycle schemes are significantly reduced. Preliminary economic analyses [23-25] suggest that such processes are economically attractive, and an important advantage of using CaO is that limestone (CaCO₃) is abundant and a relatively inexpensive material when used at the industrial scale.

CO₂ capture by CaO-based sorbents is based on the reversible chemical reaction:

$$\operatorname{CaO}_{(s)} + \operatorname{CO}_{2(g)} \xrightarrow[]{\text{Carbonation}} \operatorname{CaCO}_{3(s)} \Delta H < 0$$
 (3)

 CO_2 separation from flue gas is possible in a multi-cycle process in a dual reactor. This involves reaction of CaO with CO_2 from flue gas in a carbonator, and regeneration of sorbent in a calciner [19]. In the ideal case, carbonation/calcination cycles can be carried out indefinitely with the only limitations due to the kinetics of the reactions and thermodynamics of the equilibrium system. The chemical equilibrium of the reaction depends on temperature, *T*, and CO_2 partial pressure, *P*_{CO}, [26]:

$$\log_{10} P_{\rm CO_2}[\text{atm}] \quad 7.079 \quad \frac{8308}{T[K]}$$
 (4)

In practice, the use of the carbonation reaction (exothermic) is limited by the maximum temperature that allows CO_2 capture at the desired concentration in cleaned flue gas (according to eq. 4) and the minimum temperature that allows a practical reaction rate. The calcination reaction is limited by the lower limit temperature necessary to obtain sufficient CO_2 concentration at the calciner outlet. Operation at elevated pressure in the carbonator and at lower pressure in the calciner can improve cycle efficiency, *i. e.*, increase the carbonation rate and obtain lower CO_2 concentrations in cleaned flue gas, allowing calcination under higher CO_2 concentrations.

CaO-based CO_2 looping technology is being intensively investigated at CANMET Energy Technology Centre-Ottawa (CETC-O) and a summary of the main R&D results is presented in this paper. The technology is currently at a pilot-plant scale demonstration stage with some important challenges remaining.

Challenges of CaO-based CO₂ looping cycles

Despite the simple chemistry of carbonation/calcination looping cycles, there are some restrictions to such processes related to the kinetics and thermodynamics of the reactions, along with undesirable side reactions such as sulphation and processes such as attrition and sintering. Flue gas from fossil fuel combustion typically contains SO_2 , which under CO_2 looping cycle conditions irreversibly reacts with CaO, forming CaSO₄. A portion of the CaO sorbent is, therefore, lost as CaSO₄, and more importantly, the CaO reaction surface is covered by this product, preventing contact of CaO and CO₂ with a resulting rapid decrease in capture capacity [27, 28]. Attrition of sorbent is a significant problem for FBC systems [29], leading to significant sorbent elutriation from the reactor, and this was confirmed in our first pilot-scale demonstration of the CO₂ looping cycle using a dual FBC reactor [30].

However, the major and most investigated challenge for CO_2 looping cycles is the decrease of reversibility for the carbonation reaction due to sorbent sintering [31, 32]. A typical multi-cycle carbonation/calcination run is presented in fig. 6. It can be seen that after only 10 cycles, conversion dropped to 40%, half the conversion in the first cycle. The loss of activity continues, and it has been shown in long series of cycles (>1000 cycles) that conversions become



constant, at the level of 7-8% [33]. It should also be mentioned that most research has been performed under ideal experimental conditions, with calcination stages in N_2 at lower temperatures, while the loss of activity occurs much faster under realistic conditions expected in real FBC systems [34, 35]. It is typically supposed that during CO₂ cycles, the sorbent morphology changes, and the sorbent loses surface area and small pores, which are the main contributors to the rapid carbonation necessary for practical systems. The most important variable that determines sorbent activity decay is the number of reaction cycles, and this is the key parameter in empirical models describing the change in carbonation levels [36, 37]. Other parameters such as temperature, duration of carbonation and calcination, sorbent type, and sorbent particle size are much less important in comparison to the number of calcination/carbonation cycles [33, 38]. However, it should be mentioned that these models cannot be applied in the case of modified sorbents that do not show monotonic conversion changes along cycles [39].

The improvement of sorbent activity for extended use in commercial plants is imperative because sorbent replacement costs strongly influence the overall cost of a CO_2 looping cycle process [25]. Reactivation by hydration currently appears to be a promising method for recovery of the sorbent activity [27, 40, 41]. Another approach is sorbent doping, but unfortunately to date, it does not appear to significantly improve sorbent activity during multiple carbonation cycles [42, 43], probably because most doping agents enhance sintering, which interestingly is also enhanced by the presence of impurities in the sorbent [35, 38, 44]. An exception is doping by Al_2O_3 , which shows fairly promising results [43, 45-47].

Thermal pretreatment of the sorbent at high temperatures has shown beneficial effects in the case of a number of sorbents [38, 39, 48]. Here, thermal pretreatment typically causes lower conversions during the early cycles, but conversions in later cycles are higher than those for the original, untreated sorbents. Thus, the overall removal capacity over the lifetime of a given limestone is greater. This effect is more pronounced in the case of sorbents with small particles obtained by synthesis [48] or grinding [39]. Our recent study [39] showed that conversions of four Canadian limestones, after grinding and pretreatment at temperatures of 1000 °C, increased along cycles, reaching ~50% in the 30th cycle. This phenomenon of increasing conversion with an increasing number of reaction cycles has been called self-reactivation. Developing sorbents with self-reactivation performance and their use for CO₂ capture would be of great interest because the economics and environmental advantages of the process to a large extent depend upon the change in sorbent activity with an increasing number of cycles [23-25].

Improvenment of sorbent performances

In our laboratory we have intensely investigated spent sorbent reactivation by steam hydration, fresh sorbent pretreatment at elevated temperature, and doping. Results of these investigations are presented in more detail below.

Spent sorbent hydration

Our research on spent sorbent reactivation was originally based on experience with reactivation of sorbent utilized for SO_2 retention [49-51]. Most efforts to improve sulphation in FBC systems are focused on the hydration of spent (partially sulphated) sorbent [51]. The most thoroughly investigated methods of hydration are by steam [49, 52-54] or liquid water [55, 56], which may also be enhanced by grinding [57] and sonication [58, 59]. In the literature [50, 60], reactivation characteristics of sorbents are connected with the nature of the partially sulphated particle pattern: uniformly sulphated, core/shell and network. It has been argued that uniformly or continuously sulphated materials do not display significant reactivation after hydration by steam [50, 60]. However, such patterns may not necessarily be similar for different batches of supposedly the same limestone, sulphated under different conditions [61]. New experimental data also indicated that uniformly sulphated samples can be reactivated given suitable hydration conditions [62].

Carbonation, like sulphation, is a gas-solid reaction with solid product formation at the surface of the reactant, CaO; therefore, similar controlling mechanisms, limits, as well as methods for reactivation, are expected. Carbonation includes a very fast initial reaction stage, which is followed by a very slow stage (see for example fig. 6) controlled by the diffusion of reacting species through the product layer of CaCO₃ [32, 63]. However, an important difference between the carbonation and sulphation processes is provided by the difference in molar volumes of the solid products, VM(CaSO₄) *vs.* VM(CaCO₃) = 46 cm³/mol *vs.* 37 cm³/mol. Thus, the sulphation product layer can block pores near the particle surface, forming a partially sulphated outer shell and inner unreacted CaO core [64]. However, the presence of an unreacted core during carbonation has not been confirmed; moreover, it has been demonstrated that only product layer formation on the interior surfaces of pores is limiting for the carbonation rate [65]. Another important difference is reversibility of carbonation, *i. e.*, the product layer may be easily removed to expose sintered sorbent surface area to hydration.

Taking into account the above analysis, sorbent hydration appears to be the most promising method for reactivation. It is based on a simple chemical reaction:

$$CaO + H_2O \rightarrow Ca(OH)_2$$
 (5)

Considering the hydration technique, hydration by steam was chosen because there is no excess water to be removed, sample drying is not required after hydration, there is no loss of sorbent with liquid reactant and particle size reduction is less pronounced.

Steam hydration experiments in our studies were performed in a laboratory-scale 2 dm³ Parr 4522 M pressure reactor, described elsewhere [66]. Four Canadian limestones were investigated: Kelly Rock, Cadomin, Graymont, and Havelock. The crushed limestones were sieved and samples of particle sizes typically used in FBC systems were examined. Spent sorbent samples were produced in a tube furnace [27, 40] and in a dual FBC pilot-scale reactor [30, 67]. Original samples (before and after reactivation) were tested with regard to CO_2 carrying capacity in looping cycles [27, 40, 68] as well as with regard to sulphation performance [40, 68, 69] in thermogravimetric analyzers (TGA).

Typical test results for sorbent reactivation for CO_2 capture are presented in fig. 7 [27]. It may be seen that spent sorbent after CO_2 cycles in the tube furnace, at the end of the first cycle in the TGA, had a carbonation degree ~35%, regardless of particle size. The shapes of curves are uncharacteristic for carbonation (no initial fast reaction stages). After reactivation, the sorbent had significantly higher activity, with a clearly visible fast stage at the start, and final value for

the carbonation conversions in the first cycle above \sim 75%, regardless of the particle size, which was significantly higher than related values for spent sorbent.

The behavior of reactivated spent sorbent in multiple carbonation cycles is shown in fig. 8. The results were exceptionally good. Carbonation in the initial cycles was higher than for the natural sorbent, with the difference increasing along cycles. As a result the reactivated sorbent displayed significantly better conversions at the end of multi-cycle carbonation. The final result is an average carbonation of ~70% during 10 cycles with reactivated sorbent. This analysis shows that steam reactivation actually improves sorbent characteristics in comparison to the original sorbent. This means that in the case of CO_2 capture, separate SO₂ capture, *i. e.*, avoidance of sorbent sulphation, in



Figure 7. Steam reactivation effect on sorbent activity during carbonation in the TGA [27]



Figure 8. Steam reactivation effect on sorbent activity during CO₂ cycles in the TGA

combination with steam reactivation, may enable use of the sorbent for prolonged times, or at least until attrition phenomena dominate. This should aid in the commercialization of the process of CO_2 separation by CaO-based sorbent in FBC systems.

Another interesting result is sorbent sample swelling, *i. e.*, increase of sample volume during hydration. The measured sample volume after hydration was ~4 times larger than that before hydration [27], which is more than the Ca(OH)₂/CaO molar volume ratio (33 cm³/mol vs. 17 cm³/mol). It is expected that the sorbent after reactivation has more than enough pore space

than is needed for storage of voluminous $CaSO_4$ during sulphation. This, and the percentage of large pores (>200 nm) noticed after sorbent reactivation gave us good reason to investigate sulphation of reactivated sorbent, *i. e.*, its ultimate use for SO₂ retention.

The TGA sulphation of reactivated samples confirms the assumption of their high activity, as presented in fig. 9. It can be seen that there are major differences



Figure 9. Steam reactivation effect on sorbent sulphation performance in the TGA

between sulphation of the original and reactivated samples. Sulphation of CaO is limited by diffusion through the product layer (CaSO₄), which forms an outer shell and hinders contact of reactants (CaO and SO₂) [70, 71], and hence, sulphation curves for CaO produced from limestone have a typical shape as shown in the figure for the original sample. The sulphation had an initial faster stage, and after 60 minutes, 30% sulphation was achieved. After this stage, sulphation became very slow because of diffusion limitations. During the next 60 minutes, only a few percent of additional sulphation occurred. The shape of the sulphation curve for the reactivated sorbent is very different. The beginning stage is faster in comparison to that for the original sorbent as there is greater surface area available for reaction for the reactivated sorbent. The shift to the slower stage is not clearly apparent, and the sulphation rate is not reduced so drastically, reaching 75% after 2 hours. Moreover, the samples after that showed a relatively high sulphation rate



Figure 10. Schematic representation of sequential SO_2/CO_2 capture enhanced by sorbent reactivation [69]

during a further 2 hours of sulphation. The final result, after 4 hours, represents almost total sulphation (>95%), calculated on the basis of the TGA data and confirmed by X-ray diffraction (XRD) quantitative analysis [69]. This showed that CO_2 looping cycles had a beneficial effect on hydration and subsequent sulphation behavior of these samples.

The superior behavior of reactivated sorbent in carbonation and in sulphation supports the idea of a new process of utilization of CaO-based sorbents in FBC systems for enhanced CO_2 capture and enhanced SO₂ retention, schematically shown

in fig. 10 [69]. A process can be developed in which the final products are ash with little or no unreacted CaO, clean flue gas with "zero" SO₂ and less than 5% CO₂, and a separated stream of concentrated CO₂ (>95%). The high S/Ca molar ratio in the ash reduces the problems of ash disposal (and disposal of spent sorbent from CO₂ cycles) and cuts waste solids production by half in terms of the amount of sorbent needed for SO₂ retention. The main limitation for this approach in FBC systems may be sorbennt attrition, and it may be worth exploring pelletization concepts to use such solids further. In the case of sorbents with high Ca/S molar ratio and/or with greater tendency to sintering (activity decay), improved performance may be obtained using the reactivated sorbent for enhancement of carbonation. An additional advantage of the proposed process is separation of CO₂ capture from SO₂ retention (sequential SO₂/CO₂ capture) because of very negative effects of sulphation on carbonation [27, 28]. In the proposed scheme, SO₂ retention occurs predominantly in the combustor, with only small concentrations of SO₂ entering the carbonator with the flue gas.

Thermal pretreatment of sorbent

The main idea of thermal pretreatment is to stabilize sorbent morphology, *i. e.*, reduce sintering and loss of surface area. That could aid in maintaining sorbent CO_2 carrying activity along cycles. An experimental parametric study on the sorbent capture capacity along CO_2 cycles [38] showed an interesting result, that with longer calcination times the sorbent has higher conversions, as shown in fig. 11. A favorable influence of the calcination time was unexpected and differed from the behavior presented in the literature. Grasa *et al.* [33] and

Lysikov *et al.* [48] showed that the calcination time is not an important parameter, and Sun *et al.* [31] found that a longer calcination time actually reduced the pore volume for pores <220 nm, which are most responsible for carbonation conversions. Moreover, sintering theory that is typically used to explain decay of sorbent capacity assumes that longer exposure of sorbent to higher temperatures should lead to more intensive sintering and loss of activity.

The results presented in fig. 11 illustrate that the sorbent does not lose activity as a

consequence of prolonged exposure to calcination conditions, and it appears that this treatment may actually improve sorbent behavior. These results are interesting because they show that prolonged exposure of the sorbent to heat may stabilize its maximum carbonation level as a function of reaction cycles and enhance its CO_2 carrying capacity. Moreover, it can be expected that some thermal pretreatment of the sorbent can reduce undesirable attrition in FBC systems because pretreated particles may have

greater hardness. Further CO_2 looping cycles were per-

formed with samples pretreated at different temperatures (800-1300 °C) in nitrogen for different duration (6-48 hours). The most interesting results are presented in fig. 12, where pretreatment was for 24 hours. It can be seen that the sample treated at 900 °C had ~20% lower conversion in the first cycle than that of the original sample. However, conversion for the pretreated sample increased and in the third cycle was $\sim 8\%$ higher than that of the original sample. In subsequent cycles, conversion was typically at least 10% greater than that of the original untreated sorbent. Also, preheating of hydrated samples modifies their conversions during cyclic carbonation. Experiments performed with samples pretreated at



Figure 11. Influence of the calcination duration on the sorbent (Kelly Rock limestone, 75-150 μ m) activity decay in 10 CO₂ cycles in TGA, isothermally at 750 °C, carbonation for 30 minutes in 50% CO₂ (N₂ balance), calcination for different durations in N₂



Figure 12. The effect of sorbent preheating for 24 hours on its carrying capacity in 30 CO₂ looping cycles in TGA, isothermally at 800 °C, carbonation for 30 minutes in 50% CO₂ (N₂ balance), calcination for 10 minutes in N₂. Sorbents: "Original" – Kelly Rock limestone, 300-425 μ m; "900 °C" – original sorbent pretreated at 900 °C; "Hydrated, 900 °C" – original sorbent spent in 20 CO₂ cycles in tube furnace, hydrated by steam and pretreated at 900 °C; "Powdered, 1000 °C" – original sorbent ground to <50 μ m and preheated at 1000 °C

higher temperatures show significant increase of conversions for the initial 6-7 cycles. This effect we have called self-reactivation. Beyond this point, the decrease in activity is less pronounced, resulting in higher conversions in comparison to those seen for the original sample. Perhaps the most interesting result is seen for powdered samples ($<50 \mu$ m). It can be seen that self-reactivation occurred for the entire 30 cycles. The highest conversion was obtained for the last cycle, when 49% carbonation was achieved. The mean value for 30 cycles was ~45%, which is very good for a natural sorbent that has not been chemically modified. These results suggest that self-reactivation will continue in subsequent cycles (*i. e.*, conversions will additionally in-



Figure 13. Schematic representation of proposed pore-skeleton model [39]

crease). This finding was supported by experiments with four Canadian limestones (Kelly Rock, Cadomin, Graymont, and Havelock), [39].

The favorable influence of sorbent thermal pretreatment and the effect of sorbent self-reactivation cannot easily be explained by considering sintering and pore distribution change models. For example, it is expected that exposure of sorbents to high temperatures leads to the formation of larger pores and the elimination of smaller pores, resulting in lower carbonation conversions. To explain these results, we propose that sorbent skeleton changes need to be considered (along with pore size changes), as

these occur during cycling [39, 48, 72]. A schematic representation of the proposed pore-skeleton model is given in fig. 13 [39]. During cycling, two different types of mass transfer in the sorbent particles must occur in parallel: bulk mass transfer connected to the formation/decomposition of CaCO₃ and ion diffusion in the crystal structure of CaO. Ion diffusion in CaO stabilizes its crystal structure but with no significant effect on particle morphology and corresponding carbonation conversions [38]. Bulk mass transfer leads to major changes of morphology, to sintering and loss of sorbent activity. During CO₂ cycles, competition occurs between ion diffusion and bulk mass transfer, and two types of structure or skeleton are formed: (1) an internal unreacted structure and (2) an external structure in which reactions proceed. The internal skeleton can be considered as a hard skeleton that stabilizes and protects the particle morphology. The external structure can be considered to be a soft skeleton that easily changes during CaCO₃ formation and decomposition. During thermal pretreatment of sorbents, bulk diffusion occurs only during calcination, but when the decomposition of CaCO₃ is completed, ion diffusion continues, which leads to skeletal structure stabilization and the formation of a hard skeleton. In the initial cycles the reaction rate is slower because the hard skeleton is less reactive; ion diffusion necessary for carbonation is more difficult in that type of skeleton because it is a more stable structure. In subsequent cycles, the outward or external (soft) skeleton is formed because of formation/decomposition of CaCO₃, which accelerates the carbonation rate. An increase of conversion with cycle number occurs because the soft part of the skeleton grows. Moreover, the smooth surface obtained during thermal pretreatment may be transformed during repeated carbonation/calcination cycles, also leading to increased conversions. At the same time, the inward hard skeleton keeps the particle morphology stable. The conversion for one sorbent after infinite cycles is the consequence of the competition between ion diffusion (formation of hard skeleton) and bulk mass transfer (sintering), which results in formation of the final morphology with a stable skeleton that determines conversions.

However, it should be mentioned that there are sorbents that do not show enhanced performance after pretreatment at high temperatures, and La Blanca (Spanish) limestone is one example [72]. It was also interesting that large particle size sorbent samples (order of magnitude of hundreds of μ m, typically used for FBC operations), regardless of the favorable influence of thermal pretreatment, did not show a self-reactivation effect [38, 39]. To highlight these findings, further experimental work was focused on La Blanca limestone and on large-particle sorbents.

In the elemental analysis of La Blanca [73], the somewhat higher Na₂O content (1.07%) in comparison to that seen with our previously investigated limestones (<0.2%) was noted [27, 40]. Another potentially significant difference was the absence of Al_2O_3 and SiO_2 in

comparison to analysis results for Canadian limestones ($Al_2O_3 - 0.33-1.44\%$; $SiO_2 - 1.03-5.34\%$).

It is known that the presence of Na⁺ ions in the crystal structure of CaO causes lattice defects, which enhance mass transfer and sintering [44] that unfavorably reflect on CO₂ capture capacity [38]. Thus, the first idea was to check if and how doping of limestone by Na₂CO₃ affects its capture capacity in a series of CO₂ looping cycles. Mixtures of Kelly Rock limestone and Na₂CO₃ were ground, and TGA runs were performed: pretreatment at 1000 °C followed by 30 CO₂ cycles. The results are presented in fig. 14 [73].



Figure 14. Effect of doping by Na_2CO_3 and thermal pretreatment (1000 °C for 6 h) of Kelly Rock limestone on its capture capacity along 30 CO_2 cycles in TGA, isothermally at 800 °C, carbonation for 30 min. in 50% CO_2 (N₂ balance), calcination for 10 min. in N₂

It can be seen that doped samples showed a drastic loss of activity. An interesting result is the increased conversions with increasing amount of dopant during the first ~ 15 cycles and the opposite effect during the remaining cycles. This, we believe, is the result of two opposing effects of Na on CaO capture capacity. The first effect is a favorable increase of Ca^{2+} diffusion in CaO/CaCO₃ in the presence of Na^+ ions. This enhanced diffusion in the product layer, in general, can be expected to accelerate gas-solid reactions at the reacting surface. For example, in sulphation, there is evidence that doping of the sorbent with Na₂O increases conversion [70]. The second effect is enhancement of bulk mass transfer in the presence of Na⁺ ions, which leads to more pronounced sintering [44]. This effect is cumulative with increasing numbers of cycles and, after ~15 cycles in the experiment explored here, becomes dominant. The sorbent surface is sintered to such an extent that conversion loss caused by it cannot be compensated by conversion growth because of enhanced diffusion in the product layer. Another effect that can contribute to sintering in CaO/Na₂O/CO₂ systems is the lower melting point of Na₂O as well as the formation of other compounds - Na2Ca(CO3)2/Na2Ca2(CO3)3 - with lower melting points in comparison to that of CaO. Scanning Electron Microscope (SEM) images of original (a) and doped/pretreated (b) Kelly Rock as well as original La Blanca sample (c) after 30 CO₂ cycles, presented in fig. 15 [73], strongly illustrate pronounced sintering and loss of surface area as a result of the presence of Na in the CaO.

The absence of Si and Al in La Blanca limestone may also lead to the poorer perfor-

mance of pretreated samples, although the evidence for a favorable effect of Si is at best ambiguous. Thus, it is known that SiO_2 reacts with CaO, producing silicates with lower melting points than those of CaO, which suggests there would be an unfavorable influence of SiO_2 , and this has been recently experimentally confirmed [35]. By contrast, there is evidence that Al in CaO improves its thermal and CO_2 capture stability [45-47]. To



Figure 15. SEM images of sorbent samples after 30 CO_2 cycles in TGA; (a) Kelly Rock limestone, (b) Kelly Rock limestone doped with 5% Na₂CO₃, ground, and pretreated at 1000 °C for 6 hours, and (c) La Blanca limestone pretreated at 1000 °C for 24 hours



Figure 16. Effect of doping by Al_2O_3 and thermal pretreatment (1100 °C for 6 hours) of La Blanca limestone on its capture capacity along 30 CO₂ cycles in TGA, isothermally at 800 °C, carbonation for 30 minutes in 50% CO₂ (N₂ balance), calcination for 10 minutes in N₂ [73]



Figure 17. SEM-EDX analyses of Al_2O_3 content at the surface of sample La Blanca, doped with 5% Al_2O_3 , pretreated at 1100 °C for 6 hours, and cycled (after 30 CO₂ cycles, see fig. 16) [73]



Figure 18. Effect of pretreatment on sorbent carrying capacity in 45 CO_2 looping cycles in TGA (isothermally at 800 °C, carbonation for 10 minutes in 50% CO_2 (N₂ balance), calcination for 10 minutes in 100% N₂) of original particle size samples (Kelly Rock: 300-425 µm, Katowice: 400-800 µm, and La Blanca: 400-600 µm) pretreated at 1000 °C for 24 hours in 100% CO_2

demonstrate such an effect, La Blanca was doped with Al₂O₃, ground and thermally pretreated. The results for conversions during carbonation/calcination cycles are presented in fig. 16 [73]. Here, a clear influence of doping by Al₂O₃ on carrying capacity of the sorbent can be seen. This means that, besides the negative effects of the high Na content of La Blanca limestone, another probable cause for the absence of a self-reactivation effect is a deficiency of Al. The influence of Al on sorbent morphology, which is the determining factor for CO₂ capture capacity, has been investigated by SEM-EDX analyses of the sorbent morphology. The results presented in fig. 17 [73] are typical for an Al₂O₃-doped sample analyzed after 30 CO₂ cycles. A quite different sample morphology, compared to those presented in fig. 15 (b and c) is apparent. Moreover, different areas of surface morphology exist, depending upon the Al₂O₃ content.

The lack of self-reactivation after pretreatment of large particle size samples was another challenge because it is desirable to use pretreated improved sorbent in FBC systems. Thus, thermal pretreatment has been investigated in more detail with different limestones and under different conditions with the aim of generating self-reactivation effects for large-particle samples typically used in FBC systems. The best results were obtained with the pretreatment occurring in a CO₂ atmosphere, rather than the N₂ atmosphere previously investigated, as presented in fig. 18 [74]. Pretreated Kelly Rock and Katowice (Polish) limestone samples showed significantly increasing conversions for the initial cycles while La Blanca again behaved quite the opposite, explained by more pronounced sintering of this limestone (see above). The role of CO₂ during pretreatment is beneficial because it appears that the CO_2 in contact with CaO helps in its recrystallization and stabilization of crystal structure, but does not significantly enhance bulk diffusion and sintering.

Mercury porosimetry of the pretreated samples showed a shift of pore size distribution with sample pretreatment/cycling [75]. The maximum in pore size distribution (about 1 μ m) appeared with loss of smaller pores. This was interesting with regard to sulphation, which is often limited by pore plugging by bulky CaSO₄ and formation of an unreacted CaO core.



Figure 19. Effect of thermal pretreatment (1000 °C for 24 hours in 100% CO₂) of Katowice limestone (400-800 μ m) on its sulphation performance in the TGA (0.5% SO₂, 1% O₂, 15%CO₂, N₂ balance)

The modification of pores during thermal pretreatment led to formation of sorbent morphology that corresponded to lower reaction rate (because of lower surface area), but lower chance for pore plugging (because of larger pores and reduced reaction rate). The typical result of sulphation of pretreated sample in comparison with its corresponding original sample is presented in fig. 19. It can be seen that conversion of pretreated sample after 15 hours is 58%, 8% higher than that for the original sample. Unfortunately, further sulphation of pretreated sample is limited by sorbent porosity (51% for pretreated sample from fig. 19), *i. e.*, available space for storage of CaSO₄; and also the unfavorable shrinkage of sorbent particles during pretreatment and especially during CO₂ cycles [35, 75]. However, regardless of these limitations, spent sorbents from CO₂ looping cycles as well as pretreated sorbents are worth considering for use in SO₂ retention.

Conclusions

CaO-based CO₂ looping cycle technology is a new, rapidly developing technology, presently in the pilot-plant demonstration stage. The major technology components are well known from other processes and easily applicable. When considering thermodynamics and sorbent costs, CaO obtained from limestone is the best candidate for use as a solid carrier of CO₂ from dilute gases to concentrated streams ready for sequestration. However, the key technology costs, which are aimed at \leq \$20 per ton of avoided CO₂, are strongly connected with the behavior of sorbent in CO₂ looping cycles in a real system, which typically is a FBC. The main hurdles for the technology are overcoming the loss and deactivation of sorbent through sulphation, attrition and sintering. The intensive research at CETC-O to improve sorbent performance was presented in this paper. To date, the most promising methods were reactivation of spent sorbent by steam, thermal pretreatment of sorbent, and doping, most likely with Al₂O₃. The combination of these methods, including pelletization, should provide us with enhanced sorbent performance.

References

- Metz, B., et al., Special Report on Carbon Dioxide Capture and Storage, Intergovernmental Panel on Climate Change, Cambridge University Press, New York, USA, 2005
- Herzog, H., What Future for Carbon Capture and Sequestration? *Environmental Science and Technology*, 35 (2001), 7 pp. 148A-153A
- [3] Bachu, S., CO₂ Storage in Geological Media: Role, Means, Status, and Barriers to Deployment, Progress in Energy and Combustion Science, 34 (2008), 2, pp. 254-273

- [4] Yang, H., et al., Progress in Carbon Dioxide Separation and Capture: A Review, Journal of Environmental Sciences, 20 (2008), 1, pp. 14-27
- [5] Alie, C., et al., Simulation of CO₂ Capture Using MEA Scrubbing: A Flowsheet Decomposition Method, Energy Conversion and Management, 46 (2005), 3, pp. 475-487
- [6] Singh, D., et al., Techno-Economic Study of CO₂ Capture from an Existing Coal-Fired Power Plant: MEA Scrubbing vs. O₂/CO₂ Recycle Combustion, Energy Conversion and Management, 44 (2003), 19, pp. 3073-3091
- [7] Anthony, E. J., Solid Looping Cycles: A New Technology for Coal Conversion, Industrial and Engineering Chemistry Research, 47 (2008), 6, pp. 1747-1754
- [8] Pennline, H. W., et al., Progress in Carbon Dioxide Capture and Separation Research for Gasification-Based Power Generation Point Sources, Fuel Processing Technology, 89 (2008), 9, pp. 897-907
- [9] Tan, Y., et al., Combustion Characteristics of Coal in a Mixture of Oxygen and Recycled Flue Gas, Fuel, 85 (2006), 4, pp. 507-512
- [10] Jia, L., et al., Experimental Study of Oxy-Fuel Combustion and Sulphur Capture in a Mini-CFBC, Energy and Fuels, 21 (2007), 6, pp. 3160-3164
- [11] Buhre, B. J. P., et al., Oxy-Fuel Combustion Technology for Coal-Fired Power Generation, Progress in Energy and Combustion Science, 31 (2005), 4, pp. 283-307
- [12] Hossain, M. M., de Lasa, H. I., Chemical-Looping Combustion (CLC) for Inherent CO₂ Separations A Review, *Chemical Engineering Science*, 63 (2009), 18, pp. 4433-4451
- [13] Ryden, M., Lyngfelt, A., Mattison, T., Chemical-Looping Combustion and Chemical-Looping Reforming in a Circulating Fluidized-Bed Reactor Using Ni-Based Oxygen Carriers, *Energy and Fuels*, 22 (2008), 4, pp. 2585-2597
- [14] Shen, L., Wu, J., Xiao, J., Experiments on Chemical Looping Combustion of Coal with a NiO Based Oxygen Carrier, *Combustion and Flame*, 156 (2009), 3, pp. 721-728
- [15] Berguerand, N., Lyngfelt, A., Design and Operation of a 10 kW_{th} Chemical-Looping Combustor for Solid Fuels – Testing with South African Coal, *Fuel*, 87 (2008), 12, pp. 2713-2726
- [16] Stanmore, B. R., Gilot, P., Review Calcination and Carbonation of Limestone During Thermal Cycling for CO₂ Sequestration, *Fuel Processing Technology*, 86 (2005), 16, pp. 1707-1743
- [17] Shimizu, T., et al., A Twin Fluid-Bed Reactor for Removal of CO₂ from Combustion Processes, Chemical Engineering Research and Design, 77 (1999), 1, pp. 62-68
- [18] Hughes, R. W., et al., Design, Process Simulation, and Construction of an Atmospheric Dual Fluidized Bed Combustion System for in situ CO₂ Capture Using High-Temperature Sorbents, Fuel Processing Technology, 86 (2005), 14-15, pp. 1523-1531
- [19] Abanades, J. C., et al., Fluidized Bed Combustion Systems Integrating CO₂ Capture with CaO, Environmental Science and Technology, 39 (2005), 8, pp. 2861-2866
- [20] Davidson, J. F., Clift, R., Harrison, D., Fluidization, 2nd ed., Academic Press, San Diego, Cal., USA, 1985
- [21] Grace, J. R., Avidan, A., Knowlton, T. M., Circulating Fluidized Beds, Blackie Academic & Professional, Glasgow, UK, 1997
- [22] Cuenca, M. A., Anthony, E. J., Pressurized Fluidized Beds, Blackie Academic & Professional, Glasgow, UK, 1995
- [23] Abanades, J. C., et al., Cost Structure of a Postcombustion CO₂ Capture System Using CaO, Environmental Science and Technology, 41 (2007), 15, pp. 5523-5527
- [24] MacKenzie, A., et al., Economics of CO₂ Capture Using the Calcium Cycle with a Pressurized Fluidized Bed Combustor, *Energy and Fuels*, 21 (2007), 2, pp. 920-926
- [25] Abanades, J. C., Rubin, E. S., Anthony, E. J., Sorbent Cost and Performance in CO₂ Capture System, Industrial and Engineering Chemistry Research, 43 (2004), 13, pp. 3462-3466
- [26] Baker, E. H., The Calcium Oxide Carbon Dioxide System in the Pressure Range 1-300 Atmospheres, Journal of the Chemical Society, 70 (1962), pp. 464-470
- [27] Manovic, V., Anthony, E. J., Steam Reactivation of Spent CaO-Based Sorbent for Multiple CO₂ Capture Cycles, *Environmental Science and Technology*, 41 (2007), 4, pp. 1420-1425
- [28] Ryu, H., Grace, J. R., Lim, C. J., Simultaneous CO₂/SO₂ Capture Characteristics of Three Limestones in a Fluidized-Bed Reactor, *Energy and Fuels*, 20 (2006), 4, pp. 1621-1628
- [29] Jia, L., et al., Attrition of Calcining Limestones in Circulating Fluidized Bed Systems, Industrial and Engineering Chemistry Research, 46 (2007), 15, pp. 5199-5209
- [30] Lu, D. Y., Hughes, R. W., Anthony, E. J., Ca-Based Sorben Looping Combustion for CO₂ Capture in Pilot-Scale Dual Fluidized Beds, *Fuel Processing Technology*, 89 (2009), 12, pp. 1386-1395

- [31] Sun, P., et al., The Effect of CaO Sintering on Cyclic CO₂ Capture in Energy Systems, AIChE Journal, 53 (2007), 9, pp. 2432-2442
- [32] Abanades, J. C., Alvarez, D., Conversion Limits in the Reaction of CO₂ with Lime, *Energy and Fuels*, 17 (2003), 2, pp. 308-315
- [33] Grasa, G. S., Abanades, J. C., CO₂ Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles, *Industrial and Engineering Chemistry Research*, 45 (2006), 26, pp. 8846-8851
- [34] Lu, D. Y., et al., Sintering and Reactivity of CaCO₃-based Sorbents for In-situ CO₂ Capture in Fluidized Beds under Realistic Calcination Conditions, *Journal of Environmental Engineering* (in press)
- [35] Manovic, V., et al., Influence of Calcination Conditions on Carrying Capacity of CaO-Based Sorbent in CO₂ Looping Cycles, Fuel (submitted)
- [36] Abanades, J. C., The Maximum Capture Efficiency of CO₂ Using a Calcination/Carbonation Cycle of CaO/CaCO₃, *Chemical Engineering Journal*, 90 (2002), 3, pp. 303-306
- [37] Wang, J. S., Anthony, E. J., On the Decay Behavior of the CO₂ Absorption Capacity of CaO-Based Sorbents, *Industrial and Engineering Chemistry Research*, 44 (2005), 3, pp. 627-629
- [38] Manovic, V., Anthony, E. J., Parametric Study on CO₂ Capture Capacity of CaO-Based Sorbents in Looping Cycles, *Energy and Fuels*, 22 (2008), 3, pp. 1851-1857
- [39] Manovic, V., Anthony, E. J., Thermal Activation of CaO-Based Sorbent and Self-Reactivation During CO₂ Capture Looping Cycles, *Environmental Science and Technology*, 42 (2008), 11, pp. 4170-4174
- [40] Manovic, V., Anthony, E. J., Sequential SO₂/CO₂ Capture Enhanced by Steam Reactivation of a CaO-Based Sorbent, *Fuel*, 87 (2008), 8-9, pp. 1564-1573
- [41] Fennell, P. S., et al., Regeneration of Sintered Limestone Sorbents for the Sequestration of CO₂ from Combustion and other Systems, Journal of the Energy Institute, 80 (2007), 2, pp. 116-119
- [42] Salvador, C., et al., Enhancement of CaO for CO₂ Capture in an FBC Environment, Chemical Engineering Journal, 96 (2003), 1-3, pp. 187-195
- [43] Sun, P., et al., Investigation of Attempts to Improve Cyclic CO₂ Capture by Sorbent Hydration and Modification, Industrial and Engineering Chemistry Research, 47 (2008), 6, pp. 2024-2032
- [44] Borgwardt, R. H., Sintering of Nascent Calcium Oxide, *Chemical Engineering Science*, 44 (1989), 1, pp. 53-60
- [45] Li, Z. S., et al., Synthesis, Experimental Studies, and Analysis of a New Calcium-Based Carbon Dioxide Absorbent, Energy and Fuels, 19 (2005), 4, pp. 1447-1452
- [46] Li, Z. S., Cai, N. S., Huang, Y. Y., Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation-Calcination Cycles for a New Ca-Based CO₂ Sorbent, *Industrial and Engineering Chemistry Research*, 45 (2006), 6, pp. 1911-1917
- [47] Wu, S. F., et al., Properties of a Nano CaO/Al₂O₃ CO₂ Sorbent, Industrial and Engineering Chemistry Research, 47 (2008), 1, pp. 180-184
- [48] Lysikov, A. I., Salanov, A. N., Okunev, A. G., Change of CO₂ Carrying Capacity of CaO in Isothermal Recarbonation-Decomposition Cycles, *Industrial and Engineering Chemistry Research*, 46 (2007), 13, pp. 4633-4638
- [49] Gora, D., et al., Steam Reactivation of 16 Bed and Fly Ashes from Industrial-Scale Coal-Fired Fluidized Bed Combustors, Fuel, 85 (2006), 1, pp. 94-106
- [50] Laursen, K., et al., Sulfation and Reactivation Characteristics of Nine Limestones, Fuel, 79 (2000), 2, pp. 153-163
- [51] Anthony, E. J., Bulewicz, E. M., Jia, L., Reactivation of Limestone Sorbents in FBC for SO₂ Capture, *Progress in Energy and Combustion Science*, 33 (2007), 2, pp. 171-210
- [52] Scala, F., Montagnaro, F., Salatino, P., Enhancement of Sulfur Uptake by Hydration of Spent Limestone for Fluidized-Bed Combustion Application, *Industrial and Engineering Chemistry Research*, 40 (2001), 11, pp. 2495-2501
- [53] Davini, P., Properties and Reactivity of Reactivated Calcium-Based Sorbents, Fuel, 81 (2002), 6, pp. 763-770
- [54] Wu, Y., Anthony, E. J., Jia, L., Steam Hydration of CFBC Ash and the Effect of Hydration Conditions on Reactivation, *Fuel*, 83 (2004), 10, pp. 1357-1370
- [55] Wu, Y., Anthony, E. J., Jia, L., An Experimental Study on Hydration of Partially Sulfated FBC Ash, Combustion Science and Technology, 174 (2002), 10, pp. 171-181
- [56] Wang, J., Wu, Y., Anthony, E. J., The Hydration Behavior of Partially Sulfated Fluidized Bed Combustor Sorbent, *Industrial and Engineering Chemistry Research*, 44 (2005), 22, pp. 8199-8204
- [57] Anthony, E. J., et al., Advanced Fluidized Bed Combustion Sorbent Reactivation Technology, Industrial and Engineering Chemistry Research, 42 (2003), 6, pp. 1162-1173

- [58] Anthony, E. J., et al., The Enhancement of Hydration of Fluidized Bed Combustion Ash by Sonication, Environmental Science and Technology, 36 (2002), 20, pp. 4447-4453
- [59] Rao, A., Anthony, E. J., Manovic, V., Sonochemical Treatment of FBC Ash: A Study of the Reaction Mechanism and Performance of Synthetic Sorbents, *Fuel*, 87 (2008), 10-11, pp. 1927-1933
- [60] Laursen, K., et al., Characteristics of Steam Reactivation Mechanisms in Limestones and Spent Calcium Sorbents, Fuel, 80 (2001), 9, pp. 1293-1306
- [61] Wu, Y., et al., Reinvestigation of Hydration/Reactivation Characteristics of Two Long-Term Sulphated Limestones which Previously Showed Uniformly Sulphating Behaviour, Fuel, 85 (2006), 14-15, pp. 2213-2219
- [62] Wu, Y., Anthony, E. J., Jia, L., Reactivation Properties of Four Long-Term Sulfated Limestones, *Energy and Fuels*, 20 (2006), 6, pp. 2421-2425
- [63] Bhatia, S. K., Perlmutter, D. D., Effect of the Product Layer on the Kinetics of the CO₂-Lime Reaction, AIChE Journal, 29 (1983), 1, pp. 79-86
- [64] Hartman, M., Coughlin, R. W., Reaction of Sulfur Dioxide with Limestone and the Influence of Pore Structure, *Industrial and Engineering Chemistry: Process Design and Development*, 13 (1974), 3, pp. 248-253
- [65] Alvarez, D., Abanades, J. C., Determination of the Critical Product Layer Thickness in the Reaction of CaO with CO₂, *Industrial and Engineering Chemistry Research*, 44 (2005), 15, pp. 5608-5615
- [66] Anthony, E. J., et al., Pacification of High Calcic Residues Using Carbon Dioxide, Waste Management, 20 (2000), 1, pp. 1-13
- [67] Manovic, V., Lu, D., Anthony, E. J., Steam Hydration of Sorbents from a Dual Fluidized Bed CO₂ Looping Cycle Reactor, *Fuel*, 87 (2008), 15-16, pp. 3344-3352
- [68] Manovic, V., Lu, D., Anthony, E. J., Sulphation and Carbonation Properties of Hydrated Sorbents from a Fluidized Bed CO₂ Looping Cycle Reactor, *Fuel*, 87 (2008), 13-14, pp. 2923-2931
- [69] Manovic, V., Anthony, E. J., SO₂ Retention by Reactivated CaO-Based Sorbent from Multiple CO₂ Capture Cycles, *Environmental Science and Technology*, 41 (2007), 12, pp. 4435-4440
- [70] Borgwardt, R. H., Bruce, K. R., Blake, J., An Investigation of Product-Layer Diffusivity for CaO Sulfation, *Industrial and Engineering Chemistry Research*, 26 (1987), 5, pp. 993-998
- [71] Hsia, C., et al., Diffusion through CaSO₄ Formed during the Reaction of CaO with SO₂ and O₂, AIChE Journal, 39 (1993), 4, pp. 698-700
- [72] Alvarez, D., Abanades, J. C., Pore-Size and Shape Effects on the Recarbonation Performance of Calcium Oxide Submitted to Repeated Calcination/Recarbonation Cycles, *Energy and Fuels*, 19 (2005), 1, pp. 270-278
- [73] Manovic, V., et al., CO₂ Looping Cycle Performance of a High-Purity Limestone after Thermal Activation/Doping, Energy and Fuels, 22 (2008), 5, pp. 3258-3264
- [74] Manovic, V., Anthony, E. J., Loncarevic, D., CO₂ Looping Cycles with CaO-Based Sorbent Pretreated in CO₂ at High Temperature, *Chemical Engineering Science* (in press)
- [75] Manovic, V., Anthony, E. J., Loncarevic, D., SO₂ Retention by CaO-Based Sorbent Spent in CO₂ Looping Cycles, *Industrial and Engineering Chemistry Research* (submitted)

Authors' affiliations:

V. Manovic (corresponding author) CANMET Energy Technology Centre-Ottawa (CETC-O), Natural Resources Canada 1, Haanel Drive, Ottawa, Ont., Canada K1A 1M1 E-mail: vmanovic@nrcan.gc.ca

E. J. Anthony CANMET Energy Technology Centre-Ottawa (CETC-O), Natural Resources Canada, Ottawa, Ont., Canada

Paper submitted: October 10, 2008 Paper revised: October 18, 2008 Paper accepted: December 26, 2008