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The Calcium Looping Cycle for CO₂ Capture from Power Generation, Cement Manufacture and Hydrogen Production

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Abstract

Calcium looping is a CO₂ capture scheme using solid CaO-based sorbents to remove CO₂ from flue gases, e.g. from a power plant, producing a concentrated stream of CO₂ (~ 95 %) suitable for storage. The scheme exploits the reversible gas-solid reaction between CO₂ and CaO(s) to form CaCO₃(s). Calcium looping has a number of advantages compared to closer-to-market capture schemes, including: the use of circulating fluidized bed reactors – a mature technology at large scale; sorbent derived from cheap, abundant and environmentally benign limestone and dolomite precursors; and the relatively small efficiency penalty that it imposes on the power / industrial process (i.e., estimated at 6–8 percentage points, compared to 9.5–12.5 from amine-based post-combustion capture). A further advantage is the synergy with cement manufacture, which potentially allows for decarbonisation of both cement manufacture and power production. In addition, a number of advanced applications offer the

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potential for significant cost reductions in the production of hydrogen from fossil fuels coupled with CO₂ capture.

The range of applications of calcium looping are discussed here, including the progress made towards demonstrating this technology as a viable post-combustion capture technology using small-pilot scale rigs, and the early progress towards a 2 MW scale demonstrator.

Keywords: Calcium Looping; CCS; CO₂ capture; Power Generation; Cement Manufacture

Contents

1. Introduction.....	3
2. Basics of the cycle	4
2.1 Sorbent deactivation.....	7
2.2 Sorbent performance	12
3. Energy efficiency, economics and integration with cement production.....	17
3.1 The impact of Ca-looping on energy efficiency of power generation	17
3.2 Economic studies on the Ca-looping cycle	19
3.3 Integration of Ca-looping and cement production	21
4. Pilot plant trials for Ca-looping technologies	28
4.1 Ca-looping for fuel-gas production without CO ₂ capture.....	28
4.2 CANMET Energy and Technology Centre.....	31
4.3 INCAR	33
4.4 Stuttgart.....	34
4.5 Other post-combustion pilot plants	35
4.6 Future scale up of post-combustion Ca-looping	36
5. Advanced applications of Ca-looping technology - H ₂ production	36
5.1 Combined shift and carbonation reactions	37
5.2 Sorption-enhanced reforming (SER)	39
5.3 In situ CO ₂ capture using solid fuels.....	42
5.4 Zero emission coal process	43
5.5 ENDEX configuration for Ca-looping.....	44
6. Conclusions.....	46
Acknowledgements.....	46
References.....	47

1. Introduction

Carbon Capture and Storage (CCS) is a range of technologies being developed to help mitigate climate change by isolating from the atmosphere a significant fraction of the CO₂ produced during fuel combustion (e.g. coal, gas and biomass). In the case of coal-fired power stations, the technology could prevent up to ~ 90 % of the CO₂ from being emitted to the atmosphere; greater net emission reduction may be possible if coal is co-fired with biomass by accounting for the CO₂ removed from the atmosphere during the biomass growth. CCS involves capture, purification and compression of the CO₂ ready for transportation to a permanent storage location. This review focuses on CO₂ capture which is the most costly stage in the CCS process; for information on the topics of transport and storage please refer to (Steeneveldt *et al.*, 2006). The CO₂ capture technology closest to market is post-combustion ‘scrubbing’ using amine-based solvents which has been used for industrial-scale separation of CO₂ for several decades. However there are issues associated with amine-scrubbing for CO₂ capture from a combustion flue-gas, including the high cost of manufacturing the solvent (e.g. MEA at ~ USD 1250 / tonne) (Rao and Rubin, 2002), the high efficiency penalty (~ 9.5–12.5 percentage points) (Xu *et al.*, 2010), degradation of the solvent due to reactions with O₂ and SO₂ (frequently present in industrial flue gases), and the handling and disposal of large quantities of degradation products / waste solvent, (which raises both environmental and health and safety concerns).

Research into a range of alternative CO₂ capture technologies, which aim to address such issues, are being pursued all over the world and one promising technology involves the use of a solid CO₂ sorbent using calcium-based materials, known as ‘The Calcium Looping Cycle’ or ‘Ca-looping’. This process offers a number of advantages, including; the use of well established fluidised bed technology; it is a high-temperature process and so high-grade excess heat can be recovered to provide additional energy to drive a steam cycle, thus

reducing the overall efficiency penalty of the process; the materials used to perform the CO₂ capture are widely available and environmentally benign (derived from limestones/dolomites); the affinity of the materials to SO₂ provides simultaneous partial desulphurisation of the industrial flue gas; and, the waste material from the process has potential uses elsewhere in industry, most notably the cement industry. These advantages are discussed in detail herein.

2. Basics of the cycle

An extensive review of the Ca-looping cycle for CO₂ capture has recently been published (Blamey *et al.*, 2010); the main features of which are summarised herein. For further information, see also reviews by Stanmore and Gilot amongst others (Stanmore and Gilot, 2005; Harrison, 2008; Anthony, 2008; Florin and Harris, 2008a; Li and Fan, 2008a), and the IEA GHG High Temperatures Solid Looping Cycles Network (IEA, 2010).

The Ca-looping process uses a CaO-based sorbent, typically derived from limestone, reacting via the reversible reaction described in Eq. 1. The forwards step is known as calcination and is an endothermic process which readily goes to completion under a wide range of conditions. The backwards step is known as carbonation.



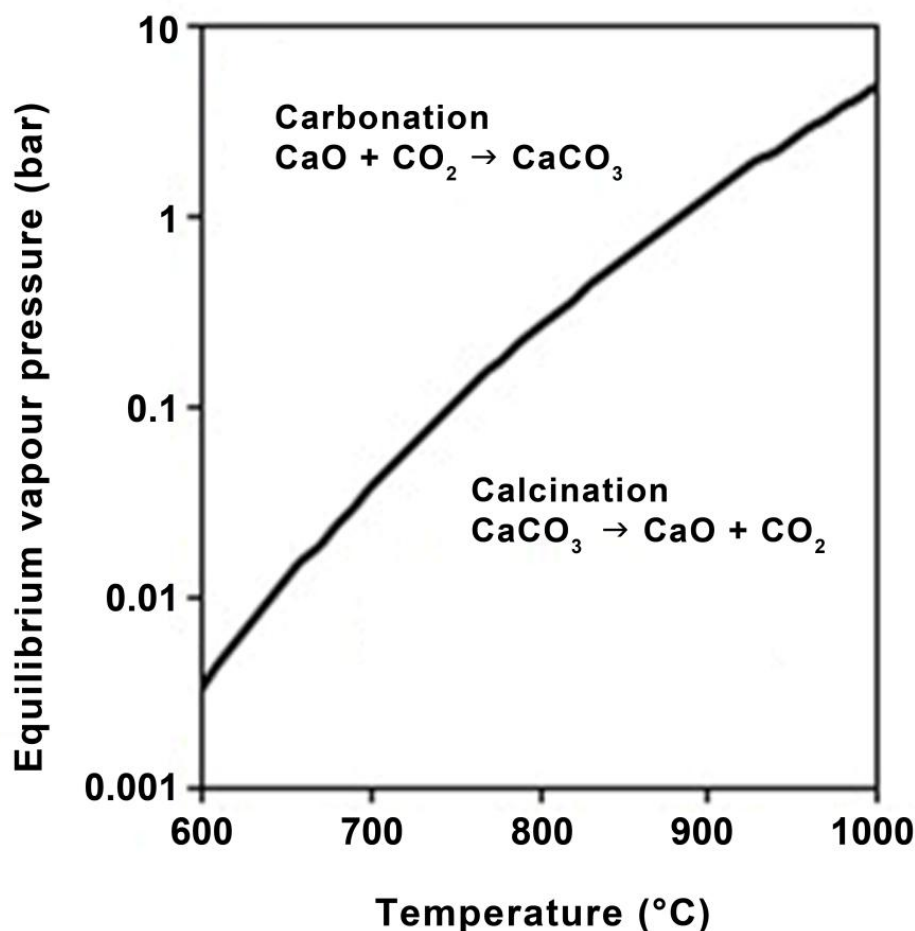


Figure 1: Equilibrium vapour pressure of CO_2 over CaO as a function of temperature (McBride *et al.*, 2002)

The equilibrium vapour pressure of CO_2 over CaO according to Eq. 1 can be calculated as a function of temperature; partial pressures of CO_2 greater than the equilibrium partial pressure at a given temperature will favour carbonation, while those lower than the equilibrium will favour calcination (see Fig. 1). As a result, if a sorbent is cycled between two vessels at suitable temperatures, carbonation of sorbent can be effected in one and calcination in the other. The objective of CO_2 capture is to obtain a pure stream of CO_2 suitable for storage; one method of achieving this is by separation of CO_2 (3–30 % by volume) from an exhaust gas obtained from power stations or industry (i.e., post-combustion CO_2 capture). A typical Ca-

looping process for CO₂ capture as proposed by Shimizu *et al.* (1999) is shown in Fig. 2. In this example, the heat necessary for calcination is provided by oxy-combustion of coal, however other methods have been suggested such as providing an external heat source (Alvarez and Abanades, 2005).

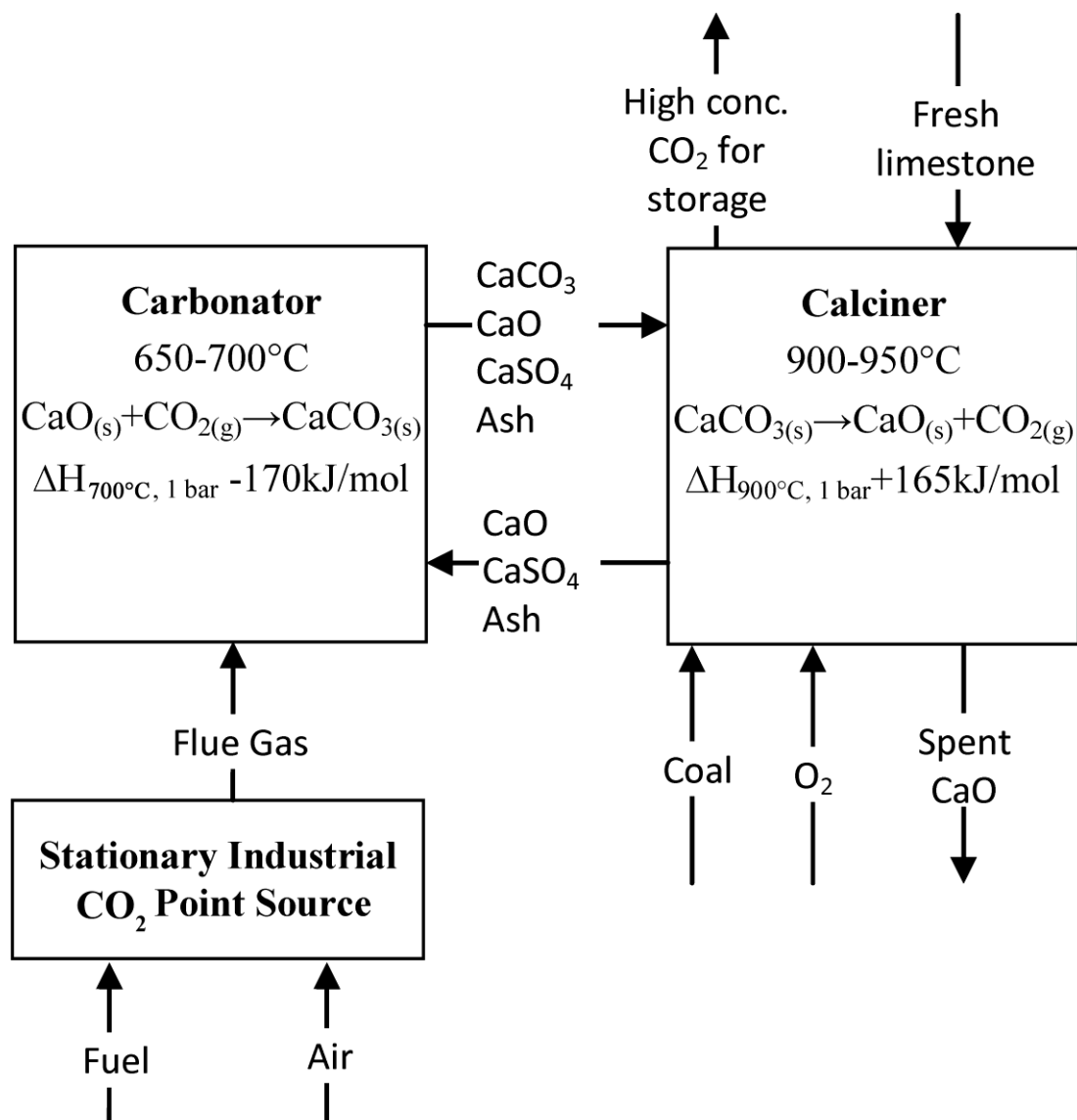


Figure 2: Typical example scheme for Ca-looping post-combustion CO₂ capture (enthalpies calculated using data provided by McBride *et al.* (2002)

The calciner temperature, (> 850 °C) is dictated by the high CO₂ partial pressure necessary to produce a near pure stream (Fig.1), and may also be chosen as a compromise between higher

temperatures, which increase the rate of calcination at the expense of rapid degradation of the sorbent (see Section 2.2) and milder temperatures which protect the sorbent; the carbonator temperature is chosen as a compromise between the higher equilibrium (maximum) capture at lower temperatures and a decreased rate of reaction. Both carbonator and calciner can use fluidised bed technology, owing to the good gas-solid contacting and uniform bed temperature, and which has the advantage of having being developed and deployed on a large scale (Cuenca and Anthony, 1995; Grace *et al.*, 1997) for circulating fluidized beds. The Ca-looping cycle can also be applied to gasification / pre-combustion techniques, where it can be used to increase hydrogen production by removing CO₂ from the products of the water gas shift (Eq. 2) and reforming reactions e.g. Eq. 9 (Harrison, 2007; Florin and Harris, 2008a), thus enhancing the maximum production of H₂. Current pilot plant trials of the Ca-looping cycle for post-combustion CO₂ capture are discussed in Section 4, while application of the Ca-looping cycle to more advanced capture techniques, including pre-combustion to generate fuel gases, are discussed in Section 5.

2.1 Sorbent deactivation

Ideally, CaO sorbent would be continually cycled between carbonator and calciner reacting with and evolving 1 mol of CO₂ per mol CaO each cycle. However, the rate of carbonation of CaO makes a transition from a fast to a very slow diffusion-controlled rate through the product layer (see inset Fig. 3) (Bhatia and Perlmutter, 1983; Mess *et al.*, 1999; Alvarez and Abanades, 2005), preventing full conversion to CaCO₃ on a timescale useful for industrial purposes. The conversion of CaO to CaCO₃ at this transition is often defined as the maximum carbonation conversion or ‘carrying capacity’ of the sorbent and is well known to decrease upon cycling of the sorbent through multiple CO₂ capture-and-release cycles (Curran *et al.*, 1967; Barker, 1973; Deutsch and Heller-Kallai, 1991; Silaban and Harrison,

1995; Aihara *et al.*, 2001; Abanades, 2002; Abanades and Alvarez, 2003; Fennell *et al.*, 2007a).

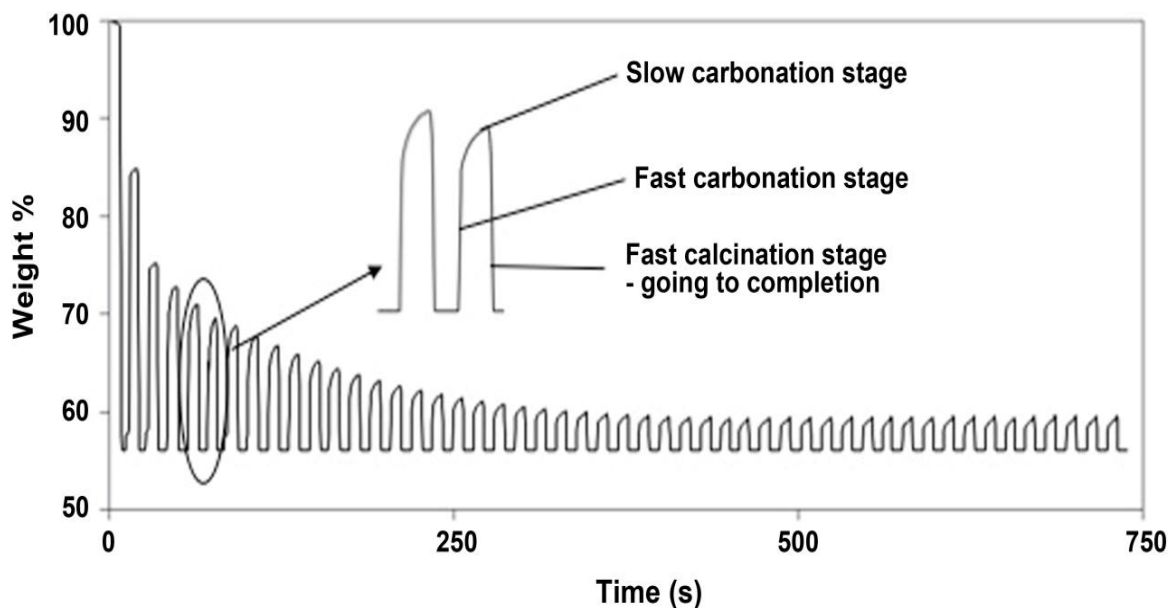


Figure 3: Carrying capacity of CaO sorbent through 50 CO₂ capture-and-release cycles represented in terms of mass change vs. time (TGA data for Havelock limestone)

Loss in sorbent reactivity can be caused by a number of factors: sintering of the porous CaO during the high temperature calcination stage (the major cause of loss in reactivity); competing sulphation / sulphidation reactions; loss of bed material through attrition causing elutriation of fines; and ash fouling.

CaO formed by calcination of CaCO₃ is very porous (Barker, 1973) because, as shown in Table 1, there is a marked reduction in molar volume from CaCO₃ to CaO resulting in a theoretical porosity of 0.54. However, CaO used for Ca-looping is prone to sintering (i.e., changes in pore shape, pore shrinkage and grain growth, at elevated temperatures), which causes a reduction in reactive surface area and a drop-off in reactivity. The transition to conditions that accelerate the rate of sintering of CaO occurs at approximately 900 °C (Borgwardt, 1989a), while increasing partial pressure of CO₂ and steam have also been found

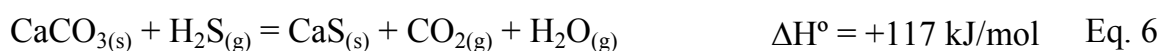
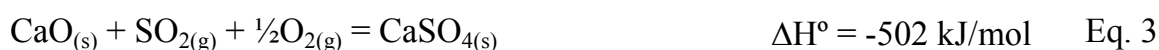
to increase the rate of sintering (Borgwardt, 1989b). Sintering of CaO can therefore be expected to be severe in the calciner, which in the example scheme in Fig. 2 is expected to be operating above 900 °C at 101 kPa CO₂. There is also a contribution of reactive sintering that is particular to cycling experiments (Gonzalez *et al.*, 2008).

Table 1. Physical properties of calcium compounds relevant to the Ca-looping cycle (Perry and Green, 1997)

Compound	Molar mass (g/mol)	Density (g/cm ³)	Molar vol. (cm ³ /mol)
CaCO ₃	100.1	2.71	36.9
CaO	56.1	3.32	16.9
CaSO ₄	136.1	2.96	46.0
CaS	72.1	2.8	25.8
Ca(OH) ₂	74.1	2.2	33.7

CaO has a very strong affinity to SO₂ and will readily form CaSO₄ in the oxidising conditions expected in post-combustion systems (see Eq. 3 for direct sulphation and Eq. 4 for indirect sulphation, i.e. sulphation of the carbonate). As a result, CaO derived from limestone has been used as a sorbent for SO₂ on an industrial scale (Smith, 2007); e.g. Drax Power Station (coal-fired, 3.96 GW) in the UK captured 90 % of its sulphur emissions using an independent wet limestone-gypsum flue gas desulphurisation plant. CaO can form CaS upon reaction with H₂S under reducing conditions (see Eq. 5 for direct sulphidation and Eq. 6 for indirect sulphidation, again, sulphidation of the carbonate). Sulphated sorbent requires very high temperatures or reducing conditions to be regenerated, though sulphided sorbent can be regenerated more readily (Lyngfelt and Leckner, 1989; Hayhurst and Tucker, 1991; Anthony

and Granatstein, 2001); both reactions can be considered as resulting in reactive sites lost for carbonation. Grace and co-workers (Ryu *et al.*, 2006; Sun *et al.*, 2007) investigated the effect of sulphate and sulphide formation on CO₂ uptake of sorbent and found that sulphate formation is a more significant problem as it results in pore blockage from the formation of CaSO₄, which has a much larger molar volume (see Table 1). This pore blockage then prevents access of CO₂ to the centre of a particle.



There has been a large volume of research published on the attrition characteristics of limestone for SO₂ capture (Anthony and Granatstein, 2001; Smith, 2007; Chen *et al.*, 2008; Saastamoinen *et al.*, 2008; Scala *et al.*, 2008; Blamey *et al.*, 2010). However, there is less research regarding limestone for CO₂ capture. Fennell *et al.* (2007a) showed that the most significant attrition occurred in the early cycles of repeated calcination / carbonation cycling experiments. Pilot plant studies published by Alonso *et al.* (2010) observed significant attrition of sorbent at the start of the experiment, while pilot plant studies published by Lu *et al.* (2008) showed significant attrition throughout operation (> 60 % of material ended up as fine material in the cyclones after 25 cycles, reducing the CO₂ capture rate significantly). For further discussion of attrition on a pilot plant scale, see Section 4. The mechanical stability of the sorbent is therefore receiving considerable attention and is likely to be a critical factor in the selection of original limestone for large-scale testing; on this basis, there is a drive

towards standardised testing of the mechanical stability of limestone to determine suitability for use in a fluidised environment (Schueppel, 2009; Zuberbuehler, 2009).

An important aspect of scale up to a typical proposed system, such as that described in Fig. 2, is the effect of fuel-combustion in the calciner. The combustion of the fuel results in two undesirable effects: the introduction of fine ash and chars into the cycle, which have the potential to deposit onto the surface of a particle and result in undesirable side reactions and low temperature melt formation; and higher local temperatures related to fuel-combustion (Joutsenoja *et al.*, 1999; Scala *et al.*, 2003; Corella *et al.*, 2006). Accordingly, Hughes *et al.* (2009) report lower reactivity of sorbent than anticipated and the formation of a dense shell on the surface of particles when combusting high-ash hardwood pellets in the calciner; a similar problem has been described by Kuramoto *et al.* (2003).

There have been a number of attempts to model the decay rate of the maximum carbonation conversion upon cycling, which focus on the reactivity towards CO₂ disregarding sulphation, attrition and ash fouling effects (Abanades, 2002; Abanades and Alvarez, 2003; Wang and Anthony, 2005; Grasa and Abanades, 2006; Lysikov *et al.*, 2007; Wang and Anthony, 2007; Gonzalez *et al.*, 2008). For descriptions of these decay equations and a discussion of their individual merits and drawbacks please refer to (Blamey *et al.*, 2010). It should be noted that most of the models proposed are semi-empirical and cannot currently be used to predict the behaviour of individual limestones from their intrinsic properties. The authors' preferred equation due to its accurate representation of the loss of reactivity over large numbers of cycles (> 20) is Eq. 7, proposed by Grasa and Abanades (2006), where a_N is the maximum carbonation conversion of the sorbent in cycle N , a_∞ is the residual (final) conversion of the sorbent after a very large number of cycles, and k is a decay rate constant.

$$a_N = (1/(1/(1-a_\infty) + kN)) + a_\infty \quad \text{Eq. 7}$$

It is likely that in a realistic system where sulphation, attrition and ash fouling are unavoidable, a_{∞} will tend to zero, however in small scale tests a residual capacity of ~ 60 mg CO₂ / g sorbent is found, which is competitive with other CO₂ sorbents (Rodriguez *et al.*, 2008b). A real system will also differ in that the residence time of the sorbent in the calciner or carbonator may not be sufficient to allow full calcination or maximum carbonation, making application of these formulas difficult; such matters are under investigation by Abanades and co-workers (Grasa *et al.*, 2009; Rodriguez *et al.*, 2010).

2.2 Sorbent performance

There is currently a great deal of work being conducted to improve sorbent performance upon cycling. This can be done by alteration of the process conditions or by sorbent enhancement. There are numerous process variables which will affect sorbent performance, the most important of which is the temperature of the calciner. However, steam partial pressure in the carbonator, the residence time of the particles in the calciner and the carbonator, the presence of ash, sulphur and other minor species, and particle size are likely to also play significant roles. The temperature of the calciner can be decreased if the partial pressure of CO₂ is reduced, thus minimising the extent of sorbent sintering upon cycling; the two simplest ways of doing this are by lowering the total pressure (Ewing *et al.*, 1979;

Alvarez and Abanades, 2005; Sakadjian *et al.*, 2007) (see also the Endex process, Section 5.5) or by introducing steam into the calciner (Alvarez and Abanades, 2005; Wang *et al.*, 2008; Wang *et al.*, 2009). The main research areas for sorbent enhancement are doping of natural limestones with trace amounts of organic salts, the production of synthetic sorbents, the hydration of spent sorbent, and thermal pre-treatment; an ideal enhanced sorbent will display high mechanical strength while maintaining its reactive surface area over repeated

cycling, without being prohibitively expensive - for economic assessments see work by Romeo and co-workers (Romeo *et al.*, 2009a; Lisbona *et al.*, 2010).

There is considerable variability in the reactivity and friability of natural limestones, which should be investigated before selecting a sorbent (Laursen *et al.*, 2000; Ryu *et al.*, 2006; Alvarez, 2007; Fennell *et al.*, 2007a). These properties depend on impurities and the conditions / age of formation. Dolomites have shown a reduced decay rate upon cycling, despite a lower initial reactivity owing to a lower amount of CaO per unit mass (Dobner *et al.*, 1977; Silaban *et al.*, 1996); natural sorbents such as shells have also been studied and have been shown to exhibit mildly increased reactivity in comparison to natural limestone in some cases (Ives *et al.*, 2008; Li *et al.*, 2009). Doping of natural limestones has been investigated; however the results have been variable (Salvador *et al.*, 2003; Fennell *et al.*, 2007b; Florin and Harris, 2008b; Sun *et al.*, 2008), even when the same dopant has been used. The efficacy of doping is highly dependent on the concentration of dopant used; too low a concentration will have no effect, too high may contribute to pore blocking and potentially agglomeration of particles. 'Synthetic sorbents' are also being developed. Examples include: precipitated CaCO₃ from a slurry bubble column (Agnihotri *et al.*, 1999; Gupta *et al.*, 2004; Florin and Harris, 2008c) to enhance the reactive surface area of the sorbent; sorbents derived from different calcium precursors, e.g. calcium acetate, calcium ethanoate (Lu *et al.*, 2006; Lu, H. *et al.*, 2008; Liu *et al.*, 2010a) with particular success using a MgO support (Liu *et al.*, 2010b) to similarly enhance the reactive surface area; dispersal of CaO within an inert porous matrix such as mayenite (Li *et al.*, 2005; Li *et al.*, 2006; Pacciani *et al.*, 2008a) to improve mechanical stability; and use of cementitious binders (Manovic and Anthony, 2009a; 2009b) to improve mechanical stability. Sorbent reactivity can be periodically improved by hydration of calcined sorbent, though this is often at the expense of

mechanical strength of the sorbent (Hughes *et al.*, 2004; Fennell *et al.* 2007b; Manovic and Anthony, 2007; Manovic and Anthony., 2008a; Sun *et al.*, 2008; Zeman, 2008). Thermal preactivation / pre-treatment, by treating sorbent at high temperature under N₂, has been found to improve long-term reactivity of sorbents (Manovic and Anthony, 2008b; 2008c).

Table 2. List of process variables used in cycling experiments for both natural and enhanced Ca-based sorbents (Key used for limestones: Key: PB = Purbeck, PN = Penrith, CD = Cadomin, GM = Glen Morrison, HL = Havelock, KT = Katowice, KR = Kelly Rock, PS = Piasek, GL = Gotland, BL = La Blanca, GM = Graymont, SB = Strassburg, DO = Dolomite)

		Carbonation Conditions			Calcination Conditions				
Sorbent	Reactor	T (°C)	PCO ₂ (atm)	t (min)	T (°C)	PCO ₂ (atm)	t (min)	No. Cyc.	Reference
Natural Sorbents									
DO	TGA	550	1	~400	800-975	0-1	5-60	up to 31	Dobner (1977)
BL, PS, CD, HL, GL, DO	TGA	650	0.1	5	850-1000	0.1-1	3-60	up to 500	Grasa and Abanades (2006)
PB, PN, CD, GM, HL	Fluidised bed with quartz tube	750	0.14	8-10	750	0 (N ₂)	8-10	30	Fennell <i>et al.</i> (2007a)
SB	TGA	850	1	3-8	720-900	0 (N ₂)	25	15	Sun <i>et al.</i> (2007)
Eggshells, mussel shells, PB	Fluidised bed with quartz tube	750	0.14	8	750	0 (N ₂)	4-10	20-54	Ives <i>et al.</i> (2008)
BL	TGA	650	0.1	10	950-1250	0.1	3-300	12-150	Gonzalez <i>et al.</i> (2008)
BL, PS, CD, HL, GL	TGA	550-700	0.1	20	900	0.2-1	10	10-100	Grasa <i>et al.</i> (2008)
KR, HL, CD, GM	TGA	650-850	0.5	30	750	0 (N ₂)	90	11	Manovic and Anthony (2008d)
HL, KT	TGA	800	0.5	20	800-	0-1	20	10	Manovic <i>et</i>

					950				<i>al.</i> (2009)
PB, KT, HL, KR	TGA	900	0.15	5	650	0.15	5	20-50	Wu <i>et al.</i> (2010)
Enhanced Sorbents									
Pressed alkoxide pellet	Quartz tube reactor with electrobalance	750	0.2	60	1000	0 (N ₂)	180	10	Aihara <i>et al.</i> (2001)
CD, KR and HL doped with NaCl and Na ₂ CO ₃	TGA	750	0.15	20	850	0.15	20	20	Salvador <i>et al.</i> (2003)
CaO and Ca ₁₂ Al ₁₄ O ₃₃ with mass ratio 3:1	TGA	700	0.2	30	850	0 (N ₂)		50	Li <i>et al.</i> (2006)
HL, PB, CD hydrated	Fluidised bed	750	-	5	750	0 (N ₂)	10	30	Fennel <i>et al.</i> (2007b)
CaO doped with lithium, Precipitated CaCO ₃	TGA	600	0.15	20	700	0 (N ₂)	20	50	Florin and Harris (2008c)
Thermally pre-treated KR, CD, GM, HL	TGA	650	0.2	30	850	0 (N ₂)	30	20	Manovic and Anthony (2008b)
Thermally pre-treated LB, KR	TGA	800	0.5	30	800	0 (N ₂)	10	30	Manovic and Anthony (2008c)
CaO-Ca ₁₂ Al ₁₄ O ₃₃ derived from acetate	TGA	690	0.15	-	850	0 (N ₂)	120	45	Martavaltzi and Lemionidou (In Press)
Calcium magnesium acetate	Fluidised bed with quartz tube	750	0.146	8	750	0 (N ₂)	8	10	Sultan <i>et al.</i> (2010)
Calcium aluminate pellets	TGA	700	0.2	10	950	1	15	30	Manovic and Anthony (2010)

All studies of sorbent enhancement should consider that sorbent reactivity is dependent on several variables: calcination temperature and time; carbonation temperature and time; CO₂ concentration in carbonation and calcination; and, the difficulty in defining ‘normal’ behaviour in a limestone, which may be used as a reference. These factors are important, in that they make comparisons between different studies difficult. For example, very different results are obtained for deactivation rates when calcination is conducted under mild vs. severe conditions (Grasa and Abanades, 2006; Manovic and Anthony, 2008b; Manovic and Anthony, 2008d; Manovic *et al.*, 2009; Wang *et al.*, 2010) and also due to increases in carbonation temperature (Manovic and Anthony, 2008d) (both of which are reported to be due to the effect of sintering, see: Section 2.1 above). Longer carbonation times can regenerate the sorbent (Barker, 1973, Lysikov *et al.*, 2007; Chen *et al.*, 2009) though the effect of this is somewhat inconsistent elsewhere (Manovic and Anthony, 2008d). A higher CO₂ concentration during carbonation has been shown to improve the uptake of some synthetic sorbents (Pacciani *et al.*, 2008b). In cases where the CO₂ concentration is higher during calcination this consistently leads to a more rapid drop-off in reactivity (Li *et al.*, 2005, Lu *et al.*, 2009); however there are cases where the effect of CO₂ concentration in calcination is only noticeable over the first five cycles (Manovic *et al.*, 2009). The presence of SO₂ leads to a reduction in carbonation reactivity owing to the competing sulphation reaction (see: Section 2.1). For a summary of the process variables used in cycling experiments investigating the performance of both enhanced and natural sorbents please refer to Table 2 above.

3. Energy efficiency, economics and integration with cement production

3.1 The impact of Ca-looping on energy efficiency of power generation

As previously mentioned, key advantages of Ca-looping include the potential for retrofitting to existing power stations or other stationary industrial CO₂ sources and the relatively low parasitic energy demand imposed on the existing processes. The Ca-looping cycle requires heat at the calciner to effect the following; the endothermic calcination of CaCO₃; raising the temperature of the recycled sorbent from carbonator to calciner temperature (+ 250 °C); and, raising the temperature of fresh limestone from ambient (+ 900 °C) which may be required to maintain the overall reactivity of the limestone in the system. As shown in Fig. 2, this heat can be provided by in-situ oxy-fired combustion of fuel in the calciner. Additional energy is also required to separate O₂ from N₂ and for CO₂ compression. Critically, because this process is operating at relatively high temperatures (> 650 °C), the majority of the energy input can be recuperated from the hot gas and solid streams exiting the system to drive a steam cycle. Heat generated by the exothermic carbonation reaction is also available which may be integrated with the steam cycle.

Accordingly, Rodriguez *et al.* (2008a) considered the parasitic energy demand simply in terms of the amount of the total fuel demand (f_p) that is diverted to the calciner, i.e., $1-f_p$; they showed $1-f_p$ to be strongly dependent on the quality of the fuel used in the calciner and calculated a minimum value of 0.3 for an ideal fuel containing no sulphur or ash (assuming a carbonator efficiency of 70 %, Ca / C molar ratio of 3 and purge flow rate of 0.13 mol/s). The sensitivity of this parameter, $1-f_p$, is shown in Table 3, with data reproduced from their work.

Abanades *et al.* (2007) incorporated the efficiency penalty owing to O₂ separation and CO₂ compression (6 % and 5 % respectively) describing the overall plant efficiency according to Eq. 8.

$$\eta_{\text{capture}} = \eta_{\text{ref}} \cdot f_p + \eta_{\text{oxy}} \cdot (1-f_p) - 0.05 \cdot f_p \quad \text{Eq. 8}$$

where: η_{ref} is the energy efficiency of the existing process, f_p is the fraction of fuel used in the main power plant η_{oxy} is the energy efficiency of the power generated by the calciner.

Assuming 40 % of total fuel consumption was allocated to the calciner (i.e. $f_p = 0.6$) (Shimizu *et al.*, 1999; Abanades *et al.*, 2004; Abanades *et al.*, 2005), the resulting energy efficiency of power generation from the additional fuel utilized in the CO₂ capture process was calculated

Table 3. Minimum efficiency penalties and associated operating parameters of Ca-looping calculated as the split of fuel use ($1-f_p$) on an existing power generation process for different types of fuels (Rodriguez *et al.* 2008a)

S / C Ratio	Ash / C Ratio	Purge / C Ratio	Sorbent Conv.	LHV (MJ / kg)	(1- f_p) Min.
N/A	N/A	0.13	0.196	34	0.30
N/A	0.25	0.18	0.255	25	0.33
0.05	N/A	0.29	0.280	34	0.35
0.12	0.56	0.41	0.290	21	0.39

as 35.6 % from a baseline of 43 % in the reference case. When heat recuperation is considered (as discussed above), Romeo *et al.* (2008) computed an efficiency penalty of only 4.5 % from 44.9 % (the supercritical steam cycle reference case) to 40.4 %. The inclusion of essential auxiliary power consumption components (O₂ separation, 47 MWe; CO₂ compression, 53 MWe; other, 15 MWe) gave a final efficiency of 26.7 % for the utilisation of the extra fuel used in the calciner to generate electricity (accounted for within the figure for the overall efficiency penalty). The study also identified the potential modifications of the

existing supercritical steam cycle for integration with Ca-looping based on the temperature and physical location of the high temperature streams exiting the Ca-looping system.

3.2 Economic studies on the Ca-looping cycle

The economics of the Ca-looping cycle have been evaluated by Abanades *et al.* (2007) considering three main cost components: the main power plant, the oxy-fired calciner and the carbonator. He calculated a likely range of costs from, 7.1 USD / tCO₂ to 31.2 USD / tCO₂ avoided, incorporating an optimistic and pessimistic estimate using data from the IPCC Special Report on CSS (i.e., for fuel cost, capital cost, variable cost and fixed charge factor) (Metz *et al.*, 2005) reflecting the impact of different cost parameters on the overall cost of capture. Mackenzie *et al.* (2007) estimated the cost of CO₂ avoided at 19 USD / tCO₂ which compares competitively with estimates for amine scrubbing, e.g. 32.5–80 USD / tCO₂ (David and Herzog, 2000; Herzog, 1998) (figures converted to 2006 USD from Canadian dollars, using mean exchange rate June 2006). Their study included a sensitivity analysis and identified the cost of limestone and the assumed Ca / C ratio as having the most significant influence on the cost (Fig. 4).

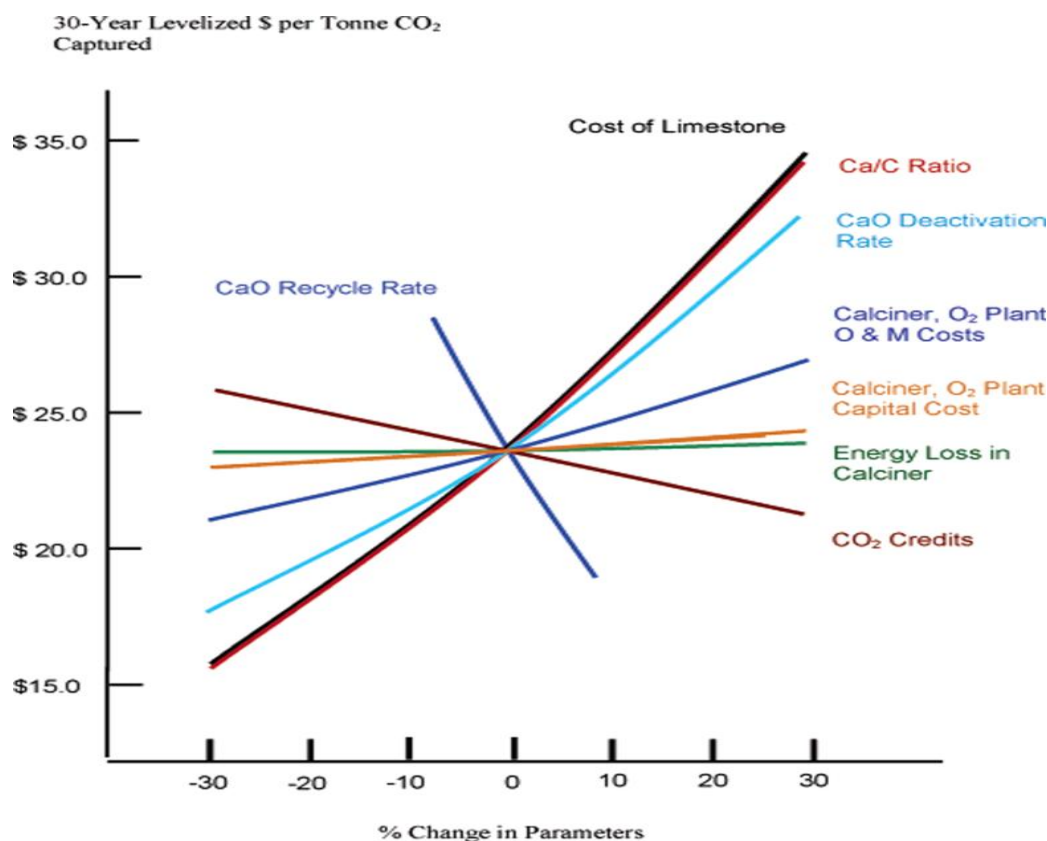


Figure 4: Sensitivity analysis showing the impact of varying critical cost parameters by +/- 30% on CO₂ capture cost (Mackenzie *et al.*, 2007)

Romeo *et al.* (2009b) examined the impact on the cost of CO₂ avoided of varying the Ca / C molar ratio and purge rate (as a percentage of the solids inventory); they showed that the impact of purge rate on the capture cost was more significant for higher Ca / C ratios (Ca / C > 4) because at higher Ca / C ratios, increasing the purge rate does not lead to an increase in CO₂ capture capacity whilst the cost rises monotonically with purge rate. The study examined the effect of these process variables purging both from the carbonator and calciner. Purging from the carbonator allows a lower possible capture cost to be reached because material is removed before a further energy-intensive calcination step is required. However, purging from the calciner allows material to be removed as CaO which can provide both an energy and CO₂ credit to cement production. Purging from the carbonator, the optimum configuration (i.e. resulting in the minimum capture cost) comprised a Ca / C ratio of 4 and a

purge rate of 2 % giving a minimum cost of 19.8 USD / tCO₂. Purging from the calciner suggested an optimum configuration of Ca / C = 5 and a purge rate of 1–2 %, giving a minimum cost of 20.5 USD / tCO₂. The results showed consistently, regardless of purge location or fuel type, that the minimum costs could be achieved with higher Ca / C ratios and lower purge rates. In all cases studied the cost of CO₂ capture remained competitive (< 29 USD / tCO₂) (figures converted to USD from euros using mean exchange rate January 2008). However, this does not take into account the potential for integration with cement manufacture, detailed below.

3.3 Integration of Ca-looping and cement production

One major advantage for the Ca-looping cycle over many competing technologies is that the exhausted / purged CaO can be used as a raw material in cement production, presenting an opportunity to partially decarbonise both power generation and the cement process.

Cement production is both a highly resource and energy intensive process. Approximately 1.5 tonnes of raw materials are required to produce 1 tonne of cement. Limestone represents ~ 85 wt.% of the raw feed whilst the remainder comprises clay (~ 13 wt. %) and additives (e.g., SiO₂, Al₂O₃, Fe₂O – < 2 wt.%) (Alsop *et al.*, 2007). The first step in the process involves limestone calcination to produce CaO which is then mixed with the other components at ~ 1400–1500 °C in the kiln to produce clinker. This is then cooled and ground with ~ 5 wt.% gypsum. The energy consumption of producing a tonne of clinker ranges from 3.1–7.5 GJ (CEMBUREAU, 1999) with over 60 % of the energy use in the process owing to heat input to the precalciner (EU, 2001) to drive the endothermic calcination of CaCO₃.

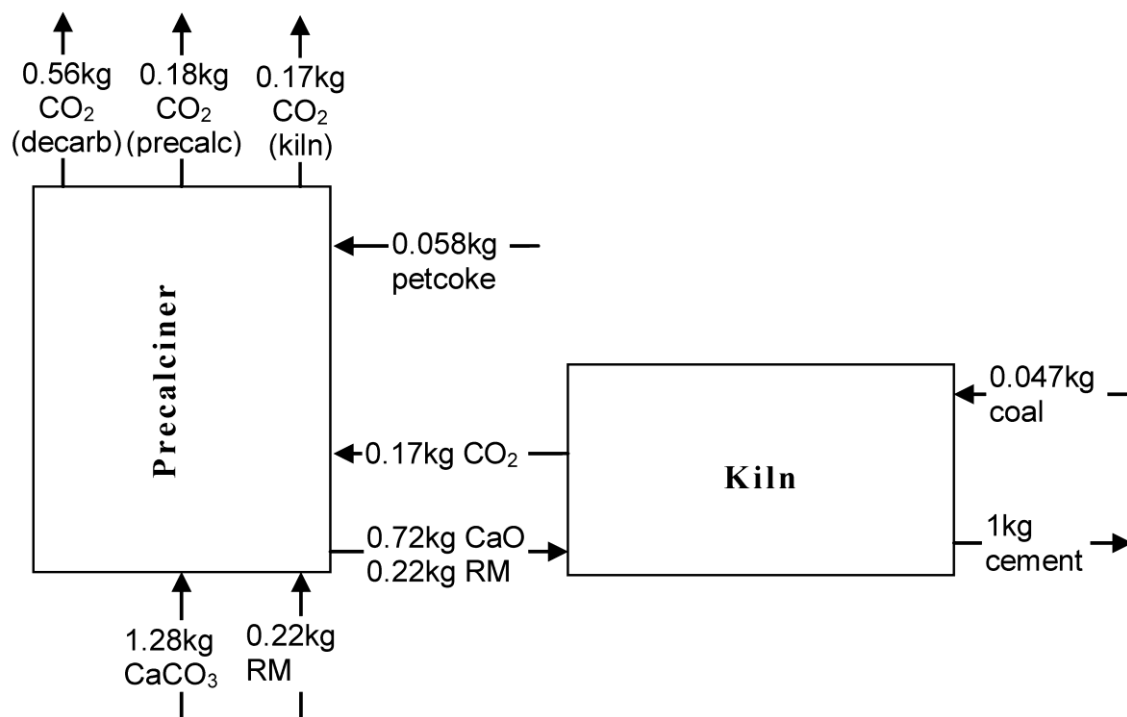


Figure 5: Mass balance on raw materials, fuels and CO_2 in a typical modern dry cement production process (RM = raw materials other than CaCO_3). Coal LHV 26.3 MJ/kg, 68.9% carbon content. Petroleum coke LHV 34.2 MJ/kg, 87.2 % carbon content. Data taken from (Alsop, 2007).

The cement production process emits between 0.6–1 kg of CO_2 per tonne of cement (ECRA, 2007) and approximately 80 % of these emissions (~ 60 % from decarbonisation, ~ 20 % from calciner fuel use) originate in the calcination stage (see Fig. 5).

A means to reducing the direct emissions of CO_2 from the calcination process has been assessed which involves driving the reaction using very hot CaO particles ($T > 1000$ °C) passed to the precaliner from a separate combustor (Rodriguez *et al.*, 2008b) (see Fig. 6). This is intended to replace the conventional method of driving the calcination reaction in the cement works (i.e. in-situ fuel combustion).

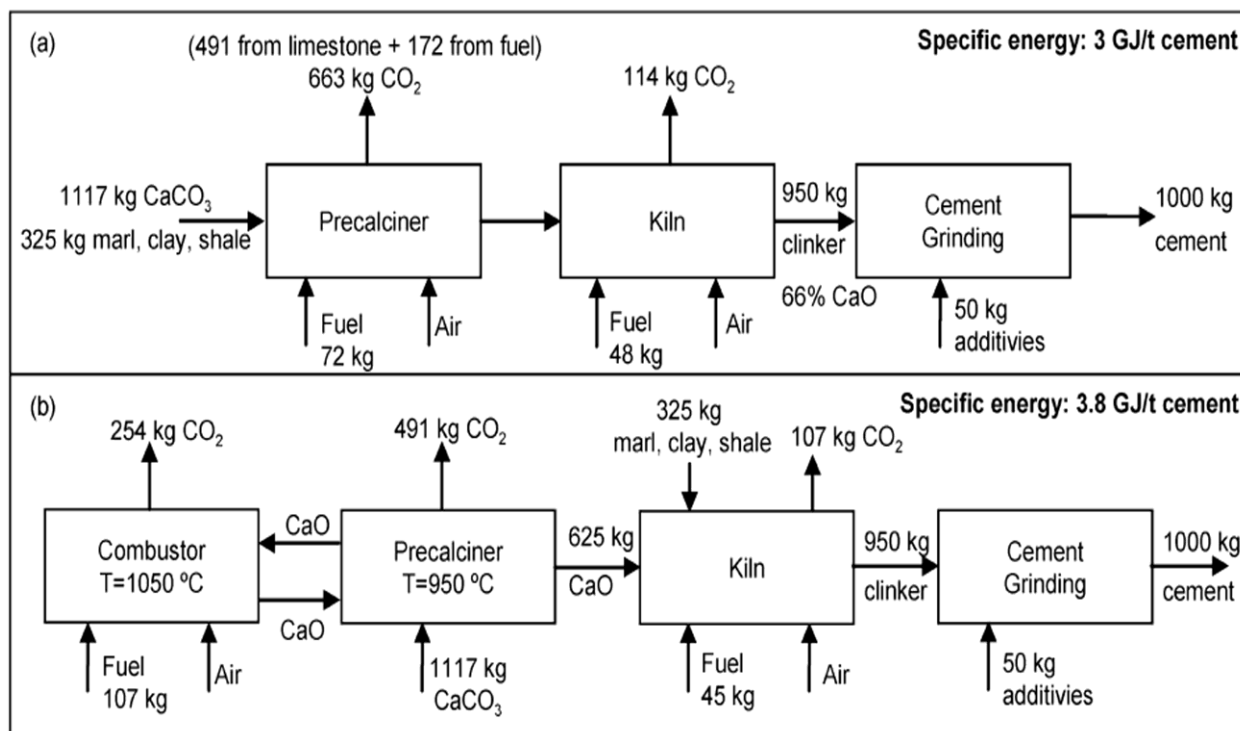


Figure 6: Mass balance on (a) a reference cement plant and (b) the novel CO_2 mitigation strategy proposed. Basis = 1 tonne of cement, LHV 25 MJ / kg, 10 % air excess. (Rodriguez *et al.*, 2008a)

Such a process would increase the energy requirement by 0.8 GJ / t cement, but allows up to 60 % of the CO_2 emissions to leave the system in a form suitable for storage (following compression and purification) at an estimated cost of 19 USD / t CO_2 . This is shown to be highly competitive with other figures for cost of CO_2 avoided determined in an economic study of CO_2 capture in the cement process using amines (144 USD / t CO_2) and using an oxy-fired kiln configuration (54 USD / t CO_2) (Barker *et al.*, 2009).

Alternatively, the purged material from the Ca-looping system (Fig. 2) which would consist predominantly of CaO (if removed at the calciner) with a proportion of ash and calcium sulphate (the proportion of which would depend on Ca-looping operating parameters) can be used in place of the CaCO_3 which is usually the main constituent of the cement feed. The ash content could also fulfil some or all of the cement aluminosilicate requirements usually supplied in the clay or in additives. This means that the direct emissions of CO_2 from the

calcination stage are avoided in the cement works, as is a substantial amount of the energy required to effect the calcination. Basic calculations (Blamey *et al.*, 2010) indicate that a reasonable purge rate of $\sim 48.9 \text{ kg / s}$ (Romeo *et al.*, 2008) would otherwise require 144 MWth, simply to calcine, thus theoretically reducing the energy required within the cement works for clinker manufacture from 3.1 GJ/t by approximately 50 %. As a result, both of the industrial processes undergo significant decarbonisation, the energy required to produce clinker in the cement plant is almost halved, the raw material costs of the cement process are vastly reduced and the issue of waste disposal from the power plant CO_2 capture process is avoided.

The inherent advantage of integrating cement manufacture with the Ca-looping process is clear. However, the potential to use waste material from the cycle to fulfil the requirement for calcareous material in the cement process may be limited by its chemical compatibility in relation to the demands or limitations imposed on cement product composition. The factors potentially limiting or having implications for the use of the deactivated CaO are discussed here. Firstly, due to the strong affinity of CaO to SO_2 (Eq. 3), a proportion of the CaO in the waste material will be in the form of CaSO_4 . The proportion will depend upon the Ca / C ratio used in the calcium loop, the composition of the fuel and the recycle / purge rate. The maximum sulphur content of ordinary portland cement (OPC) in the U.S. is 2.5 % as specified by ASTM C150; above this level, sulphur leads to expansion and cracking of the cement paste upon hydration. (This expansion is dependent upon the alumina content; therefore this value increases to 3 % for cements with higher levels of aluminates).

The proportion of sulphur contained in the final cement product is also known to impact upon the formation of the four major cement compounds which determine the strength properties of the cement (Fig. 7). An increase in sulphur content within the 0–3 % range have been shown to lead to a decrease in ‘alite’ (the cement compound which provides long-term

strength development) and an increase in ‘Belite’ (the compound providing short-term strength development) irrespective of the Silica Modulus (the ratio of silica to aluminium and iron oxides in the cement). A desirable level of SO_3 in OPC clinker is 0.6 % (Alsop *et al.*, 2007).

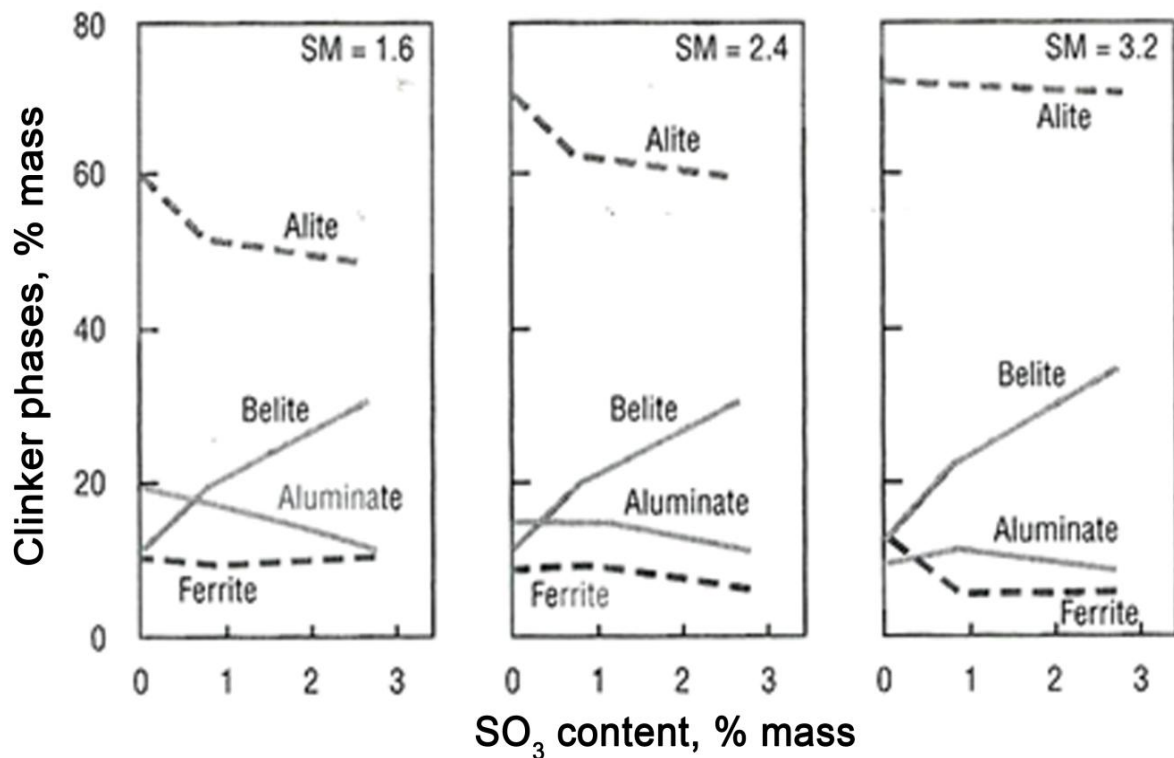


Figure 7: The effect of cement product SO_3 content and Silica Modulus (SM) on major phase formation (Bhatty and Miller, 2004)

It should also be noted that excess sulphur entering the cement works can lead to operational problems arising from cycles of evaporation in the kiln and condensation in the precalciner leading to blockages. However, in modern cement plants reasonable sulphur levels in the system and the resulting circulation can be controlled using a kiln by-pass line to remove unwanted vapourised components from the kiln (in particular K_2O , Cl and Na_2O_3 as well as SO_3).

Another potential issue is that of trace elements released from fuel use in the Ca-looping calciner. The in-situ combustion of solid fuels is likely to result in partial or total vapourisation of trace elements contained in the fuel. Repeated exposure of the solids to the combustion environment over a long series of cycles could lead to a build-up of certain trace elements in the solids, either through physical or chemical attachment to the calcium oxide, calcium sulphate or the ash. These elements would therefore be present in the waste material and passed to the cement works. A key concern for the cement industry when considering the use of a marginal raw material is its trace element content, the incorporation of the elements into the clinker and their effects on the production process and on cement performance (Bhatty, 1995). Highly volatile elements such as cadmium, mercury, selenium and thallium tend to leave the cement process either in the cement kiln dust (CKD) or in the emissions and pose less of a concern for operation of the plant or for the final cement product. Less volatile elements are likely to incorporate into the clinker causing a variety of desired or undesired effects. For example, the presence of beryllium in quantities as low as 0.25 % has been shown to severely affect the setting and strength properties of cement (Bhatty, 2003) due to its impact on alite crystals. A summary of the effects of trace elements on cement performance is given in Table 4. For more detailed information refer to (Bhatty *et al.*, 2004).

Table 4. An overview of the effects on cement performance of higher than normal levels of trace elements in cement product. Elements listed are those commonly found in coal and petroleum coke.

Element	Impact
Sb	Incorporates into clinker as calcium antimonates, reduces alite and belite size.
As	Can form low-volatile calcium arsenates known to reduce alite formation.
Ba	Improves burnability of materials.
Be	Severely reduces alite formation affecting setting and strength properties.
Cr	Reduces alite formation but also improves grindability of clinker.
Pb	Effects uncertain.
Ni	Replaces Ca and therefore increases free lime in kiln (reduces burnability).
Ag	No known effect.
V	Incorporates into alites forming larger crystals; increases free lime and imparts a tan colour.
Zn	Enters belite and alite, reduces free lime; improves clinkering reactions.
Sr	Small amounts favour alite formation; larger amounts favour belite formation.

In addition to chemical compatibility, both attrition and agglomeration of the exhausted material could impact on its use as a raw feed to the cement process. Typically the cement feed is made up of particles with the following size distribution: 88 μm (83 %), 88–300 μm (15 %) and > 300 μm (2 %) (Alsop *et al.*, 2007). If the material is too fine due to attrition the particles would become entrained in the exhaust gas and lost in the CKD. However if the feed is too coarse the load on the kiln would be increased due to a reduction in material burnability

(i.e. the ease by which the raw materials form the clinker phases, measured in terms of the fuel consumption required to achieve these phases). This can be overcome by subjecting the material to grinding, however a grinding stage would result in a loss of the sensible heat provided by the purged CaO stream which could otherwise be used to reduce the load on the kiln.

4. Pilot plant trials for Ca-looping technologies

Several independent projects have been initiated in order to scale-up Ca-looping technology, including pilot plant trials with CO₂ capture in Spain, Canada and Germany (up to ~ 120 kWth). In addition, larger scale demonstrations are planned (~ 2 MWth). To date, these projects have demonstrated good levels of CO₂ capture efficiency (~ 80–90 %), with future work needing to focus on process efficiency and generating a CO₂ stream suitable for storage. The most relevant pilot studies are discussed below.

4.1 Ca-looping for fuel-gas production without CO₂ capture

The Ca-looping process has been developed on a large scale for improving the heating value of product gas from gasification processes by removing CO₂ and driving gasification (see Section 5); however, the emphasis has not, as yet, been on producing CO₂ suitable for storage. In the 1960s-1980s Consolidation Coal Company developed the CO₂ Acceptor Process, culminating in pilot plant trials in Rapid City, South Dakota, USA (Curran, 1967; Fink *et al.*, 1974; Basu, 2006); unfortunately, many of these results are not in the public domain. The CO₂ Acceptor Process consisted of two bubbling fluidised beds with solid

Table 5. Summary of current Ca-looping pilot plant trials

University	Nominal size	Calciner technology	Carbonator technology	Additional features	Operations
University of Vienna, Vienna, Austria	100 kWth	CFBC	CFB gasifier / carbonator	Fast internally circulating fluidized bed	Increased H ₂ production from biomass from 40 % to 75 % v/v, while allowing a lower gasification temperature and lower tar emissions
CANMET Energy and Technology Centre, Ottawa, Canada	75 kWth	CFBC, ID 100 mm, height 5 m	BFB, two stages designed to separate combustion/sulphation and carbonation, ID 100 mm, height 5 m	CO ₂ recycling in calciner to allow oxy-firing	Good levels of CO ₂ capture from simulated flue gas and fuel gas; attrition and accelerated sorbent deactivation found to be a problem
INCAR-CSIC, Oviedo, Spain	30 kWth	CFBC, ID 100 mm, height 6 m	CFB, ID 100 mm, height 6.5 m	Two interconnected circulating fluidised bed reactors; allows continuous operation	Good levels of CO ₂ capture from simulated flue gas; in situ capture from biomass combustion
University of Stuttgart, Stuttgart, Germany	10 kWth	BFB, ID 70 mm, height 12.4 m	CFB, ID 114 mm	Solid looping rate between the beds is controlled by a cone valve; allows continuous operation	Good levels of CO ₂ capture
Ohio State University, Columbus, USA	120 kWth	Rotary kiln	Entrained bed	Capture from stoker boiler; hydrator between calciner and carbonator	Good levels of CO ₂ capture; hydration vessel resulted in the reactivity of the sorbent being maintained upon cycling
Technical University of Darmstadt, Germany	1 MWth	CFBC, horizontal cross section, 37 m ² , 1.5 MWth	CFB, horizontal cross section, 194 m ² , 1 MWth	Ratio of calciner: carbonator 2:1	Construction in progress

particle streams linking the two; one gasifier / carbonator operating at 10 bar and 825 °C under steam; and one combustor / calciner operating at 1000 °C.

More recently, the AER (Adsorption Enhanced Reforming) process has been developed by a consortium under the European Commission's 6th Framework Programme to enhance the steam gasification of biomass. Pilot plant investigations of the AER process have been performed at the Vienna University of Technology, Austria, using so-called Fast Internally Circulating Fluidized Bed (FICFB) technology. The reactor consists of a dual fluidised bed system with a gasifier / carbonator operating at 600–700 °C at atmospheric pressure and a combustor / calciner, which can handle 100 kWth fuel power. Much work has been done on suitability of sorbents for the process, with a focus on finding a sorbent with a suitable mechanical strength and reactivity without susceptibility for melt formation (Pfeifer *et al.*, 2007; Soukup *et al.*, 2009). AER operation can increase H₂ production from biomass – in comparison to an analogous process without CO₂ sorbent, which has been scaled up and is available commercially – from ~ 40 % to ~ 75 % v/v – while allowing a lower gasification temperature and producing lower tar emissions (due to catalytic cracking by CaO) (Pfeifer *et al.*, 2009). The process has been modelled (Proell and Hofbauer, 2008) and has been subject to much larger trials in an 8 MWth fuel input CHP unit in Guessing, Austria (Koppatz *et al.*, 2009). The trials at Guessing were deemed successful in demonstrating the feasibility of the AER process on an industrial scale, and future work will focus on varying process parameters such that the observed H₂ production of 50 % can be increased to that observed on a smaller scale. While results from the AER process should be watched keenly for application of Ca-looping techniques for CO₂ capture with storage in mind, it would take considerable modification of the existing setup to be directly applicable.

4.2 CANMET Energy and Technology Centre

The CANMET Energy and Technology Centre, Ottawa (CETC-O), a division of Natural Resources Canada, have a 75 kWth dual fluidised bed system setup (see Fig. 8), which has been used to test the Ca-looping cycle for CO₂ capture. Hughes *et al.* (2005) published the early design and process analysis of the facility. The dual fluidised bed consists of two reactors; one is a CFBC calciner upgraded for operation with oxy-fuel using flue gas recycle; and the other a BFB combustor / carbonator, divided into two stages allowing separate combustion / sulphation and carbonation. Lu *et al.* (2008) described more than 50 h of operating experience with three different calciner operating modes; electrically heated, and oxy-combustion with biomass (low-ash wood pellet) and bituminous coal (high-volatile medium-sulphur eastern bituminous). Operation was continuous following an initial calcination period. CO₂ capture of ~ 95 % was achieved in the first few cycles of operation, dropping to 71 % after 25 cycles. In oxy-fuel experiments, CO₂ concentrations of ~ 85 % were observed, which are expected to be improved upon as the unit design is improved. Attrition was found to be a significant problem in the system with ~ 50 % of the limestone (Havelock), which started in the range 0.4–0.8 mm, becoming smaller than 0.1 mm and becoming collected in cyclones. The authors conclude that attrition made a significant contribution to the decay in reactivity of the sorbent and is therefore an important consideration in Ca-looping processes.

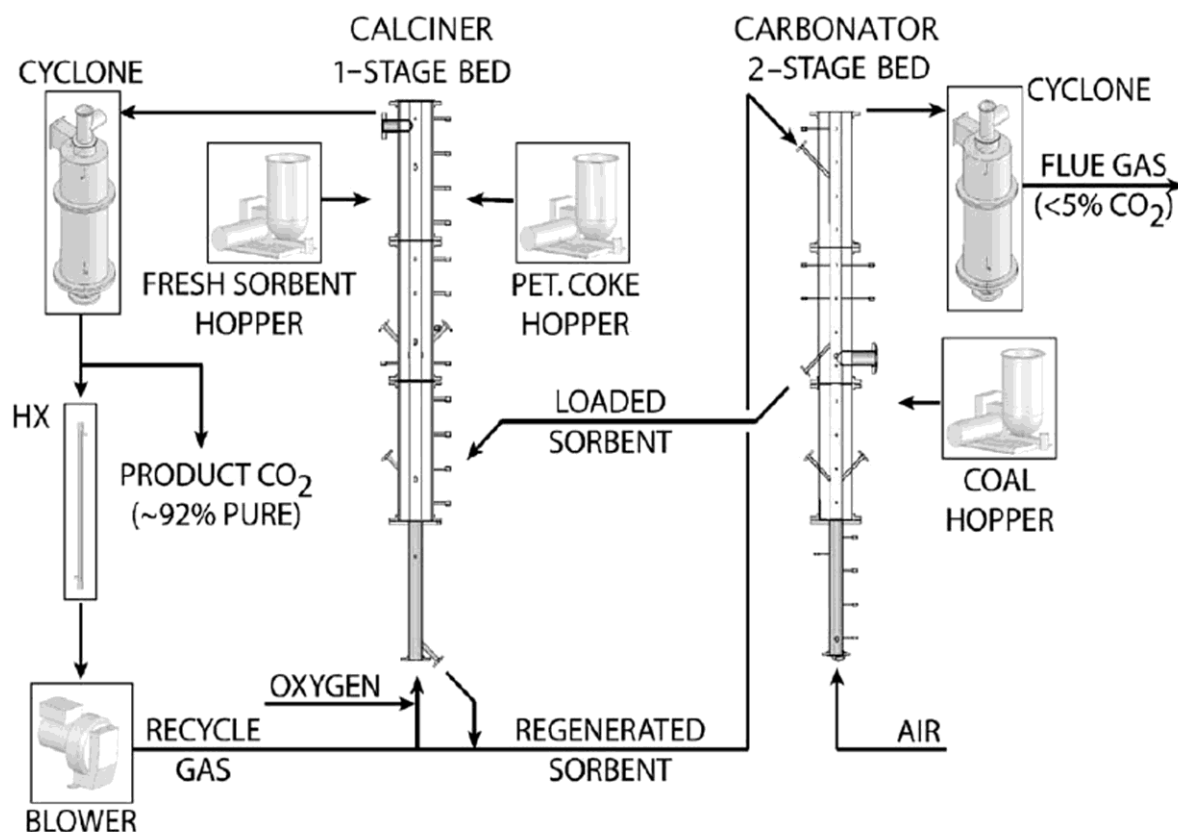


Figure 8: Schematic diagram of the 75 kWth pilot plant at CETC-O (Hughes *et al.*, 2005)

Symonds *et al.* (2009a) used the same system in a batch fashion to investigate CO₂ capture from a simulated syngas in comparison to post-combustion capture. The only modifications to the system described above were the addition of a steam generator before the carbonator and a shell-and-tube heat exchanger for steam condensation after the carbonator. Two different calcination environments were tested: pure fibre/hardwood blend wood pellets in O₂ air enriched and in oxy-fuel fired conditions. Three different carbonation conditions were tested: CO₂ (8 %) in air, CO₂/ steam (8 / 17 %) in air, and simulated syngas (N₂ / CO₂ / CO / H₂ / H₂O, 12 / 8 / 42 / 21 / 17 %). Results obtained showed deterioration in sorbent performance with the more severe calcination environment and improvement in sorbent performance when steam was added. A further improvement was observed using simulated syngas (as observed in previous tests on a smaller scale (Symonds *et al.*, 2009b).

The reactor used is the adaptation of a system previously used by Anthony and co-workers (Salvador *et al.*, 2003; Abanades *et al.*, 2004; Jia *et al.*, 2007); reviews by Anthony and co-workers (Anthony and Granatstein, 2001; Anthony *et al.*, 2007; Anthony, 2008). Salvador *et al.* (2003) and Abanades *et al.* (2004) both used mild (15 % CO₂, balance air) calcination conditions and achieved high CO₂ capture efficiencies: the former highlighted that promising sorbent enhancement strategies demonstrated in the TGA do not necessarily translate to the larger scale; and the latter showed that performing repeated cycles of full carbonation and calcination showed similar trends in reactivity to those seen in lab-scale tests, while developing a model to calculate CO₂ concentration profiles within the reactor. Jia *et al.* (2007) focused on attrition showing a marked difference in the extent of attrition between Cadomin and Havelock (both Canadian) limestones with most of the attrition occurring over the first couple of calcinations; the authors also reported a marked decrease in attrition rates of partially sulphated sorbent at the expense of sorbent reactivity, though sulphation extent would have to be carefully controlled to limit deactivation of the sorbent for CO₂ capture (Lu *et al.*, 2009).

4.3 INCAR

INCAR-CSIC has developed a 30 kW test facility comprising two interconnected circulating fluidised bed (CFB) reactors. Continuous experiments for several hours using relatively mild calcination conditions (air-fired, 800–900 °C) have been performed, following a relatively long start-up time to complete initial calcination. Once a steady state was reached, CO₂ capture efficiencies were consistent and stable between 70 % and 90 %, depending on the ‘freshness’ of sorbent (maximum activity of material 0.2–0.3, average T = 650 °C). Attrition during the first cycle was intense and therefore fresh limestone was added periodically batch-wise. Once the material had been calcined, solids had a typical particle size below 100 µm

and attrition was no longer a serious problem (Abanades *et al.*, 2009). Gonzalez *et al.* (In Press) presented the results of attrition analysis on experiments in the test plant at INCAR. They found that for one limestone, there was a marked decrease in average particle size at the start of operation (from an initial size of 100–400 μm to 90 % of the solids being less than 100 μm), which then appeared to stabilise on continued operation. A second limestone was also tested, which had a smaller initial particle size and showed minor change during continuous operation (all less than 100 μm). The authors present a literature review on attrition of limestones before successfully applying several attrition models to their results. In a separate work, Abanades *et al.* (2009) investigated validation of in situ CO_2 capture using CaO from biomass combustion – i.e. combusting biomass in the carbonator – using the 30 kW test plant. They obtained a CO_2 capture efficiency of higher than 70 % with sufficiently high solids circulation rates of CaO and solids inventories with a carbonator operation temperature of 700 °C.

4.4 Stuttgart

The University of Stuttgart has a 10 kWth pilot plant consisting of a CFB carbonator and BFB calciner (air blown) with the solid looping rate between the beds controlled by a cone valve (Charitos *et al.*, 2008; Hawthorne *et al.*, 2008). A hydrodynamic study of the apparatus has been published (Charitos *et al.*, 2010). A parametric study has been performed on the apparatus with the riser used as the calciner and BFB as the carbonator and a CO_2 capture efficiency of > 90 % was reported. The CO_2 capture efficiency was found to decrease with decreasing CaO looping ratio (CaO looping rate between beds / CO_2 flow to carbonator) and space time (number of moles of CaO in carbonator / CO_2 flow to carbonator) (Charitos *et al.*, 2009).

4.5 Other post-combustion pilot plants

Ohio State University has developed a 120 kWth plant to develop a process named the Carbonation-Calciation Reaction (CCR) process. The CCR process is described as the following: CaO / Ca(OH)_2 is injected into an entrained bed reactor, whereupon it reacts with CO_2 and SO_2 between 450 and 650 °C; it is then calcined at a high temperature between 850 and 1300 °C. The calciner could be a flash or entrained bed calciner, a fluidized bed, or a rotary kiln. There is a third unit, the hydrator, used to 'reactivate' the sorbent (see Section 2.2). The pilot facility consists of a stoker furnace, whose flue gas is fed into an entrained bed carbonator operating at 500-625 °C, the solids from which are passed into an electrically heated rotary calciner operating at 980 °C. In work published by Wang *et al.* (2010), the calcined sorbent was removed, hydrated off-line, and passed to the flue gas duct. They were successful in achieving CO_2 capture efficiencies of > 90 % and SO_2 capture efficiencies of ~ 100 %. By investigating the capture efficiencies of various sorbents at various Ca / C ratios, they found considerably better capture efficiencies at lower Ca / C ratios for sorbent derived from Ca(OH)_2 with an average size of 3 μm than sorbent derived from pulverised lime (average size of 18 and 300 μm) and ground lime (600 μm). The use of the hydration vessel resulted in the reactivity of the sorbent being maintained upon cycling. However, the use of particles as low as 3 μm in an industrial-scale process for cyclical CO_2 capture incorporating CFB reactors may be extremely challenging due to the difficulty in repeatedly separating such small particles from a gas stream; the collection efficiency of cyclones (an integral part of CFB design) rapidly drops off at particle diameters below 5 - 20 μm (Ray *et al.* 1997), depending on cyclone conditions.

4.6 Future scale up of post-combustion Ca-looping

The European Commission, under the 7th Framework Programme, has recently part-funded a € 6.87 million project for the development of post-combustion CO₂ using Ca-looping in a large test facility. The project, named 'CaOling' (CaO looping), brings together HUNOSA (Spain), Natural Resources Canada (Canada), Foster Wheeler (Spain), CSIC (Spain), Lappeenranta University of Technology (Finland) and Imperial College London (UK). The project focus is the development of a 2 MWth Ca-looping pilot plant built to capture CO₂ from the flue gases from a 50 MWe CFB coal power plant at La Pareda, operated by HUNOSA. The project is seen as a necessary step towards a pre-industrial demonstration plant (10s of MWth in scale).

The Technical University of Darmstadt is also developing a demonstration plant for CO₂ capture using post-combustion Ca-looping technologies (LISA – LImeStone-based Absorption of CO₂) and construction of a 1 MWth capture plant as an extension to a 1052 MWe hard coal-fired power plant (net efficiency 45.6 %) is underway.

The projected efficiency loss for 87 % CO₂ capture of the unit is estimated to be < 3 % points (less than e.g. amine scrubbing), with CO₂ compression a further 3 %. The carbonator is to be a CFB unit with a thermal duty up to 1 MWth operating at 650 °C, and the calciner is to be a CFB unit with a thermal duty up to 1.5 MWth operating at 900 °C. The plan is to demonstrate CO₂ capture from coal, biomass and / or RDF combustor (1 MWth) (Epple, 2009; Strohle *et al.*, 2009a; 2009b).

5. Advanced applications of Ca-looping technology - H₂ production

Looking further into the future, Ca-looping technology underpins a range of advanced power schemes for the production of electricity and / or hydrogen coupled with the production of a concentrated stream of CO₂ suitable for storage, or alternative industrial processes. These

include: combined shift-carbonation (i.e., Han and Harrison, 1994) sorbent enhanced reforming (SER) (e.g., Balasubramanian *et al.*, 1999; Johnsen *et al.*, 2006), in situ CO₂ capture, e.g., HyPr-RING (Lin *et al.*, 2004a), Endex configuration (Ball and Gray, 1999), (Sceats, 2009) and the zero-emission coal concept (ZECA) (Gao *et al.*, 2008a; 2008b). These processes, which offer significant potential for efficiency and economic improvements, although involving higher technical complexity, are discussed in turn below.

H₂ is an important chemical feedstock in the chemical and petroleum sectors and there is an increasing interest in the use of H₂ as a clean-green energy carrier in a future H₂ energy economy, owing to debatable environmental and efficiency benefits. At present, most H₂ (i.e., 96 %) is produced from fossil fuels, resulting in an equivalent amount of CO₂ being released to the atmosphere to that if the fuel was burnt directly (ignoring efficiency losses)—undermining the potential benefits of a H₂ energy economy. Given the enormous increase in production that would be necessary to support a transition to a H₂ energy economy, there is clear scope for improved methods of production coupled with CCS (Franzese *et al.*, 2009).

5.1 Combined shift and carbonation reactions

Although we classify H₂ production as an ‘advanced application’ of Ca-looping technology, a process coupling the carbonation reaction (Eq. 1) with the water-gas shift reaction (Eq. 2) for the production of hydrogen and the separation of CO₂ was patented in 1931 by Gluud *et al.* (US patent, 1931). Although no data was offered, the patent describes the production of H₂ by reacting equivalent quantities of steam and CO over a bed of CaO and some amount of MgO at temperatures between 300 °C and 600 °C at atmospheric pressure; in addition, they described the production of a pure stream of CO₂ and sorbent regeneration by calcining the sorbent at 900–1000 °C in an apparatus that was externally heated. In this process, the removal of CO₂ gas as solid CaCO₃ shifts CO conversion beyond the standard equilibrium balance, and thus promotes the output of H₂. Combining the shift and carbonation reactions

represents a process simplification and improves efficiency by eliminating the need for the input of an excessive quantity of steam.

Fig. 9 shows thermodynamic modeling results for the combined shift and carbonation reaction system predicting the H_2 mol fraction as a function of temperature and pressure. In the presence of CaO, the H_2 mol fraction is increased in the 400–600 °C temperature range due to the removal of CO_2 from the gas phase altering the equilibrium balance. Above this temperature, the conditions favour calcination and therefore H_2 production returns to the level predicted for the system without CaO present. Increasing the pressure to 15 atm is shown to improve H_2 production above 700 °C due to carbonation taking place at higher temperatures.

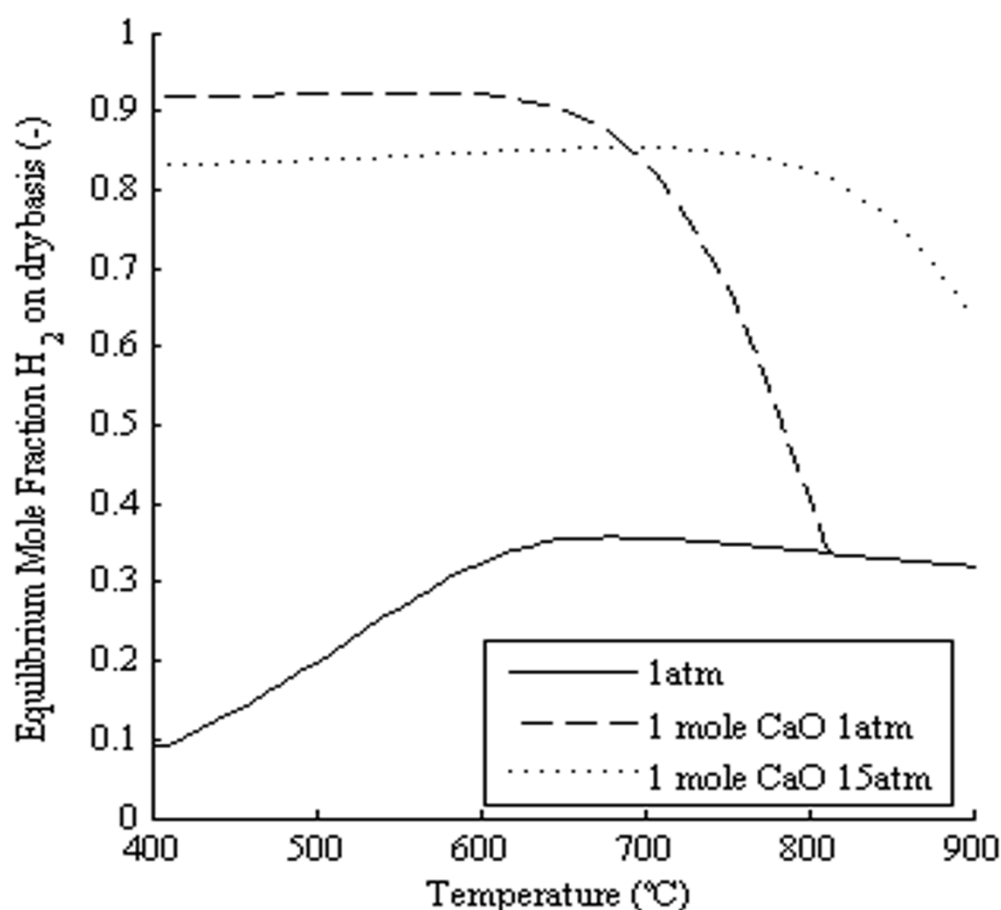


Figure 9: H_2 mole fraction as a function of temperature and pressure with and without the presence of CaO predicted by thermodynamic equilibrium modeling. Inputs: 1 mole CO, 1 mole H_2O , 1 mole CaO. Thermodynamic data from (McBride *et al.*, 2002)

More recently, Han and Harrison (1994) have published results from their study of the combined shift and carbonation reactions conducted in a laboratory-scale fixed bed reactor. Their study investigated temperature (400–650 °C), pressure (5 atm and 15 atm), synthesis gas composition, gas residence time and sorbent type (i.e. limestone and dolomite precursors). The optimal temperature for the process represents a trade-off between thermodynamic and kinetic limitations, whereby a higher temperature improves the rate of reaction; however there is an upper temperature limit owing to equilibrium constraints from the exothermic carbonation and shift reactions. Han and Harrison (1994) reported near complete equilibrium conversion of CO (> 0.995) and CO₂ capture at temperatures ≥ 500 °C; improved CO conversion was observed at 15 atm compared to 5 atm, which is expected owing to the increase in the CO₂ partial pressure relative to the equilibrium CO₂ pressure over CaO, and thus providing a greater driving force for CO₂ capture at higher temperatures. The same issue of decay in CO₂ capture capacity through multiple cycles undermines the economic efficiency of this advanced application; and thus, Müller *et al.* (2009) have investigated the cyclic stability of a variety of Ca-based sorbents for the combined carbonation and shift reactions using an atmospheric pressure fixed bed reactor. They reported superior performance using a synthetic sorbent derived from calcium magnesium acetate, compared to natural limestone and dolomite precursors, when tested through five reaction-regeneration cycles.

5.2 Sorption-enhanced reforming (SER)

Sorption-enhanced reforming of hydrocarbons for H₂ production involves an additional degree of complexity by combining hydrocarbon reforming, e.g., steam methane reforming (SMR) according to Eq. 10 with the carbonation and the water-gas shift reactions in a single reaction step. This process, which is achieved using CaO mixed with a reforming catalyst also exploits the advantage of removing CO₂ from the reaction system, promoting a high

equilibrium conversion of CO and producing a concentrated stream of H₂ > 98 vol. % (dry basis) according to Eqs. (1, 2 & 9) (Balasubramanian *et al.*, 1999; Harrison, 2008).



The reforming reaction is strongly endothermic, however, when combined with the exothermic carbonation and water-gas shift reactions, the overall reaction scheme is thermally balanced. On this basis, the potential energy savings of SER compared to standard SMR is reported to be in the order of 20 % (Ortiz and Harrison, 2001). There is also the advantage of reducing the number of process steps by eliminating the shift reactors. However, some additional heat is required for calcination of CaCO₃ for sorbent regeneration.

The predicted improvement in the H₂ yield between SMR and SER according to thermodynamic equilibrium as a function of temperature is shown in Figs. 10 and 11. For temperatures below 800 °C, the improvement in H₂ production due to the capture of CO₂ by CaO can be observed. Above this temperature decomposition of CaCO₃ results in a drop-off in the level of H₂ produced and an increase in the level of CO.

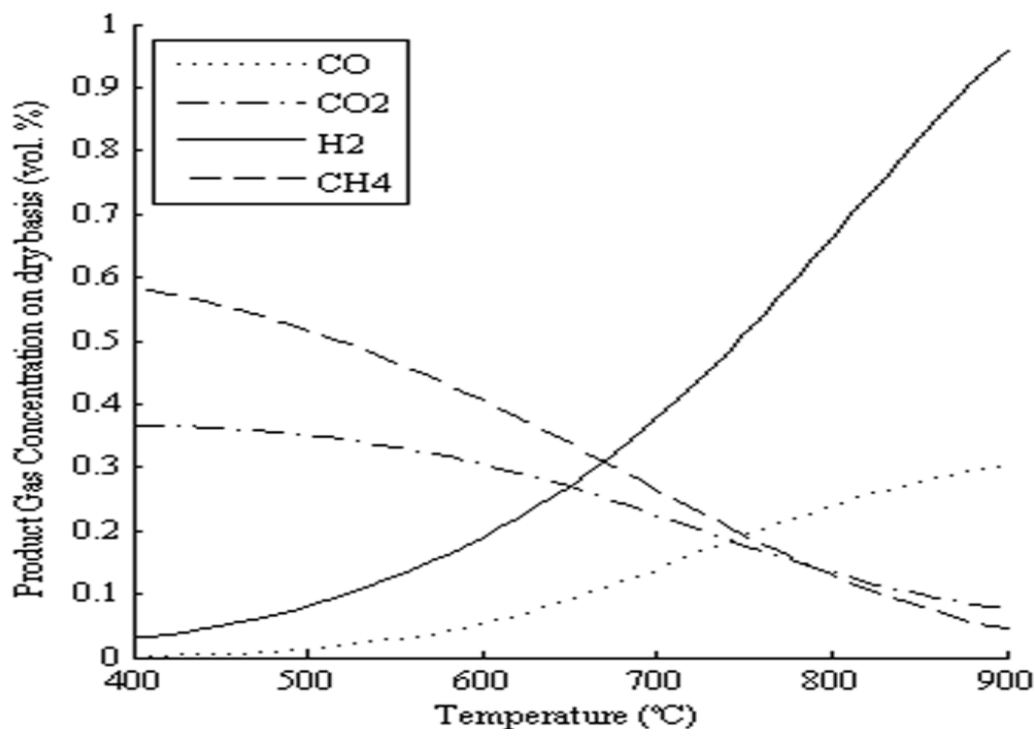


Figure 10: Product gas concentration of methane reforming at 15 bar pressure as a function of temperature. Inputs: 1mole CH₄, 1 mole CO, 2 mole H₂O. Thermodynamic data from (McBride *et al.*, 2002)

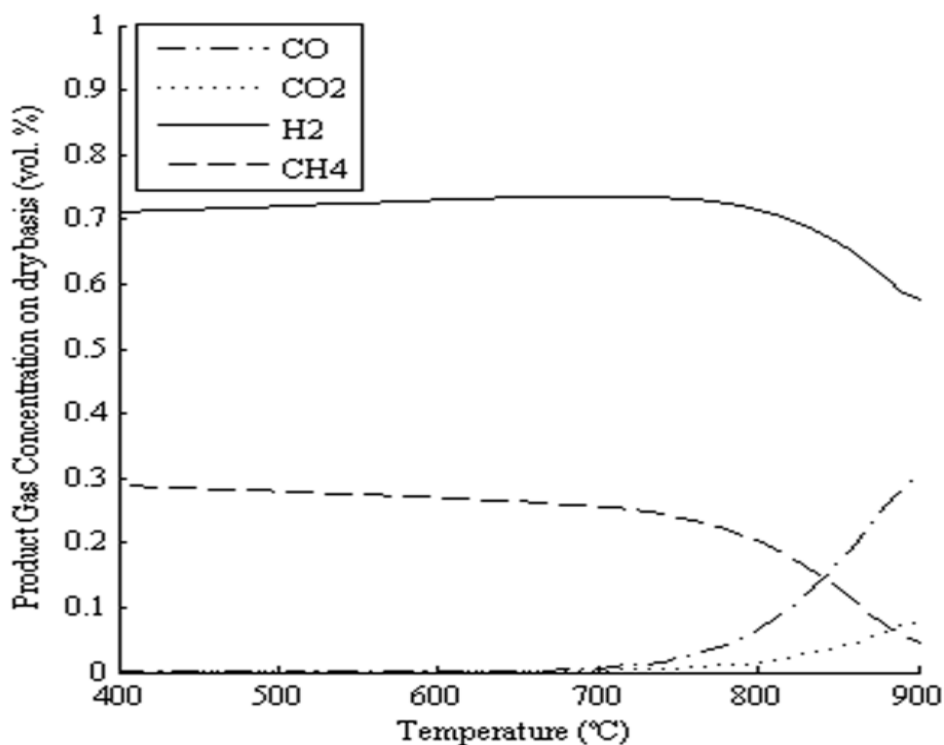


Figure 11: Product gas concentration of sorbent enhanced reforming at 15 bar pressure as a function of temperature. Inputs: 1mole CH₄, 1 mole CO, 2 mole H₂O, 1 mole CaO. Thermodynamic data from (McBride *et al.*, 2002)

The process has been demonstrated experimentally at the lab-scale, for a range of temperatures and pressures, and using fixed-bed (e.g., Balasubramanian *et al.*, 1999) and fluidised-bed reactors (e.g., Johnsen *et al.*, 2006). Balasubramanian *et al.* (1999) used a pressurised fixed-bed reactor, with reagent grade CaO and a commercial reforming catalyst (NiO supported on Al₂O₃) and reported a H₂-rich product gas consisting of 94.7 vol. % H₂, 5.2 vol. % CH₄ and carbon oxides in the order of ppms (dry basis, pre-breakthrough at 650 °C, 15 atm and S / C = 4). Johnsen *et al.* (2006) used an atmospheric-pressure bubbling fluidised bed reactor, which they operated cyclically between the reforming/carbonation conditions and calcination. They reported a H₂ concentration of 98–99 vol. % (dry basis) at 600 °C which was maintained through four reforming-regeneration cycles using a dolomite-derived sorbent and commercial reforming catalyst; although the H₂ yield decreased with cycle number corresponding to the decay in the capture capacity of the dolomite-derived sorbent. The strategies developed for reactivation/preactivating sorbent, discussed above, are also relevant to this advanced application; however the use of sorbent and catalyst mixtures and combined sorbent-catalysts (e.g., Martavaltzi and Lemonidou, In Press) is likely to increase the complexity of reactivation/pre-activation strategies and there remains considerable scope for further developments.

5.3 In situ CO₂ capture using solid fuels

A number of researchers have investigated the possibility of using the integrated reaction scheme for the gasification of solid fuels, e.g., coal and biomass. Lin *et al.* (2004a) developed a process they named the ‘HyPr- RING’, involving the high-pressure steam-gasification of coal in the presence of CaO. They used a continuous pressurised reactor to gasify sub-bituminous coal in the presence of CaO at 650 °C and pressures up to 60 atm (steam partial pressure 30 atm). They observed an

increasing trend in the H₂ concentration corresponding with increasing pressure and reported a maximum concentration of 77 vol. % (dry basis) at 60 atm (Lin *et al.*, 2004b). More recently, Florin and Harris (2008a) examined the potential of coupling steam gasification with in situ CO₂ capture at atmospheric pressure with low-rank fuels, including biomass. The addition of CaO was shown to significantly increase the output of H₂ during the primary pyrolysis of biomass by the water-gas shift reaction; the presence of CaO was also observed to increase the H₂ output by tar cracking and char decomposition, based on combined TGA-MS experiments. A similar concept for the combustion of biomass has been demonstrated at the pilot scale, discussed above, Abanades *et al.* (2009).

5.4 Zero emission coal process

Even more ambitious than the schemes outlined above is the zero emission coal (ZEC) process, which is a gasification concept that was developed at Los Alamos National Laboratory (LANL) and pursued by the Zero Emission Coal Alliance (ZECA) – a North American consortium of private industry and government agency partners. The ZEC process first involves high-pressure gasification of coal in H₂ (hydrogasification) to produce CH₄, via the exothermic methanation reaction according to Eq. 10.



CH₄ is then fed to a high-pressure reformer/carbonator (analogous to the SER process) to produce a H₂-rich product gas. Overall, the reaction scheme results in the production of an additional 2 moles of H₂ for every 2 moles required for methanation (i.e., according to Eq. 1, 2 & 9). In the proposed process, some of the H₂ product gas is recycled to the gasifier and the remainder is used to produce electricity in a high-temperature solid oxide fuel cell (SOFC);

waste heat from the SOFC is used in a calciner to regenerate the CaO-based sorbent and produce a pure stream of CO₂ for storage by mineral carbonation (Ziock, 2003).

This novel concept is no longer being pursued by ZECA, in fact their website is now defunct; although, they have published a study of the conceptual design/economics and predicted overall efficiency to be about 70 %, including CO₂ capture and compression (Nexant). Fundamental technical elements of this concept require further RD&D, including transferring large quantities of sorbent across a significant pressure drop as well as challenges associated with the integration of the different process elements, considering reaction kinetics and the production of electricity using hydrogen fuel cells/ gas turbines. However, several critical aspects have been investigated at the laboratory scale, e.g., Jia and Anthony (2003); Gao *et al.* (2008a; 2008b). Gao *et al.* (2008a; 2008b) modified a high-pressure wire-mesh reactor (WMR) to study the hydrogasification step – obtaining data on the effects of temperature, pressure and H₂/steam ratio on the extent of conversion of different coals, tar formation and the reactivity of residual chars. Owing to the influence of short-lived H radicals on the overall conversion of the coal, the WMR obtained more representative results for a large-scale gasifier than would e.g. a thermogravimetric analyser (Kandiyoti *et al.*, 2006). Lignites were shown to be the most reactive with conversions > 75 % in pure H₂ and up to 86 % with the injection of 50/50 (vol.) H₂ and steam mixtures (950 °C, about 70 atm). On the basis of their results, which showed temperatures of 900–1000 °C and long residence times (> 10 s) to be critical for acceptable fuel conversions, they concluded that fluidised bed technology would be best suited for the hydrogasification step. Work along these lines is currently being carried out at Imperial College in collaboration with Cambridge University.

5.5 ENDEX configuration for Ca-looping

The ENDEX configuration for Ca-looping proposes a ‘reversed’ application of the conventional Ca-looping technology in order to eliminate some of the key technological

challenges, including decay in CO₂ capture capacity through multiple cycles and process heat integration—fundamental to the cost efficiency of post-combustion capture and hydrogen production (Ball and Sceats, In Press). The configuration is reversed in the sense that the calcination is carried out at a lower temperature (650–760 °C) than the carbonation (760–850 °C), thus heat is transferred from the exothermic carbonator to the endothermic calciner. This configuration is made thermodynamically feasible by elevating the carbonator pressure and running the calciner at sub-atmospheric pressure (i.e. < 0.03 atm CO₂ partial pressure at 700 °C – see Fig. 1). Another unique characteristic of the proposed process is operation with short solid residence times in the carbonator to drastically limit the extent of conversion to about 2–4 % (Sceats, 2009). In the conventional process, as discussed above, maintaining a high extent of carbonation to minimise heat input to the calciner is a critical challenge. However, with the Endex configuration, it is asserted that the reduced temperature in the calciner and the limited carbonation extent will eliminate the drop-off in CO₂ capture capacity with cycling. There is limited experimental data available in the literature to demonstrate these benefits: Grasa *et al.* (2009) reported a minor decrease in the rate of decay in CO₂ capture capacity for one limestone sorbent partially carbonated (1 min vs. 5 min) through 60 conventional Ca-looping cycles, using a TGA. The implications of rapid cycling of material on the mechanical stability of the sorbent particles must also be examined. Moreover, a number of engineering concerns remain regarding the novel process configuration which requires transport of sorbent particles through a pressure gradient, and the disadvantage of producing a sub-atmospheric stream of CO₂ that must be pressurised before transport and storage. The requirement to compress the flue gas imposes an additional energy penalty. Some of these issues may be resolved with further experimental work and experience with the planned 10 MWth demonstrator in Australia (Sceats, 2009).

6. Conclusions

The Ca-looping cycle has multiple potential benefits as a CO₂ capture process for both post- and pre- combustion applications. It requires careful integration with the steam cycle of a power station if it is to be incorporated as a post-combustion CO₂ capture process inexpensively. The degradation of the sorbent's ability to take up CO₂ is manageable, though further work into both maintaining the overall reactivity of the sorbent and regenerating that reactivity, for multiple cycles of reaction, is ongoing. Such work will lead to further improvements in the efficiency of the CO₂ capture process. However, even without improvements in the reactivity, the overall cost of CO₂ capture is low (~ 19 USD / tonne avoided), owing to the cheap sorbent (essentially, crushed rock) and the low energy penalty (~ 6–8 %, including compression). These benefits are even more pronounced when the Ca-looping process is integrated into cement production, where the use of the spent sorbent can result in a reduction of the energy required in the cement works on the order of 50 %.

Multiple demonstrations are currently being planned or have been conducted. Current projects look set to test the process at the scale of 1–2 MWth within 3 years. Soon after that, projects on the order of 10 MWth are planned, with rapid expansion to full scale thereafter.

In the future, the role of CaO looping for H₂ production, via the water-gas shift reaction may become more important, with savings both in terms of overall energy usage and CO₂ emitted to the atmosphere. The versatility of the cycle, coupled with the cheapness of the raw materials used, point to widespread usage in the future.

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