Process Analysis of CO_2 Capture from Flue Gas Using Carbonation/Calcination Cycles

Li Zhen-shan and Cai Ning-sheng
Key Lab for Thermal Science and Power Engineering of MOE, Department of Thermal Engineering,
Tsinghua University, Beijing 100084, China

Eric Croiset
Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ont., Canada N2L 3G1

DOI 10.1002/aic.11486

Process analysis of CO_2 capture from flue gas using Ca-based carbonation/calcination cycles is presented here. A carbonation/calcination system is composed essentially of two reactors (an absorber and a regenerator) with Ca-based sorbent circulating between the two reactors (assumed here as fluidized beds). CO_2 is, therefore, transferred from the absorber to the regenerator. Because of the endothermicity of the calcination reaction, a certain amount of coal is burned with pure oxygen in the regenerator. Detailed mass balance, heat balance and cost of electricity and CO_2 mitigation for the carbonation/calcination cycles with three Ca-based sorbents in dual fluidized beds were calculated and analyzed to study the effect of the Ca-based sorbent activity decay on CO_2 capture from flue gas. The three sorbents considered were: limestone, dolomite and $CaO/Ca_{12}Al_{14}O_{33}$ (75/25 wt %) sorbent. All results, including the amount of coal and oxygen required, are presented with respect to the difference in calcium oxide conversion between the absorber and the regenerator, which is an important design parameter. Finally, costs of electricity and CO_2 mitigation costs using carbonation/calcination cycles for the three sorbents were estimated. The results indicate that the economics of the carbonation/calcination process compare favorably with competing technologies for capturing CO_2. © 2008 American Institute of Chemical Engineers *AIChE J,* 54: 1912–1925, 2008

Introduction

It is now well accepted that the release of CO_2 from fossil fuel combustion contributes to the enhanced greenhouse effect with possible disastrous effect on climate change. In recent years, many countries, including China, are paying more and more attention to the effects of increased CO_2 emissions. The emissions of CO_2 into the atmosphere have been reported to account for half of the greenhouse effect that causes global warming.[1] An approach to reduce CO_2 release from large point sources is CO_2 (or carbon) capture and storage (CCS). The estimated costs for CO_2 transportation (US\$1–3 per ton per 100 km),[2] and sequestration (US\$4–8 per ton of CO_2)[3] are small compared to the cost of CO_2capture, estimated at US\$35–55 per ton of CO_2 captured.[4] Therefore, reducing the cost of CO_2 capture is absolutely necessary to make CCS more economically attractive. The high-cost of CO_2 capture stems from the considerable amount of energy required in the separation process.[4]

There are three main options for capturing CO_2 from flue gases: (1) post combustion capture (e.g., chemical absorption where CO_2 is separated essentially from nitrogen in the flue gas stream), (2) precombustion capture (typically, coal gasification with CO_2 capture followed by combusting the hydro-

---

Correspondence concerning this article should be addressed to C. Ning-sheng at cains@tsinghua.edu.cn.

gen produced in combined cycles), and (3) oxyfuel combustion where nitrogen is removed prior to combustion. This article focuses on post-combustion capture, and presents an alternative to the state-of-the-art amine scrubbing process. In the proposed process, CO_2 is captured via carbonation/calcination reactions (CCR) with CaO.

The carbonation reaction of lime (CaO) with CO_2 has been proposed by many researchers to separate CO_2 from gaseous mixtures.[5–16] This separation principle was first patented by DuMotay and Marechal to aid the gasification of carbon by steam.[5] The carbonation reaction was also applied to coal gasification gases in the acceptor gasification process.[6] Recently, a number of power plant concepts[7–9] with near zero emissions were proposed to produce H_2, and/or electricity from fossil fuels by integrating CO_2 separation, based on the carbonation reaction of CaO. In the sorption enhanced methane steam reforming process, the addition of a Ca-based sorbent to the reforming reactor can remove selectively CO_2 from the products, thereby shifting the equilibrium of reforming reactions, and resulting in process simplification, improved energy efficiency, and increased reactant conversion and product yield.[10–13] Carbonation/calcination cycles were also proposed to capture CO_2 from flue gas in combustion systems.[14–16] In such processes CaO is carbonated to $CaCO_3$ at a relatively lower-temperature in the flue gas (about 873–973 K), removed from the absorber, and then decomposed back to CaO and CO_2 in a regenerator at higher-temperatures (>1,173 K). The regenerated lime then returns to the absorber, and the heat required for the decomposition of $CaCO_3$ in the regenerator is supplied by burning coal, biomass or petroleum coke in a gas atmosphere that includes high concentrations of O_2, CO_2, or steam.

In the CCR process, the CO_2 sorbents are used repeatedly, and the cyclic reaction/regeneration characteristics of these sorbents are very important for practical application. All naturally occurring Ca containing sorbents, such as limestone and dolomite, suitable for CO_2 separation process undergo decay in their capacity of capturing CO_2 during multiple carbonation/calcination reaction cycles. Alternative sorbents have been developed with better stability over many cycles, although they too deactivate over time. The purpose of this article is to assess the potential effect of Ca-based sorbent activity decay on CO_2 capture from flue gas using carbonation and calcination cycles in fluidized beds. A detailed design and analysis of the process is presented. The relationship between suitable operating conditions in the CCR process and multiple cycles characteristics for different Ca-based sorbents are discussed. Finally, an economic evaluation of the process for the three sorbents is also given.

Introduction to carbonation/calcination cycles

The process is shown in Figure 1. This process consists of dual fluidized-bed reactors, one is the absorber, and the other the regenerator, both operating at atmospheric pressure and being connected with solid transportation lines. The carbonation/calcination cycles may be summarized as follows: the flue gas from the conventional combustion system is introduced into the absorber, whose temperature is maintained between 873 and 973 K. This temperature range is best for the carbonation reaction of CaO with CO_2 (Eq. 1) to occur effectively.[12] Sulfur dioxide capture is also expected to be very effective since the higher calcium requirements for CO_2 removal will result in an equivalent Ca/S molar ratio on the order of 20–30.[16] Fluidized-bed combustors are intrinsically low-producers of NO, and are amenable to NH_3 injection if very low-emissions of NO are desired.[16] Since the carbonation is an exothermic reaction, steam can be produced and utilized to generate electricity by immersing heat-transfer surface in the absorber.[14] $CaCO_3$ so produced is transported to the regenerator where the temperature is maintained at about 1,223 K. The decomposition of $CaCO_3$ is endothermic, and the required heat is supplied by burning coal, biomass or petroleum coke with pure oxygen diluted with CO_2 and steam. This allows for the decomposition reaction of $CaCO_3$ (Eq. 2) to take place at atmospheric pressure in almost pure CO_2, thus, generating a nearly pure CO_2 stream. In a cyclic mode, the sorbent alternates between carbonation and calcination. Therefore, the sorbent itself is virtually not consumed, and its role in the process is to act as a carbon carrier. However, both the fuel and O_2 are consumed due to heat-and high-temperature requirement for $CaCO_3$ decomposition

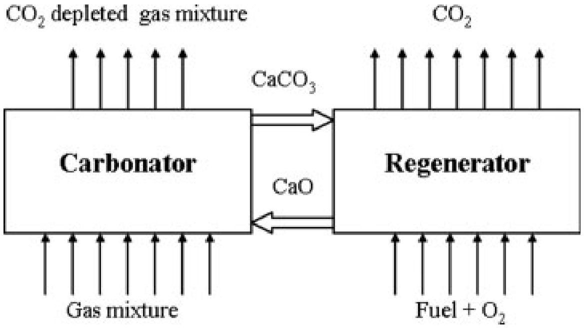

Figure 1. Carbonation/calcination cycles process for a Ca-based sorbent.

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \text{(Eq. 1)}$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Eq. 2)}$$

In the CCR process, CaO has a high CO_2 capture capacity, 393 g of CO_2/kg-CaO, assuming a 50% conversion of CaO over multiple cycles, resulting into lower sorbent requirements, smaller reactor sizes, and lower pressure drop across the reactor.[17] It is also clear that there are plentiful sources of cheap, widely available sorbent. Because of high-absorption capacity, CaO-based absorbers are more compact than other sorbents-based processes, and the cost of CO_2 capture could eventually be lower. The oxygen required in the regenerator is only 1/3 that required for an oxyfuel process, reducing air separation unit (ASU) capital and operating costs accordingly.[16,18]

Process Analysis of CO_2 Capture using Carbonation/Calcination Cycles

Process description and parameters definition

A more detailed description of the process, with the notation given in Figure 2. The total molar flow rate of inlet flue

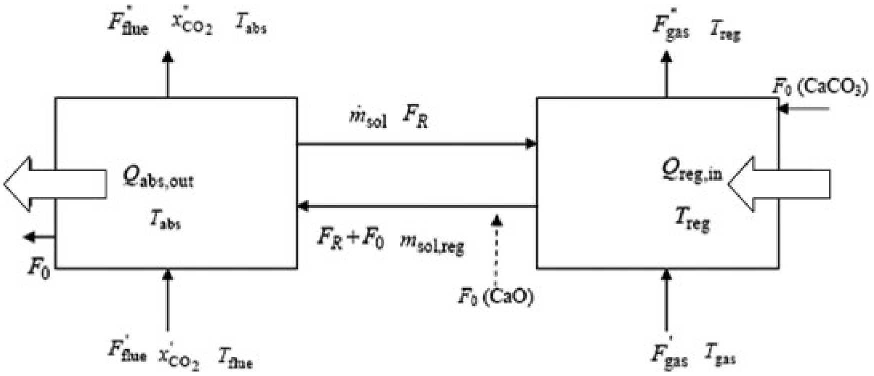

Figure 2. Process variables definition for the carbonation-calcination cycle to capture CO_2.

gas is F'_{flue} (kmol/s). This total flow rate is the sum of the flow rates of each flue gas component F'_i, where i = CO_2, O_2, N_2 and H_2O. The mole fraction of CO_2 in inlet flue gas is x'_{CO_2}, and the inlet flue gas temperature is T_{flue} (K). After the flue gas enters the absorber, the CO_2 reacts with the sorbent at a temperature T_{abs} (K), and the product is $CaCO_3$. The molar flow rate of the flue gas leaving the absorber is F''_{flue} (kmol/s), which is the sum of each partial flow rates F''_i, where i = CO_2, O_2, N_2 and H_2O. The fraction of CO_2 in outlet flue gas decreases to x''_{CO_2}. CaO is used repeatedly in the process of carbonation and calcination cycles; $CaCO_3$ formed during carbonation is then heated and calcined to regenerate CaO at higher-temperature. The gas product leaving the calcination process is mostly CO_2. Unfortunately, sorbent activity declines with increasing the number of cycles, and fresh sorbent must then be continuously injected into the system. The molar flow rate of fresh sorbent is F_0 (kmol/s). If Ca in the fresh sorbent is in the form of $CaCO_3$, the fresh sorbent is injected into the regenerator, whereas if it is in the form of CaO, it is injected into the absorber. At the same time, some of the spent sorbent is discharged. In order to prevent accumulation of materials in the system, the molar flow rate of spent sorbent to be discharged is also F_0 (kmol/s). F_R (kmol/s) is the sorbent molar flow rates from the absorber to the regenerator, and the corresponding mass flow rate is m_{sol} (kg/s). The mass flow of sorbent returning from the regenerator to the absorber is $m_{sol,reg}$ (kg/s). The temperatures of absorber and regenerator are T_{abs} (K) and T_{reg} (K), respectively. A hot gas with a flow rate F'_{gas} (kmol/s) enters the regenerator at temperature T_{gas} (K). $CaCO_3$ decomposes in the regenerator, and the molar flow rate of the gas exiting the regenerator is F''_{gas} (kmol/s) at temperature T_{reg} (K).

The temperature of the absorber is lower than that of the regenerator, and the solid leaving the regenerator will carry a significant amount of heat. In addition, the carbonation is exothermic, so a quantity of heat $Q_{abs,out}$ (kJ/s) must be removed from the absorber in order to maintain its temperature at T_{abs}. Likewise, the heat required to maintain the temperature of the regenerator at T_{reg} is $Q_{reg,in}$ (kJ/s).

Since the carbonation reaction is exothermic and the absorber must be kept at a lower temperature than that of the regenerator, heat must be removed from the absorber. One way of doing so is to discharge the spent sorbent from the absorber.

The mole flow rates of flue gas from the coal-fired power plant,[14] and the temperature of the absorber and the regenerator are shown in Table 1.

In the aforementioned carbonation/calcination process, the CO_2 conversion is defined as follows

$$X_g = \frac{F'_{CO_2} - F''_{CO_2}}{F'_{CO_2}} \tag{1}$$

The numerator of Eq. 1 represents the amount of absorbed CO_2

$$F_{CO_2} = F'_{CO_2} - F''_{CO_2} \quad \text{(kmol/s)} \tag{2}$$

The mass of absorbed CO_2, is, therefore

$$m_{CO_2} = M_{CO_2} \cdot F_{CO_2} \quad \text{(kg/s)} \tag{3}$$

where M_{CO_2} is the CO_2 molecular weight (kg/kmol).

The conversion of CaO, X, is the actual mass of CO_2 absorbed divided by the mass of CO_2 that would be absorbed if the sorbent was fully carbonated

$$X = \frac{M_{\text{actual}} - M_{\text{f,reg}}}{M_{\text{f,abs}} - M_{\text{f,reg}}} \tag{4}$$

where $M_{\text{f,fabs}}$ is the molar mass of the fully carbonated sorbent, $M_{\text{f,reg}}$ is the molar mass of the fully calcined sorbent, and M_{actual} is the actual molar mass of the sorbent in its

Table 1. Flue Gas composition for Absorber and Inlet and Outlet Temperatures of Absorber and Regenerator

	CO_2 (kmol/s)	O_2 (kmol/s)	N_2 (kmol/s)	H_2O (kmol/s)	Absorber Temperature (K)	Regenerator temperature (K)
Inlet	2.91	0.65	14.73	1.26	423	423
Outlet	0.49	0.65	14.73	1.26	873	1223

partially carbonated state. The solids in the two reactors are assumed to be well stirred, and the conversion of the solids, is, therefore, equal to the conversion of the solid flows leaving these reactors. Since CO_2 is transferred from the absorber to the regenerator, the average conversion is higher in the absorber X_{abs}, than in the regenerator X_{reg}, and the difference in conversion ΔX, is

$$\Delta X = X_{abs} - X_{reg} \tag{5}$$

ΔX is an important parameter, and has an important impact on the carbonation and calcination cycle.

Sorbent activity decay

When the sorbent is recycled between the absorber and regenerator, the CaO average conversion in the absorber is given by[19]

$$X_{abs} = \sum_{N=1}^{N=\infty} \frac{F_0 F_R^{N-1}}{(F_0 + F_R)^N} \cdot X_N \tag{6}$$

Note that Eq. 6 is valid whether the fresh sorbent is fed to the regenerator (case of $CaCO_3$) or to the absorber (case of CaO). All researchers found that the conversion of CaO to $CaCO_3$ in the carbonation step decreases with increasing the number of carbonation/calcination cycles. Therefore, when Eq. 6 is used to calculate the CaO average conversion, the decay characteristic of the sorbent must be known. Based on published experimental data on repeated CaO carbonation/calcination cycles for different conditions, Abanades[19] found that the decay in conversion was only dependent on the number of cycles and gave the following equation to describe CaO reactivity decay

$$X_N = f^{N+1} + b \tag{7}$$

where X_N denotes the conversion of CaO to $CaCO_3$ in the Nth cycle and f and b are constants.

Later, Abanades and Alvarez[20] developed a new formula using two parameters, f_m and f_w,

$$X_N = f_m^N(1 - f_w) + f_w \tag{8}$$

The decay behavior of the absorption capacity has been examined by Wang and Anthony,[21] and they proposed a new simple equation

$$X_N = \frac{1}{1 + kN} \tag{9}$$

This equation was shown to better describe the reported data using only one parameter (k) than Eq. 8, especially for dolomite[22] and $CaO/Ca_{12}Al_{14}O_{33}$ (75/25 wt %)[23–24] (for simple, cement notation CaO/C12A7 be used for $CaO/Ca_{12}Al_{14}O_{33}$ sorbents). However, a disadvantage of Eq. 9 is the difficulty to obtain the limit of an infinite sum when incorporating Eq. 9 into Eq. 6.

In this work, a different equation—Eq. 10—was adopted to describe the activity decay of three types of Ca-based CO_2 sorbents: limestone, dolomite and CaO/C12A7

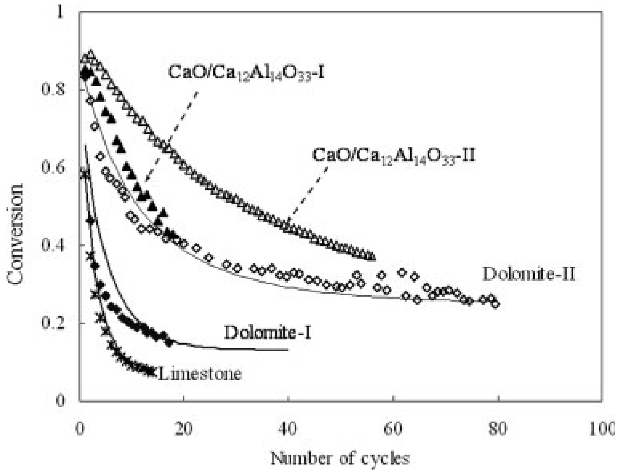

Figure 3. Comparison between experimental and modeling results, Eq. 11 for three Ca-based sorbents.

$$X_N = a_1 f_1^{N+1} + a_2 f_2^{N+1} + b \tag{10}$$

Incorporating Eq. 10 into Eq. 6, and calculating the limit of the infinite sum of the geometric series yields

$$X_{abs} = \frac{a_1 f_1 F_0}{F_0 + F_R(1 - f_1)} + \frac{a_2 f_2 F_0}{F_0 + F_R(1 - f_2)} + b \tag{11}$$

The experimental results of multiple carbonation/calcination cycles for dolomite-II shown in Figure 3 were obtained at calcination temperature 1,173 K, and CO_2 fraction 10 vol %.[22] For CaO/C12A7-II sorbent shown in Figure 3,[24] a pure CO_2 stream was introduced into TGA at both carbonation and calcination steps, this would result into carbonation happening at higher-temperature, such as 1,073 K, when the temperature of TGA was raised to 1,253 K from carbonation temperature. In fact, 873–973 K is best temperature range for the carbonation reaction of CaO with CO_2 to occur effectively, and the calcination temperature for $CaCO_3$ decomposition should be maintained above 1173 K in pure CO_2 atmosphere. Therefore, new experiments were carried out for dolomite and CaO/C12A7 sorbents, and the temperatures and the CO_2 fraction of carbonation and calcination were 923 K, 15% and 1,223 K, 100%, respectively, the final experimental results were shown in Figure 3 (dolomite-I and CaO/C12A7-I), and used for subsequent analysis. The values of a_1, a_2, b, f_1 and f_2 are specific to the sorbents, and are shown in Table 2. Comparison between experimental and modeling results is shown in Figure 3.

Mass Balances

Case of $CaCO_3$ fresh sorbent (limestone and dolomite)

Solids material balance for the absorber yields

$$(F_R + F_0)[M_{CaCO_3} X_{abs} + M_{CaO}(1 - X_{abs})] \\ = (F_R + F_0)[M_{CaCO_3} X_{reg} + M_{CaO}(1 - X_{reg})] + F_{CO_2} M_{CO_2} \tag{12}$$

Table 2. Parameters for Eq. 11 for Three Sorbents.*

	a_1	a_2	f_1	f_2	b	x_{CAO}[a]	Reference[b]
Limestone	1.0	0.0	0.712	0.0	0.074	1.0	20
Dolomite-I	0.35	0.43	0.78	0.85	0.13	0.58	this work
$CaO/Ca_{12}Al_{14}O_{33}$-I	0.35	0.33	0.88	0.95	0.25	0.75	this work

*Calcination performed in pure CO_2 for all sorbents.

[a] x_{CaO} is the mass fraction of CaO upon complete calcinations.

[b] Reference for experimental data.

or

$$(F_R + F_0)\Delta X \underbrace{(M_{CaCO_3} - M_{CaO})}_{=M_{CO_2}} = F_{CO_2}M_{CO_2} \tag{13}$$

So, finally

$$(F_R + F_0)\Delta X = F_{CO_2} \tag{14}$$

The total mass flow rate of sorbent from absorber to regenerator (m_{sol}), and from regenerator to absorber ($m_{sol,reg}$) can then be determined as follows

$$m_{sol} = F_R M_{abs} + F_R M_{CaO}(1 - x_{CaO})/x_{CaO} \tag{15}$$

$$m_{sol,reg} = (F_R + F_0)M_{reg} + (F_R + F_0)M_{CaO}(1 - x_{CaO})/x_{CaO} \tag{16}$$

with

$$M_{abs} = M_{CaCO_3}X_{abs} + M_{CaO}(1 - X_{abs}) \tag{17}$$

$$M_{reg} = M_{CaCO_3}X_{reg} + M_{CaO}(1 - X_{reg}) \tag{18}$$

Case of CaO *fresh sorbent* (CaO/C12A7)

In a similar manner as for $CaCO_3$, the solid material balance for the absorber leads to the following equation

$$F_R\Delta X + F_0 X_{abs} = F_{CO_2} \tag{19}$$

m_{sol} remains the same as in Eq. 16, whereas $m_{sol,reg}$ becomes

$$m_{sol,reg} = F_R M_{reg} + F_0 M_{CaO} + (F_R + F_0)M_{CaO}(1 - x_{CaO})/x_{CaO} \tag{20}$$

One will notice that if the sorbent is completely calcined in the regenerator (i.e., $X_{reg} = 0$), then Eqs. 14 and 19 are equal, as well as Eqs. 16 and 20. In that case, there would be no need to distinguish the case of $CaCO_3$ as fresh sorbent from the case of CaO as fresh sorbent.

In the process of CO_2 capture using carbonation and calcination cycles, ΔX is an important parameter. Recall that , ΔX is the difference between the conversion in the absorber and the conversion in the regenerator (Eq. 5). Injection of fresh sorbent is necessary to compensate for the decrease in sorbent activity over several cycles. For a given sorbent and a given X_{abs}, F_0 and F_R are determined by solving simultaneously Eqs. 11, and either 14 or 19, depending on the nature of the fresh sorbent. Figure 4 and 5 show, in the case of limestone, how F_0 and F_R vary as a function of , ΔX and CaO conversion (X_{abs}). When X_{abs} is fixed, Figures 4 and 5 show that F_0 and F_R decrease with increasing , ΔX. At low-values of X_{abs} a large amount of sorbent is required to absorb a fixed amount of CO_2, thus, the large values of $F_{R,}$ as shown in Figure 5. At the same time, since the CaO conversion is low, the activity loss of Ca-based sorbent has negligible effect on the CO_2 capture process; only a small amount of fresh sorbent F_0, is needed, as shown in Figure 4. As X_{abs} increases, a smaller amount of recycled sorbent F_R, is required (see Figure 5), but because of higher CaO conversion the effect of sorbent activity loss becomes more and

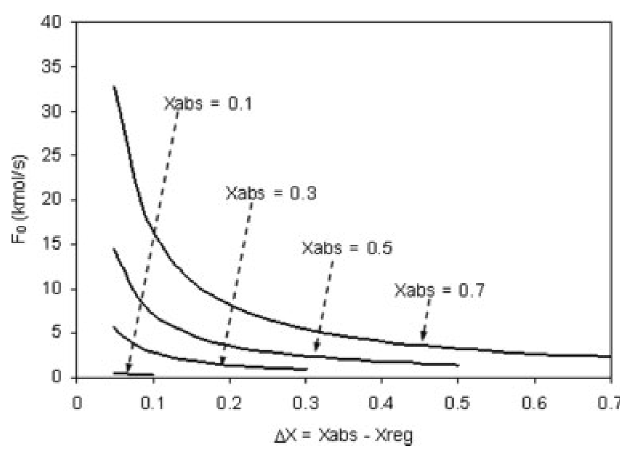

Figure 4. Change of parameters F_0 with ΔX and X_{abs} (case of limestone sorbent).

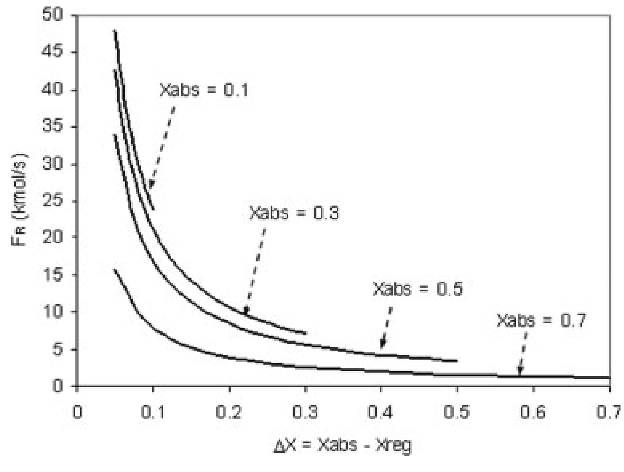

Figure 5. Change of parameters F_R with ΔX and X_{abs} (case of limestone sorbent).

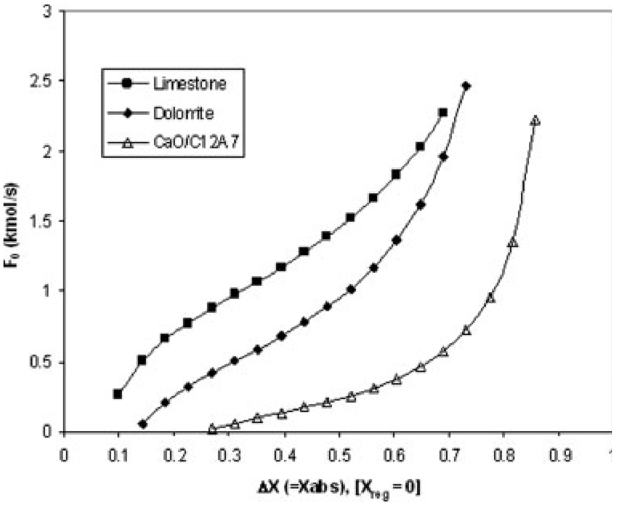

Figure 6. Changes in F_0 with ΔX for limestone, dolomite, and CaO/C12A7 sorbents.

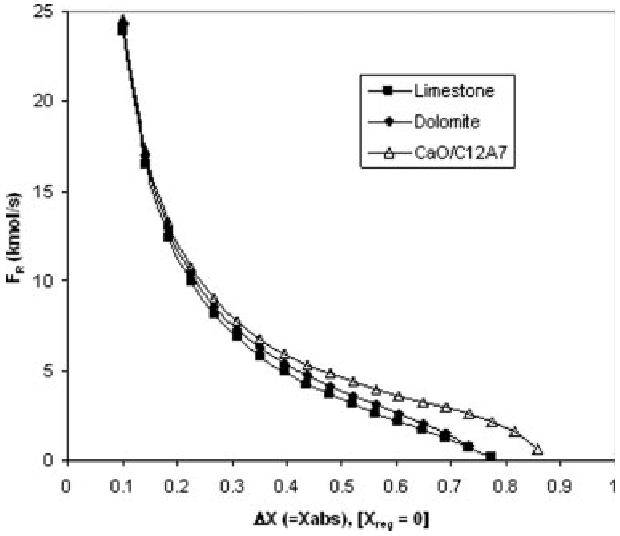

Figure 7. Changes in F_R with ΔX for limestone, dolomite, and CaO/C12A7 sorbents.

more important, and, therefore, a larger amount of fresh sorbent is needed (see Figure 4).

From Figure 4 and 5, it can be seen that F_0 and F_R increase rapidly with decreasing ΔX. That is, X_{reg} has also an important effect on the values of F_0 and F_R. When is equal to zero, ΔX is equal to X_{abs}, in this case, F_0 and F_R approach their minimum values. It should be noted that in practice, because calcination is much faster than carbonation, it is very likely that X_{reg} will be small. In the following, it is assumed that $CaCO_3$ decomposes completely in the regenerator, therefore, X_{reg} is equal to zero and $\Delta X = X_{abs}$. In Figures 4 and 5, this corresponds to the points furthest to the right on each curve.

Figure 6 shows the changes in F_0 with ΔX for three sorbents: limestone, dolomite, and CaO/C12A7 when $X_{reg} = 0$. It can be seen from Figure 6 that F_0 can vary significantly from one sorbent to the other, because the activity loss for each sorbent is different. Indeed, the amount of fresh sorbent required is closely related to the activity loss of the sorbent. The faster the sorbent loses its activity, the higher the value of F_0. Figure 6 illustrates the fact that limestones deactivates at the fastest rate, followed by dolomite, and finally CaO/C12A7. The behaviors of limestone and dolomite are, nonetheless, relatively close, except at very high-value of ΔX (or X_{abs}) This is related to Figure 3 where limestone and dolomite showed similar conversion vs. number of cycles. Another important observation from Figure 6 is that there is a practical maximum limit in terms of CaO conversion, which is sorbent dependent. These maximum limits of ΔX are around 0.7 for both limestone and dolomite, and 0.9 for CaO/C12A7. Compared to other sorbents, the activity of limestone declines rapidly, and, thus, a large amount of fresh sorbent has to be added into the reactor.

Figure 7 shows the evolution of sorbent circulation rate (F_R) with ΔX for limestone, dolomite and CaO/C12A7 sorbents. When increasing ΔX, F_R decreases for the three sorbents. For high values of ΔX (i.e., high X_{abs} here), a large quantity of fresh sorbent must be added into the absorber in order to compensate for sorbent activity loss (recall Figure 4). In this case, F_R is quite small, approaching zero, as shown in Figure 7. Again, because the activity loss versus number of cycles for dolomite and limestone are similar, so is F_R for these two sorbents, as seen in Figure 7.

The mass flow rates, m_{sol} and $m_{sol,reg}$ from the absorber to regenerator, and from the regenerator to absorber, are determined not only by F_R and F_0, but also by x_{CaO}, the fraction of CaO in the sorbent. m_{sol} and $m_{sol,reg}$ are important for reactor design and system operation. It can be seen from Figures 8 and 9, that m_{sol} and $m_{sol,reg}$ decrease with increasing ΔX for all sorbents. This is because the sorbent activity loss becomes more and more important with increasing ΔX, and, thus, the amount of fresh sorbent increase, resulting in a smaller amount of recycled sorbent. The sequence for m_{sol} and $m_{sol,reg}$ is: dolomite > CaO/C12A7 > limestone, as shown in Figures 8 and 9. Dolomite corresponds to the highest recirculation mass flow rate, because it contains only 58 wt % CaO, the balance being mainly MgO. MgO is inert and contribute to the large total mass of recirculated materials.

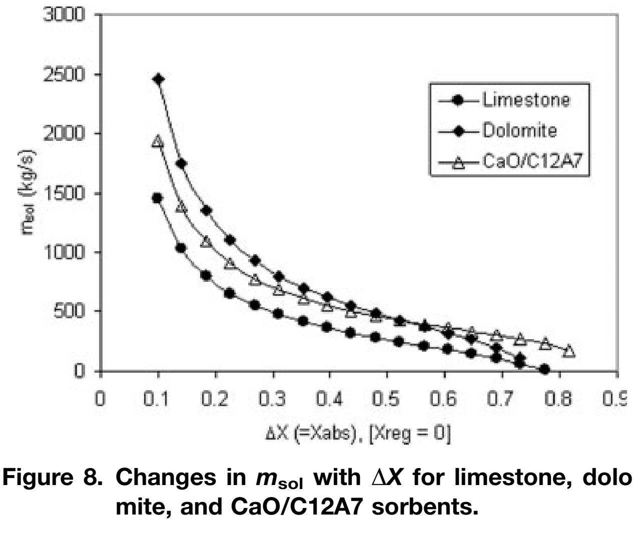

Figure 8. Changes in m_{sol} with ΔX for limestone, dolomite, and CaO/C12A7 sorbents.

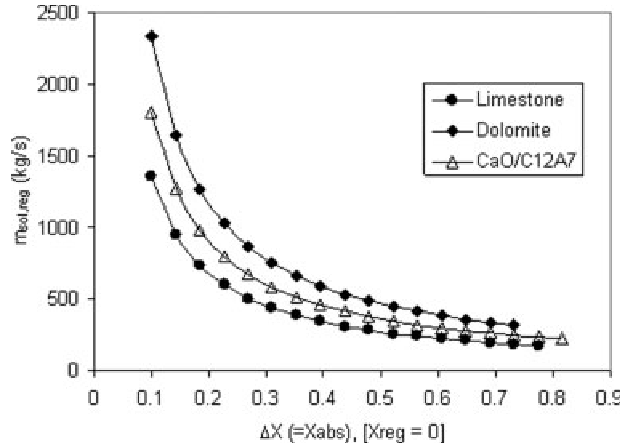

Figure 9. Changes in $m_{sol,reg}$ with ΔX for limestone, dolomite, and CaO/C12A7 sorbents.

Similarly, CaO/C12A7 contains 25 wt % of $Ca_{12}Al_{14}O_{33}$, and, thus, the total mass is higher than that of limestone (which is mostly $CaCO_3$).

Heat Balances

In the absorber, the heat carried by the solid sorbent from the regenerator and produced by the carbonation reaction must be removed in order to keep a suitable absorber operating temperature.

Case of $CaCO_3$ fresh sorbent (limestone and dolomite)

The heat removed is $Q_{abs,out}$ (kJ/s), and the heat balance equation for the absorber is

$$\begin{aligned} Q_{abs,out} &= (-\Delta H)_{abs,carb}\cdot F_{CO_2} + (F_R+F_0) \\ &\cdot (C_{p,reg}\cdot T_{reg} - C_{p,abs}\cdot T_{abs}) + (F'_{flue}\cdot C'_{p,flue}\cdot T_{flue} - F''_{flue}\cdot C''_{p,flue}\cdot T_{abs}) \\ &+ \frac{(F_R+F_0)M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,reg}\cdot T_{reg} - C_{p,inert,abs}\cdot T_{abs}) \end{aligned} \tag{21}$$

The heat balance for the regenerator is

$$Q_{reg,in} = A_{reg} + (F''_{gas}\cdot C''_{p,gas}\cdot T_{reg} - F'_{gas}\cdot C'_{p,gas}\cdot T_{gas}) \tag{22}$$

$$\begin{aligned} A_{reg} &= F_R\cdot(C_{p,reg}\cdot T_{reg} - C_{p,abs}\cdot T_{abs}) \\ &\quad + F_0\cdot(C_{p,reg}\cdot T_{reg} - C_{p,0}\cdot T_0) \\ &+ \frac{F_R M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,reg}\cdot T_{reg} - C_{p,inert,abs}\cdot T_{abs}) \\ &\quad + \frac{F_0 M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,reg}\cdot T_{reg} - C_{p,inert,0}\cdot T_0) \\ &+ \left[\frac{F_0 M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}} + F_R\Delta X + F_0(1-X_{reg})\right](-\Delta H)_{reg,calc} \end{aligned} \tag{23}$$

with

$$C_{p,abs} = C_{p,CaCO_3}X_{abs} + C_{p,CaO}(1-X_{abs}) \tag{24}$$

$$C_{p,reg} = C_{p,CaCO_3}X_{reg} + C_{p,CaO}(1-X_{reg}) \tag{25}$$

The amount of CO_2 released in the regenerator is

$$\begin{aligned} F_{CO_2,reg} &= F_R\Delta X + F_0(1-X_{reg}) + \frac{F_0 M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}} \\ &\quad + \frac{C_{ar}}{100\cdot M_C}\cdot m_{coal} \end{aligned} \tag{26}$$

where C_{ar} is the mass fraction of carbon in the coal (as received).

Case of CaO fresh sorbent (CaO/C12A7)

The heat balance equation for the absorber is

$$\begin{aligned} Q_{abs,out} &= (-\Delta H)_{abs,carb}\cdot F_{CO_2} + F_R\cdot(C_{p,reg}\cdot T_{reg} - C_{p,abs}\cdot T_{abs}) \\ &\quad + F_0\cdot(C_{p,0}\cdot T_0 - C_{p,abs}\cdot T_{abs}) \\ &\quad + (F'_{flue}\cdot C'_{p,flue}\cdot T_{flue} - F''_{flue}\cdot C''_{p,flue}\cdot T_{abs}) \\ &+ \frac{F_R M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,reg}\cdot T_{reg} - C_{p,inert,abs}\cdot T_{abs}) \\ &+ \frac{F_0 M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,0}\cdot T_0 - C_{p,inert,abs}\cdot T_{abs}) \end{aligned} \tag{27}$$

The heat balance for the regenerator is

$$Q_{reg,in} = A_{reg} + (F''_{gas}\cdot C''_{p,gas}\cdot T_{reg} - F'_{gas}\cdot C'_{p,gas}\cdot T_{gas}) \tag{28}$$

$$\begin{aligned} A_{reg} &= F_R\cdot(C_{p,reg}\cdot T_{reg} - C_{p,abs}\cdot T_{abs}) \\ &+ \frac{F_R M_{CaO}(1-x_{CaO})}{x_{CaO}M_{inert}}(C_{p,inert,reg}\cdot T_{reg} - C_{p,inert,abs}\cdot T_{abs}) \\ &\quad + F_R\Delta X\cdot(-\Delta H)_{reg,calc} \end{aligned} \tag{29}$$

The amount of CO_2 released in the regenerator is

$$F_{CO_2,reg} = F_R\Delta X + \frac{C_{ar}}{100\cdot M_C}\cdot m_{coal} \tag{30}$$

The required amount of coal for sorbent regeneration is

$$m_{coal} = \frac{Q_{reg,in}}{Q_{heatvalue}}\,(\mathrm{kg/s}) \tag{31}$$

where $Q_{heatvalue}$ is the high-heating value of coal (MJ/kg-daf).

The corresponding required amount of O_2 for sorbent regeneration is

$$\begin{aligned} F_{O_2} &= \frac{(\frac{8}{3}\cdot(C_{ar}+0.375\cdot S_{ar}) + 8\cdot H_{ar} - O_{ar})}{100\cdot M_{O_2}}\cdot m_{coal}\cdot\alpha_{O_2} \\ &= \beta m_{coal}\alpha_{O_2}\quad(\mathrm{kmol/s}) \end{aligned} \tag{32}$$

where α_{o_2} is the excess oxygen coefficient.

The coal composition used in this study is shown in Table 3, and the excess oxygen coefficient α_{o_2}, was chosen as 1.06. When calculating heat balance, the heat capacity of the solid sorbent is required to calculate the heat carried by the solid material. The values of C_p's for all solids and gases at different temperature were obtained from.[25]

Table 3. Analysis of Bituminous Coal employed for this Design (wt %)[14]

C	H	O	Moisture	Ash	HHV(MJ/kg-daf)	α_{O_2}
69.2	4.0	9.3	9.8	17.5	33.2	1.06

Maintaining the absorber and regenerator temperatures at their desired values is very important. From thermodynamic calculations, a CO_2 partial pressure of nearly 101325 Pa can be achieved for Eq. 1 for a temperature of 1,173 K. However, to ensure complete calcination of $CaCO_3$ the regenerator should be operated at a slightly higher-temperature. We then propose a design temperature of the regenerator of 1,223 K. From an equilibrium view point, for achieving CO_2 capture efficiencies higher than 80% for typical coal boilers, the carbonation temperature should be in the range of 873–973 K, therefore, the temperature difference between the absorber and regenerator is about 350 K. Because hot solids from the regenerator enter the absorber, and because the reaction of CaO with CO_2 is exothermic, heat must be removed from the absorber in order to maintain the carbonation temperature of ~873 K. The required amount of heat to be removed from the absorber is $Q_{\mathrm{abs,out}}$ (kJ/s). At the same time, heat is required for the regenerator to heat up the sorbent, and to supply heat for the endothermic $CaCO_3$ decomposition reaction. The amount of flue gas is fixed and then, for a given CO_2 removal efficiency, the amounts of heat to be released for carbonation and required for calcination depend on the solid circulation rate between the absorber and regenerator, which in turn, as seen in the mass balance section, depends on ΔX. Figure 10 gives the change of $Q_{\mathrm{abs,out}}$ with ΔX for three sorbents. This figure shows that the heat to be evacuated from the absorber decreases when increasing ΔX. This is related to the decrease in solid circulation rate at higher ΔX (see Figures 7–9). When the solid circulation rate decreases, the heat carried by hot solid from the regenerator reduces, resulting in a decrease of $Q_{\mathrm{abs,out.}}$

From Figure 10, it is also seen that for a given ΔX, the sequence for increasing $Q_{\mathrm{abs,out}}$ is: dolomite > CaO/C12A7 > limestone. The MgO and C12A7 contained in dolomite, and CaO/C12A7 sorbents do not react with CO_2, and can be considered as inert that act as heat sinks. Although it is beneficial for reducing $Q_{\mathrm{abs,out}}$, there are some disadvantages for using sorbents containing a high-portion of inert materials. On the one hand, a higher mass of sorbent is needed to capture a certain amount of CO_2 as the active CaO fraction is lower. On the other hand, more energy is required for the calcination process to heat up the larger fraction of inert material. In Figure 10, $Q_{\mathrm{abs,out}}$ is the lowest for limestone because its carbonation performance is the lowest, and because it corresponds to the lowest solid circulation flow rate (see Figures 7–9). Note that in the case of CaO/C12A7, $Q_{\mathrm{abs,out}}$ is lower than dolomite, because fresh CaO/C12A7 is injected directly into the absorber, which contributes to remove some heat from the absorber.

Figure 11 gives the change of $Q_{\mathrm{reg,in}}$ with ΔX for three sorbents. When increasing ΔX, $Q_{\mathrm{reg,in}}$ for limestone and dolomite first decreases and then increases, whereas for CaO/C12A7 $Q_{\mathrm{reg,in}}$ continuously decreases with ΔX. We have seen that the solid circulation rate decreases when increasing ΔX (see Figure 7–9). Therefore, less heat is carried out by the hot solid leaving the regenerator, resulting in a decrease in $Q_{\mathrm{reg,in}}$. This effect of ΔX on $Q_{\mathrm{reg,in}}$ is counterbalanced by a simultaneous increase in fresh sorbent input, F_0, (see Figure 6) fed directly into the regenerator in the case of limestone and dolomite. As F_0 increases, more heat is required to heat up the fresh sorbent. For limestone and dolomite, the resulting $Q_{\mathrm{reg,in}}$ depends, thus, on F_R and F_0, whose change with ΔX are in the opposite directions, hence, the characteristic curves for limestone and dolomite in Figure 11. In the case of CaO/C12A7, fresh sorbent is injected directly into the absorber and not in the regenerator. There is, therefore, no effect of F_0 on $Q_{\mathrm{reg,in}}$ for CaO/C12A7, and only F_R affects $Q_{\mathrm{reg,in}}$. Thus, $Q_{\mathrm{reg,in}}$ continuously decreases as ΔX increases, as shown in Figure 11 for CaO/C12A7.

The amounts of coal and pure oxygen required are determined directly by the amount of required heat for the regenerator (see Eqs. 31 and 32). It is clear from Eqs. 31 and 32 that both m_{coal} and F_{O_2} are linear functions of $Q_{\mathrm{reg,in}}$. Thus, as seen in Figure 12, the profiles of m_{coal} and F_{O_2} vs. ΔX are the same as that of $Q_{\mathrm{reg,in}}$ in Figure 11.

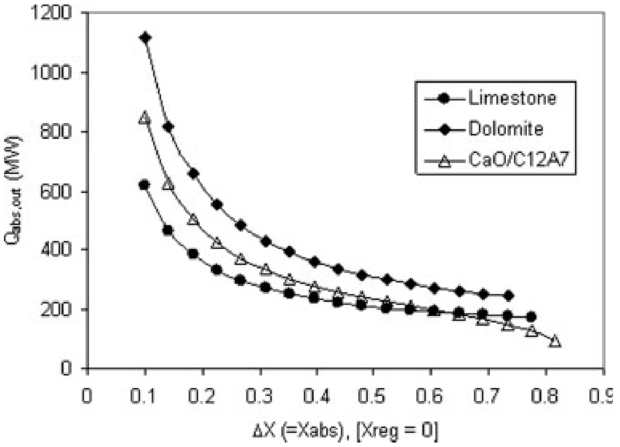

Figure 10. Change of $Q_{\mathrm{abs,out}}$ with ΔX for three sorbents.

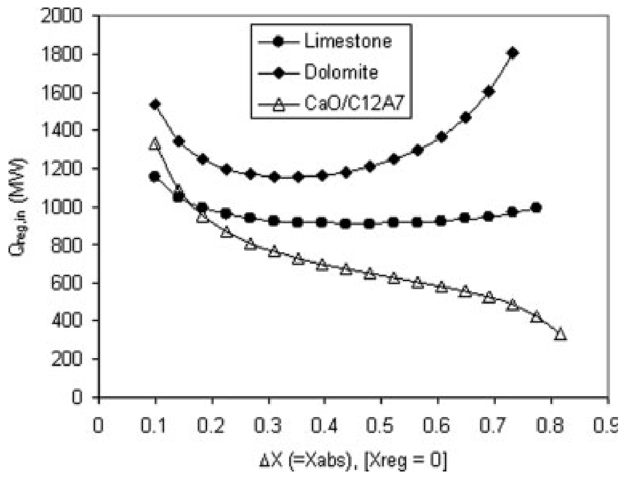

Figure 11. Change of heat required for the regenerator with ΔX for three sorbents.

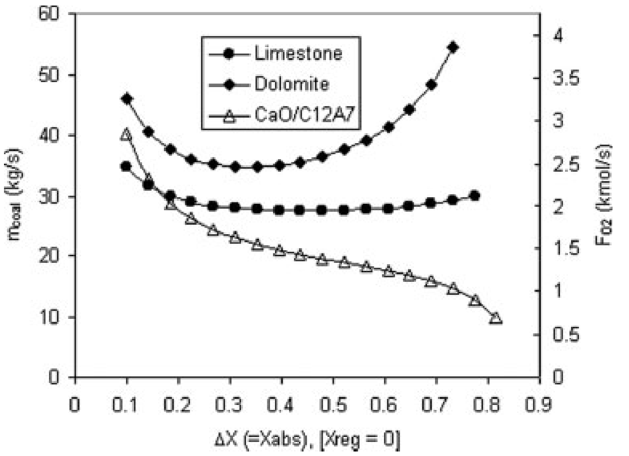

Figure 12. Variation of the amount of required coal and pure oxygen for the regenerator as a function of Δ*X* for three sorbents.

Figure 12 suggest that to minimize the amount of coal and pure oxygen to be consumed, one should operate at $\Delta X \approx 0.35$ for limestone and dolomite, and as high as possible ΔX for CaO/C12A7. Note, however, that for limestone m_{coal} and F_{o_2} do not vary much for ΔX between 0.3 and 0.7.

Amount of CO_2 to be captured from the regenerator

The amount of CO_2 released in the regenerator $F_{co_2,\text{reg}}$, is shown in Figure 13. This figure shows that the amount of CO_2 released in the regenerator differs depending on the sorbent. For most of the range of ΔX considered here, dolomite leads to the highest amount of CO_2 released, followed by limestone and then CaO/C12A7. All the CO_2 released in regenerator is to be compressed for transport and storage. Figure 13 shows that, even if the amount of CO_2 captured from the flue gas (F_{CO_2}) remains constant, the amount of CO_2 released in the regenerator can vary significantly, thus, affecting directly the electricity demand for the compressors.

It is important to recall that, in addition to the CO_2 contained in the flue gas, there are other sources of CO_2 to be captured from the regenerator. For CaO/C12A7, the other source of CO_2 is from burning coal with pure oxygen to provide heat to the regenerator. For limestone and dolomite, CO_2 is also released from the fresh sorbent itself ($CaCO_3$ based sorbent). All this additional CO_2 will have a significant impact on the compression duty.

As shown in Figure 14, when increasing ΔX, the CO_2 released from the sorbent in the case of limestone and dolomite increases due to the increase in fresh sorbent input, whereas for CaO/C12A7 it is zero, because the active material is CaO. The amount of CO_2 released in the regenerator from the flue gas continuously reduces with increasing ΔX, the balance being captured as calcium carbonate discharged from the carbonator (F_0). For limestone and dolomite, Figure 14a and b indicate that only half of the CO_2 compressed is CO_2 originating from the flue gas, and this fraction decreases as ΔX increases. For high ΔX, almost all the CO_2 compressed originates from the sorbent and from burning coal. For CaO/C12A7 57% of the CO_2 compressed comes from the flue gas at $\Delta X = 0.23$, this values increasing to 60% at $\Delta X = 0.35$, and to 64% at $\Delta X = 0.65$.

Plant performance

The integration of the CO_2 capture plant with the main power plant is similar to that presented by Shimizu and coworkers,[14] and is shown in Figure 15. The main power plant is a supercritical plant with an efficiency of 38.3% (HHV). In all cases, the amount of coal fed to the main power plant is constant and equal to 1380 MWth, as in.[14] The power of the main combustor, is, therefore, constant at 529 MW_e. Additional power can be generated from the heat released by the absorber, and from heat recovered from the absorber and regenerator exits. It is assumed here that the steam produced for generating electricity from the CO_2 capture plant is at 839 K and 170 atm (subcritical), and that the steam turbines have an efficiency of 42.6%.[14] The values reported in Figure 15 are for the case of CaO/C12A7 with $\Delta X = 0.268$. Assuming that internal power consumption for the CO_2 capture plant is equal to 8% of the gross power, the efficiency of the whole system in the case of CaO/C12A7, with $\Delta X = 0.268$ is 32.8% (HHV). Figure 16 gives the overall efficiency for all three sorbents at different ΔX. CaO/C12A7 shows the highest efficiency, which decreases as ΔX increases. This is because this sorbent do not content any CO_2 in the form of carbonate, thus, less CO_2 needs to be compressed, thereby increasing the overall efficiency. One will notice that the difference in efficiency between limestone and dolomite is not big at lower ΔX because, as mentioned previously. For CaO/C12A7, the efficiency remains more or less constant (ca. 32%) for ΔX up to 0.6, but quickly decreases, thereafter, because of the increase in fresh sorbent (see Figure 6). Dolomite is the worse in terms of overall efficiency, again because it contains carbonate and inert material MgO, and calcium conversion of dolomite is higher than that of limestone, but 42% of this sorbent is MgO. The weight fractions (grams of CO_2 captured per gram of parent sorbent) of dolo-

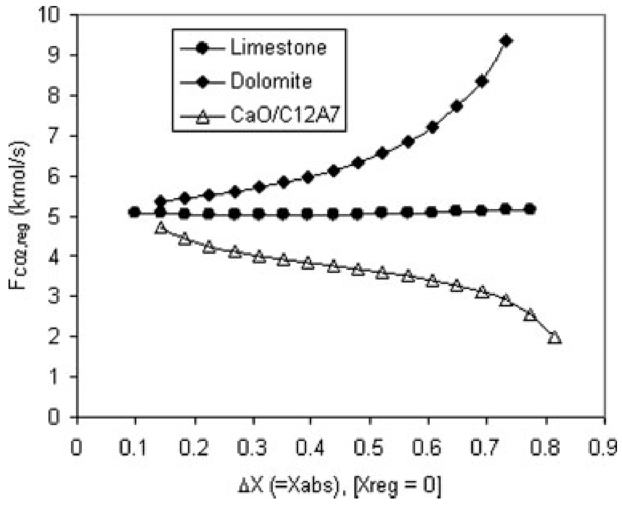

Figure 13. Variation of the amount of CO_2 released in the regenerator as a function of Δ*X* for three sorbents.

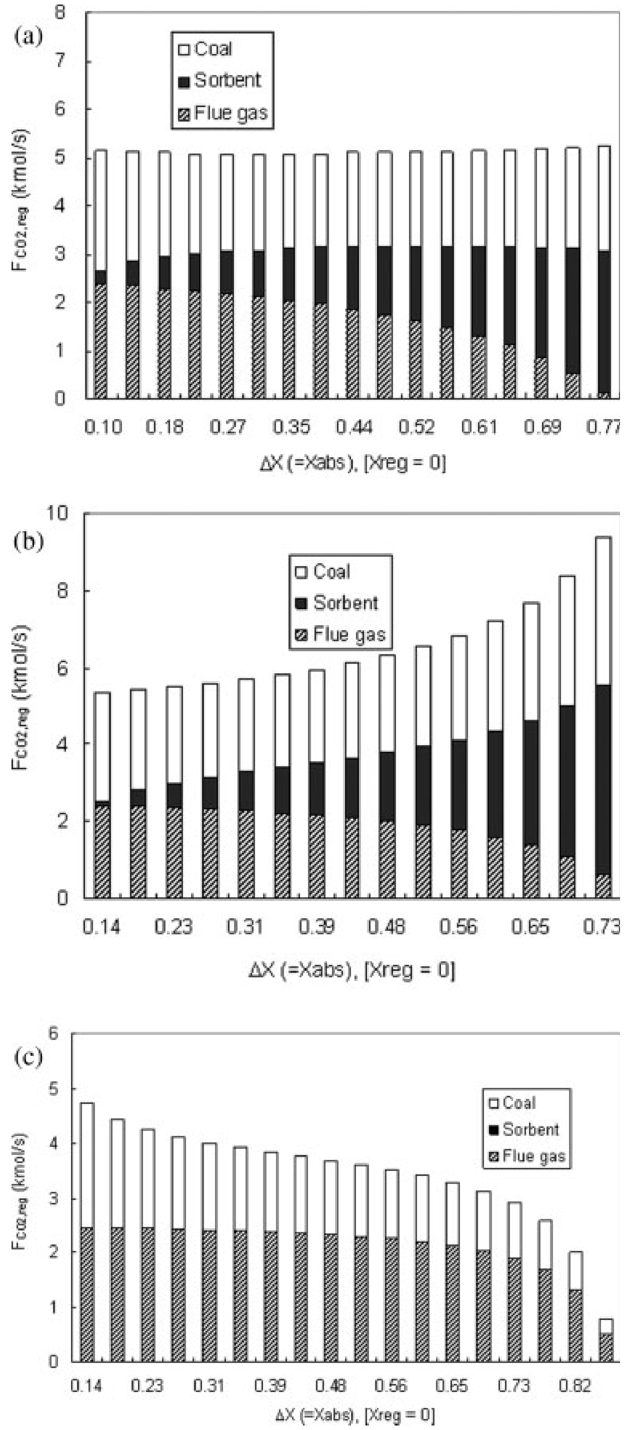

Figure 14. Variation of the amount of CO_2 released from coal, sorbent and flue gas in the regenerator as a function of ΔX for three sorbents.

(a) Limestone sorbent; (b) dolomite sorbent; (c) CaO/C12A7 sorbent.

mite is similar to the limestone. However, a higher mass of sorbent is needed to capture a certain amount of CO_2 as the active CaO fraction is lower. Therefore, more energy is required for the calcination process to heatup the larger fraction of inert material.

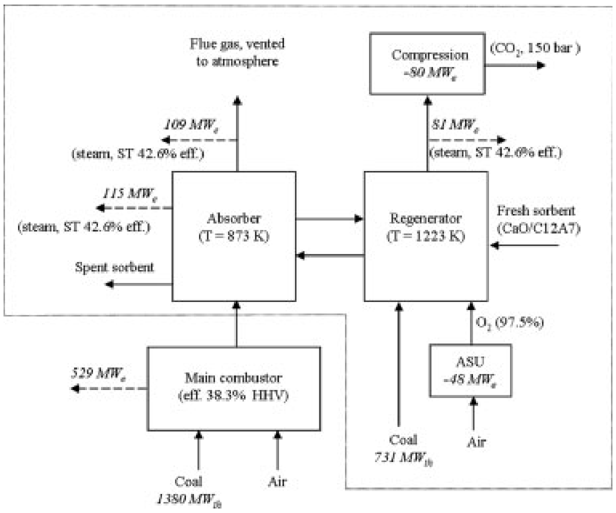

Figure 15. Heat balance for the entire system.

The value of power generated/consumed are for the case of CaO/C12A7 with ΔX = 0.268.

As indicated in Figure 15, the CO_2 capture process is also a significant power producer; in the case of CaO/C12A7 with ΔX = 0.268, the total net electrical power generated is 692 MW, of which 305 MW comes from the carbonator/regenerator process (ca. 44%). The amount of electricity produced from the CO_2 capture process, and, therefore, the total amount of electricity generated, decreases as ΔX increases, as seen in Figure 17. This is essentially due to the reduction in materials being recirculated (see Figure 7), and, therefore, the amount of heat that can be recovered. However, comparison between Figures 16 and 17 shows that the reduction in electricity generated is accompanied by a reduction in efficiency for three sorbents.

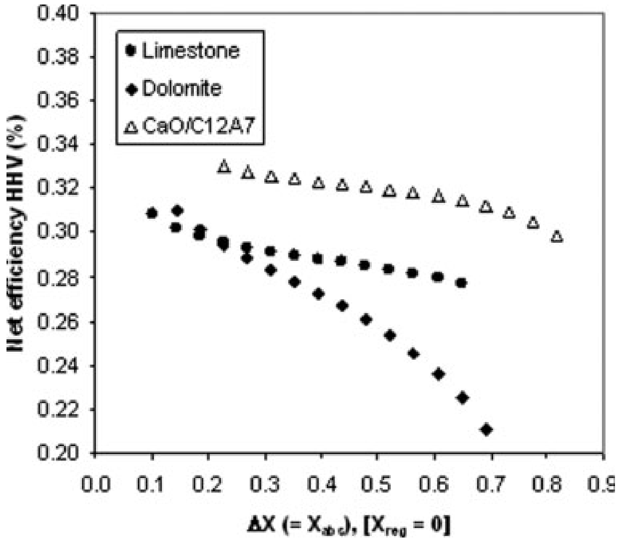

Figure 16. Net efficiency of the overall system (main combustor + CO_2 capture process).

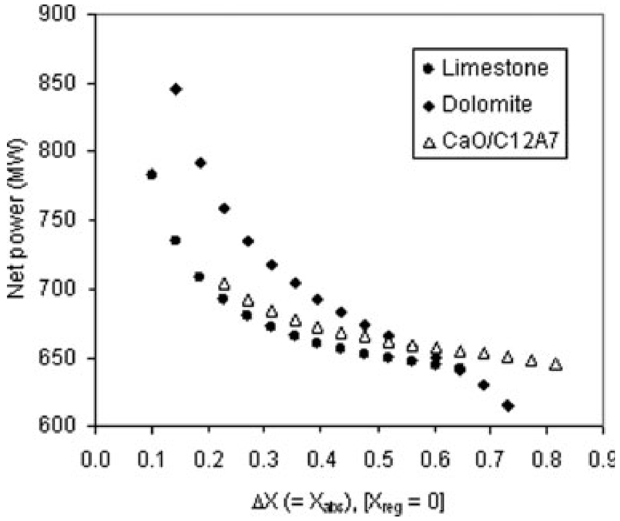

Figure 17. Total net electricity generated.

Recall that the net power generated from the main combustor is constant and equal to 529 MW.

Cost analysis

The assumptions for the cost analysis are: interest rate of 8%, project duration of 20 years, and annual capacity factor (ACF) of 0.8. Tax and CO_2 credit were not taken into account, neither the possible benefit of selling the spent sorbent. When not specified, all reported values are in USD 2005. When necessary, the Marshall and Swift index was used to convert cost in USD 2005.

Capital cost estimation

- Main combustor: supercritical PC plant with 38.3% efficiency (HHV). Capital cost of \$1,511/kW (adapted from a 2006 EPA report[26]).
- Air separation unit: the power requirement is set at 26 MJ/kmol O_2,[27,28] and the capital cost at 57 M\$/(kmol O_2/s).[28]
- CO_2 compression: used data from a UC Davis report.[29]
- Calciner/carbonator: used data from MacKenzie et al.[27] where they evaluated the capital cost of the calciner/carbonator at 64 M\$ (2005 CAD), including 25% indirect cost for 1.38 kmol/s of CO_2 captured. In this study, it is assumed that the capital cost of calciner/carbonator is based on the amount of CO_2 released from the regenerator and, converting the cost from MacKenzie et al.[27] we estimated the capital cost as 46 M\$/(kmol/s CO_2 captured). The calciner/carbonator is certainly the component whose cost is associated with the most uncertainties.
- For the balance of plant of the capture plant we used an EPA report (see Appendix A4),[26] for a subcritical plant, because a subcritical steam cycle was assumed in this work for the capture plant. The balance of plant (excluding calciner/carbonator) was then estimated at 1,054 \$/kW_{gross}.

Production cost estimation

- Cost of fuel: \$3/GJ
- Cost of sorbent: limestone: 26.7 \$/t,[30] dolomite: 30 \$/t,[30] CaO/C12A7:130 \$/t. The cost of CaO/C12A7 (formula CaO/$Ca_{12}Al_{14}O_{33}$) was determined assuming that limestone and Al_2O_3 (\$500/t) are the main components during fabrication, to which 20% manufacturing cost was added.
- The operating labor, maintenance, administrative and support labor, as well as consumable were estimated based on data found in an EPA report,[26] and equal to 5.3, 7.3, 2.1, and 14.3 \$M per year, respectively.

Cost data are reported in terms of cost of electricity (COE), and CO_2 capture cost expressed as \$ per ton of CO_2 avoided. The CO_2 mitigaton cost is calculated according to

$$\text{CO}_2\,\text{mitigation cost}\,(\$/\text{tonne CO}_2\,\text{avoided}) = \frac{(\text{COE})_{\text{capture}}-(\text{COE})_{\text{no capture}}}{(\text{CO}_2)_{\text{no capture}}-(\text{CO}_2)_{\text{capture}}}\quad\frac{[\$/\text{MWh}]}{[\text{t}_{\text{CO}_2}/\text{MWh}]} \tag{33}$$

where the indices "capture" and "no capture" denote a power plant with and without CO_2 capture, respectively.

Cost analysis results

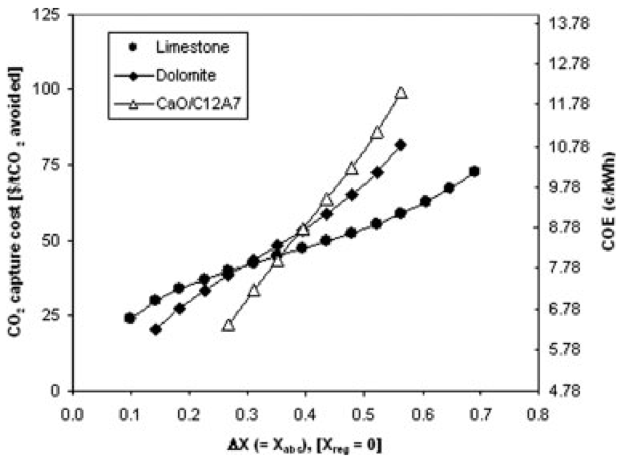

Figure 18. Change in COE and mitigation cost as a function of ΔX for limestone, dolomite and CaO/C12A7.

As shown in Figure 18, the cost of electricity and CO_2 mitigation cost have identical profiles when plotted as a function of ΔX. For comparison, the COE for a conventional supercritical power plant is estimated at 4.7 ¢/kWh. Figure 18 clearly shows that for all sorbents both the COE and mitigation cost increase as ΔX increases. This is due to the increase in fresh sorbent to be supplied to the system at higher ΔX (see Figure 6). Although in Figure 6, the fresh sorbent flow rates of CaO/C12A7 is smallest among three sorbents for most of the ΔX range, Figure 18 shows a much more important difference between these three sorbents, because the cost of CaO/C12A7 is more than four times that of dolomite and limestone. Figure 18 also shows that CaO/C12A7 has the lowest COE and capture cost, and limestone the highest ones if ΔX being lower than 0.35. Although the cost analysis points toward designing this capture process for low-values of ΔX, one should recall that low-values ΔX are also associated with large amounts of solid recirculation within the process (see Figure 7). This implies large amounts of heat to be released from the absorber (and, thus, large

Table 4. Cost Analysis Comparison Between MacKenzie[27] and this Work

Sorbent type	Capital cost	Operation cost (including sorbent)	Fuel	Tax	Total COE	CO_2 mitigation cost
Limestone (Mackenzie[27])	2.35	0.92	1.51	0.79	5.56	20.4 \$/t CO_2 capt.
Limestone $X_{abs} = 0.23$	3.25	1.83 (57% sorbent)	2.41	–	7.52	37 \$/t CO_2 avoid.
Limestone $X_{abs} = 0.1$	3.14	1.06 (30% sorbent)	2.33	–	6.54	24 \$/t CO_2 avoid.
Dolomite $X_{abs} = 0.14$	3.12	0.87 (15% sorbent)	2.32	–	6.31	20.7 \$/t CO_2 avoid.
CaO/C12A7 $X_{abs} = 0.27$	3.00	1.16 (35% sorbent)	2.20	–	6.35	21.7 \$/t CO_2 avoid.

For MacKenzie data, cost have been converted to 2005 USD assuming 1 CAD = 0.86 USD. Costs reported in ¢/kWh (except mitigation cost). The values in between brackets for the operating cost represents the portion of operating cost due to sorbent cost. COE for the base supercritical plant is 4.7 ¢/kWh.

heat transfer area required), and large amounts of heat to be supplied to the regenerator, as well as anticipated increased difficulty of operation as the amount of solid recirculation increases. It is obvious that synthesized sorbent with high-performance, and low-cost would be highly beneficial for the CO_2 capture process from flue gas using carbonation/calcination cycles. However, there are some uncertainties in this analysis. One factor that was not considered is the possibility that sulfation might also cause sorbent activity loss. SO_2 was found to impede cyclic CO_2 capture because of pore blockage by sulfate products, resulting primarily from direct sulfation during the later stage of each cycle for simultaneous CO_2 and SO_2 removal.[31] This case can be dealt with in this study by assuming that SO_2 already has been removed before entering into carbonator. The second factor that is not considered is the subject of sorbent attrition. Experimental work by Jia et al.[32] in a small pilot-scale CFBC suggested that multiple carbonation/calcination cycles resulted in severe fragmentation during the first one or two calcination periods. They found that partial sulfation can dramatically reduce fragmentation, albeit with the risk of reduction of reaction reversibility. A way to retain both sorbent reactivity and particle strength is required for this process. Third factor that is not considered is the effect of coal ash on sorbent reactivity. Coal ash may react with CaO, especially in calciner, and if so, they will have a deleterious or positive effect on carbonation and particle strength. Because of a lack of detailed experimental results regarding the effect of coal ash on sorbent performance, this was not included in this study.

Comparison with published data and other CO_2 capture technologies

To our knowledge, articles from MacKenzie et al.[27] and Abanades et al.[33] are the only two publications presenting cost analysis for the calcinations/carbonation process for capturing CO_2. In their work, MacKenzie et al. considered capturing CO_2, using limestone as sorbent, from a 360 MW net PFB whose electric generation efficiency is 40.7%. It was not clear to us if the heat recovered from the carbonator and calciner was also used to generate additional electricity. This might be an important difference with the process described in this article. The size of their CO_2 capture process was also smaller; capture of 1,900 kt/yr CO_2 vs. 3,400 in this case. Another difference is their project life of 30 years as opposed to 20 years in this study. Note that sensitivity analysis (not shown here) indicated that increasing the project life from 20 to 30 years yielded a decrease in COE of approximately 7%. Finally, MacKenzie analysis included tax, which is not the case in our study. Despite these differences, it is felt that, considering the very limited amount of data published for this process, a comparison is still meaningful. Comparison between MacKenzie results, and our results is shown in Table 4. MacKenzie[27] reported a fresh limestone makeup flow of 7.5%, which, in our case, corresponds to X_{abs} (or ΔX) equals to 0.23. Our results indicate higher COE and CO_2 mitigation cost, even without including tax. This is due to higher capital, operating and fuel costs. Table 4 also shows results for limestone with X_{abs} of 0.1 (best situation for limestone in term of cost), as well as dolomite at X_{abs} of 0.14 and CaO/C12A7 at X_{abs} of 0.27. In all cases, the COE is higher than that of MacKenzie, but the CO_2 capture cost is in the same order of magnitude, especially for dolomite. The best situation, as far as cost is concerned is that of dolomite with X_{abs} of 0.14. In this case, a low-fresh sorbent makeup is needed (15% of the operating cost is attributed to the sorbent cost).

Comparison with other CO_2 capture technologies is presented in Table 5. Data reported in Table 5, other than those for the carbonation/calcination process are taken from the review of Beér.[34] Table 5 shows that the carbonation/calcinations process compares well with the other technologies, showing the lowest COE, comparable to that of the IGCC with CO_2 capture. What is remarkable is that the lowest COE is obtained despite the largest capital cost (2,576–2,702 \$/kW) among all technologies. This is because the carbonation/calcinations process requires less heat and/or electricity for the capture process than its counterparts, and also because a significantly large amount of heat can be recovered

Table 5. Comparison of COE with other CO_2 Capture Technologies

	COE ¢/kWh	Capital cost \$/kW	%COE increase	Efficiency %, HHV
Amine, subcritial	8.16	2500	+70%	25.1
Amine, supercritial	7.69	2400	+61%	29.3
Amine, ultra supercritial	7.34	2340	+57%	34.1
Oxyfuel	6.98	2300	+46%	30.6
IGCC	6.51	2120	+27%	31.2
Calc./Carb.	6.31~6.54	2576~2702	+36%~+40%	31.0~32.8

The % COE increase represents in the % COE increase from the plant without CO_2 capture. For the carbonation/calcinations the base plant is that of a supercritical plant.

to generate electricity. The efficiency of this process (31.0–32.8% HHV) is also among the highest. Percentage increase in COE is also reported because it can be best used for comparison between different studies; the carbonation/calcinations shows among the lower percentage increase in COE. Note that for the CCR process, the base COE was that of a supercritical plant.

Conclusion

A design and analysis of a CO_2 capture process based on carbonation/calcination cycles with two fluidized-bed reactors was presented. The design and operating conditions of this process system are highly dependent on the Ca-based sorbent used. It was found that the difference in conversion of sorbent between absorber and regenerator, ΔX, was an important design variable affecting greatly all other parameters (e.g., fresh sorbent makeup, amount of coal and oxygen required in the regenerator, etc.). In practical operation, because of the fast calcination reaction, it is very likely that calcination in the regenerator will be nearly complete. This was assumed in most of the analysis presented here, and, thus, ΔX was equivalent to the conversion in the absorber.

At low ΔX the activity loss of Ca-based sorbent has negligible effect on the CO_2 capture process, and only a small amount of fresh sorbent is needed. However, in that case, a large amount of sorbent must be recirculated between the absorber and the regenerator. As the sorbent conversion in the absorber increases, the amount of recycled sorbent decreases, but because of higher CaO conversion the effect of sorbent activity loss becomes more and more important, and, therefore, a larger amount of fresh sorbent is needed. The required amount of fresh sorbent can vary significantly from one sorbent to the other because the activity loss for each sorbent is different; limestone requires considerably more fresh sorbent makeup than dolomite and CaO/C12A7.

The heat to be removed from the absorber decreases when increasing ΔX, and the sequence is: dolomite > CaO/C12A7 > limestone. More heat must be removed from the absorber for dolomite and CaO/C12A7, because they contain inert material that can be considered as heat sinks. When increasing ΔX, the heat required for sorbent regeneration for limestone and dolomite first decreases and then increases, which is due to the balance between the amount of sorbent recirculated and fresh sorbent makeup. For CaO/C12A7 the heat required in the regenerator continuously decreases because fresh sorbent is injected directly into the absorber and not into the regenerator. The amounts of coal and pure oxygen required are determined directly by the amount of required heat for the regenerator.

The economic analysis (COE and CO_2 mitigation cost) indicated that dolomite and CaO/C12A7 are promising sorbents. Limestone is not attractive because of its fast activity loss, and, thus, because of the very large amount of makeup sorbent required. Although CaO/C12A7 has higher adsorption capacity and cyclic stability than that of limestone and dolomite, its cost, more than four times that of limestone and dolomite, makes the process more expensive, except at very low ΔX, where the amount of fresh sorbent is the lowest. Using dolomite and CaO/C12A7 the COE increases by 36%–40% compared to the base COE of a supercritical plant, while capturing 85% of CO_2, which is lower than any other competing CO_2 capture technologies, except IGCC with CO_2 capture. It is obvious that synthesized sorbent with high-performance and low-cost would be highly beneficial for the CO_2 capture process from flue gas using carbonation/calcination cycles.

Acknowledgment

This work was supported by the National Basic Research Program of China (No. 2006CB705807).

Notation

C_{ar} = the mass fraction of carbon in the coal (as received)
$C_{p,0}$ = the specific heat of fresh sorbent, kJ/(kmol K).
$C_{p,CaCO_3}$ = the specific heat of $CaCO_3$, kJ/(kmol K)
$C_{p,\ CaO}$ = the specific heat of CaO, kJ/(kmol K)
$C'_{p,\ flue}$ = the specific heat of inlet flue gas, kJ/(kmol K)
$C''_{p,\ flue}$ = the specific heat of outlet flue gas, kJ/(kmol K)
$C''_{p,\ gas}$ = the specific heat of outlet gas from regenerator, kJ/(kmol K)
$C'_{p,\ gas}$ = the specific heat of intlet gas into regenerator, kJ/(kmol K)
$C_{p,inert,reg}$ = the specific heat of inert material in regenerator, kJ/(kmol K)
$C_{p,inert,abs}$ = the specific heat of inert material in absorber, kJ/(kmol K)
$C_{p,inert,0}$ = the specific heat of inert material in fresh sorbent, kJ/(kmol K)
F_0 = the molar flow rate of fresh sorbent, kmol/s
F_{CO_2} = the amount of absorbed CO_2, kmol/s
$F_{CO_2,reg}$ = the amount of CO_2 released in the regenerator, kmol/s
F'_{flue} = the total molar flow rate of inlet flue gas, kmol/s
F''_{flue} = the molar flow rate of the flue gas leaving the absorber, kmol/s
F'_{gas} = the gas-flow rate entering the regenerator, kmol/s
F''_{gas} = the molar flow rate of the gas exiting the regenerator, kmol/s
F_{O_2} = the corresponding required amount of O_2 for sorbent regeneration, kmol/s
F_R = the sorbent molar flow rates from the absorber to the regenerator, kmol/s
F'_i = (i = CO_2, O_2, N_2 and H_2O) = the flow rates of each flue gas components, kmol/s
F''_i = (i = CO_2, O_2, N_2 and H_2O) = the flow rates of each flue gas components leaving the absorber, kmol/s
H_{ar} = the mass fraction of hydrogen in the coal (as received)
M_{actual} = the actual molar mass of the sorbent in its partially carbonated state, kg/kmol
M_C = the C molecular weight, kg/kmol
M_{CaO} = the CaO molecular weight, kg/kmol
M_{CaO_3} = the $CaCO_3$ molecular weight, kg/kmol
M_{CO_2} = the CO_2 molecular weight, kg/kmol
$M_{f,abs}$ = the molar mass of the fully carbonated sorbent, kg/kmol
$M_{f,reg}$ = the molar mass of the fully calcined sorbent, kg/kmol
m_{coal} = the required amount of coal for sorbent regeneration, kg/s
m_{CO_2} = the mass of absorbed CO_2, kg/s
M_{inert} = the molecular weight of inert material in sorbent, kg/kmol
m_{sol} = the mass flow rate of sorbent from the absorber to the regenerator, kg/s
$m_{sol,reg}$ = the mass flow of sorbent returning from the regenerator to the absorber, kg/s
N = cycle number
O_{ar} = the mass fraction of oxygen in the coal (as received)
$Q_{abs,out}$ = the heat required to be removed from absorber, MJ/s
$Q_{heatvalue}$ = the high-heating value of coal, MJ/kg-daf
$Q_{reg,in}$ = the heat required for sorbent regeneration in regenerator, MJ/s
S_{ar} = the mass fraction of sulfur in the coal (as received)

T_{abs} = the temperature of absorber, K
T_{flue} = the inlet flue gas temperature, K
T_{gas} = the temperature of gas entering the regenerator, K
T_{reg} = the temperatures of regenerator, K
X = the conversion of CaO
X_{abs} = CaO conversion in absorber
X_g = the CO_2 conversion
X_N = the conversion of CaO to $CaCO_3$ in the *N*th cycle
X_{reg} = CaO conversion in regenerator
x_{CaO} = the mass fraction of CaO upon complete calcination
x'_{CO_2} = the mole fraction of CO_2 in inlet flue gas
x''_{CO_2} = the fraction of CO_2 in outlet flue gas
ΔX = the difference in conversion
constants = $a_{1,}$, a_2, f_1, f_2, f, b, f_m, f_w, and k
α_{o_2} = the excess oxygen coefficient
$(-\Delta H)_{abs,carb}$ = the reaction heat of carbonation in absorber, kJ/kmol
$(-\Delta H)_{reg,calc}$ = the reaction heat of calcination in regenerator, kJ/kmol

Literature Cited

1. Climate Change 1995: The Science of Climate Change,Contribution of Working Group I to the Second Assessment Report of the Intergovernmental Panel on Climate Change; Houghton JT, Meira Filho LG, Callander BA, Harris N, Kattenberg A, Maskell K. eds. Cambridge University Press: Cambridge, U.K; 1996.
2. Freund P. Making deep reductions in CO_2 emissions from coal-fired power plant using capture and storage of CO_2. *Proc Inst Mech Eng*. 2003;217 (Part A):1.
3. Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO_2 separation; application of chemical-looping combustion. *Chem Eng Sci*. 2001;56:3101.
4. Singh D, Croiset E, Douglas PL, Douglas MA. Techno-economic study of CO_2 capture from an existing coal-fired power plant: MEA scrubbing vs. O_2/CO_2 recycle combustion. *Energy Conv and Manag*. 2003;44:3073.
5. Squires AM. Cyclic use of calcined dolomite to desulfurize fuels. undergoing gasification. *Adv Chem Ser*. 1967;69:205.
6. Curran GP, Fink CE, Gorin E. CO_2 acceptor gasification process. *Adv Chem Ser*. 1967;69:141.
7. Lackner K, Ziock H J, Harrison DP. Patent WO 01/42132 A1; 2001.
8. Lyon RK, Cole JA. Unmixed combustion: An alternative to fire. *Comb and Flame*. 2000;121:249.
9. Lin SY, Suzuki Y, Hatano H, Harada M. Developing an innovative method, HyPr-RING, to produce hydrogen from hydrocarbons. *Energy Conv and Manag*. 2002;43:1283–1290.
10. Williams R. Hydrogen Production. U.S. Patent 1,938,202; 1933.
11. Gorin E, Retallick W B. Method for the Production of Hydrogen. U.S. Patent 3,108,857; 1963.
12. Balasubramanian B, Lopez A, Kaytakoglu S, Harrison DP. Hydrogen from methane in a single-step process. *Chem Eng Sci*. 1999;54:3543.
13. Kato Y, Ando K, Yoshizawa YJ. Study on a regenerative fuel reformer for a zero-emission vehicle system. *Chem Eng Japn*. 2003; 36:860.
14. Shimizu T, Hirama T, Hosoda H, Kitano K, Inagaki M, Tejima K. A twin fluid-bed reactor for removal of CO2 from combustion processes. *Trans IChemE*. 1999;77:62.
15. Abanades JC, Anthony EJ, Wang JS, Oakey JE. Fluidized bed combustion systems integrating CO_2 capture with CaO. *Environ Sci Technol*. 2005;39:2861.
16. Hughes RW, Lu DY, Anthony EJ, Macchi A. Design, process simulation and construction of an atmospheric dual fluidized bed combustion system for in situ CO_2 capture using high-temperature sorbents. *Fuel Proc Technol*. 2005;86:1523.
17. Gupta H, Fan LS. Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. *Ind Eng Chem Res*. 2002;41:4035.
18. Abanades JC, Rubin ES, Anthony EJ. Sorbent cost and performance in CO_2 capture systems. *Ind Eng Chem Res*. 2004;43:3462.
19. Abanades JC. The maximum capture efficiency of CO_2 using a carbonation/calcination cycle of $CaO/CaCO_3$. *Chem Eng J*. 2002; 90:303.
20. Abanades JC, Alvarez D. Conversion limits in the reaction of CO_2 with lime. *Energy & Fuels*. 2003;17:308.
21. Wang J, Anthony EJ. On the decay behavior of the CO_2 absorption capacity of CaO-based sorbents. *Ind Eng Chem Res*. 2005;44:627.
22. Grasa G.S., Abanades J.C. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. *Ind Eng Chem Res*. 2006;45: 8846.
23. Li ZS, Cai NS, Huang YY, Han HJ. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide sorbent. *Energy Fuels*. 2005;19:1447.
24. Li ZS, Cai NS, Huang YY. Effect of preparation temperature on cyclic CO_2 capture and multiple carbonation-calcination cycles for a new Ca-based CO_2 sorbent. *Ind Eng Chem Res*. 2006;45:1911.
25. Barin I, Sauert F, Schultze-Rhonhof E, ShuSheng W. *Thermochemical data of pure substances*. 2nd ed. Weinheim: VCH; 1993.
26. *Environmental Footprints and Costs of Coal-Based Integrated Gasification Combined Cycle and Pulverized Coal Technologies*. Prepared by: Nexant, Inc. epa.gov/air/caaac/coaltech/.
27. MacKenzie A, Granatstein DL, Anthony EJ, Abanades JC. Economics of CO_2 capture using the calcium cycle with a pressurized fluidized bed combustor. *Energy & Fuels*. 2007;21:920.
28. Andersson K, Johnsson F. Process evaluation of an 865 MWe lignite fired O_2/CO_2 power plant. *Energy Conv and Manag*. 2006;47:3487.
29. Collum DL, Ogden JM. Techno-Economic Models for Carbon Dioxide Compression, Transport, and Storage & Correlations for Estimating Carbon Dioxide Density and Viscosity. http://its.ucdavis.edu/.
30. US Geological Survey. Mineral Commodities Suymmaries 2005. United States Government Printing Office: Washington, DC; 2005 (available at http://minerals.usgs.gov/minerals).
31. Sun P, Grace JR, Lim CJ, Anthony EJ. Removal of CO_2 by calcium-based sorbents in the presence of SO_2. *Energy & Fuels*. 2007;21:163.
32. Jia L, Hughes R, Lu D, Anthony EJ, Lau I. Attrition of calcining limestones in circulating fluidized-bed systems. *Ind Eng Chem Res*. 2007;46:5199.
33. Abanades JC, Grasa G, Alonso M, Rodriguez N, Anthony EJ, Romeo LM. Cost structure of a postcombustion CO_2 capture system using CaO. *Environ Sci & Technol*. 2007;41:5523.
34. Beér JM. High efficiency electric power generation: The environmental role, *Progr Energy and Comb Sci*. 2007;33:107.

Manuscript received May 14, 2007, and revision received Feb. 15, 2008.