

CaO-based Sorbents for Capturing CO₂ in Clean Energy Processes

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Using CaO-based regenerative sorbents to capture CO₂ in fossil fuel based power generation and H₂ production is a promising technology for reduction of CO₂ emission. A major challenge for this technology is the decay of sorbent activity with increasing cycles of sorption/regeneration. Evaluation of long-term sorbent activity currently requires large amounts of experimental work. In this study a method for determination of the long-term activity has been proposed, which can greatly reduce the experimental work for process evaluation and sorbent development.

1. Introduction

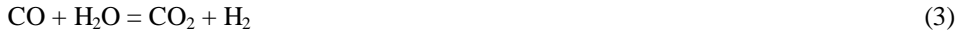
Emissions of CO₂ from fossil fuel combustion are major contributors to global warming. To curb CO₂ emissions, CO₂ capture and sequestration options are being actively studied. Among various options for capturing and concentrating CO₂ from flue gases, absorption by mineral sorbents at high temperatures appears to be attractive (Blamey et al., 2010). CaO sorbent from the calcination of limestone can take up CO₂ via the carbonation reaction:



The sorbent can be regenerated by decomposing the CaCO₃ into CaO and CO₂ in a separate reactor (calciner) via calcination, the reverse reaction of Reaction 1. The heat for calcination can be supplied by burning high-carbon fuel with pure oxygen. The product of the combustion in the calciner is predominantly CO₂, which together with the CO₂ from decomposition of CaCO₃ form a CO₂ stream for sequestration or use; alternatively the heat may also be supplied by other means. The regenerated sorbent is then sent back to the carbonator, and heat is released during subsequent sorption of CO₂ through the exothermic reaction of the sorbent (Eq. 1). In this way, the heat energy consumed in the calcination is transferred into the carbonator at high temperature and is available for steam or heat generation. High energy efficiency and cost-effectiveness for a number of applications incorporating this process have been projected.

The carbonation/calcination cycle can also be used to absorb CO₂ and enhance hydrogen production by reforming (Eq. 2) or the water-gas shift reaction (Eq. 3)





Production of H_2 through these reactions is limited by chemical equilibrium. Adding CaO-based sorbents in the reformer or shift reactor to remove CO_2 through Reaction (1) will move the equilibrium toward the product side. Thus, the conversion of CH_4 and CO to H_2 is increased, with the additional benefit of recovering the captured CO_2 in a calciner.

Unfortunately, the sorbent activity decreases with increasing cycles of carbonation/calcination, indicating a decay of the carbonation activity, as illustrated in Fig. 1. Sintering has been suggested to be the major cause for the activity decay.

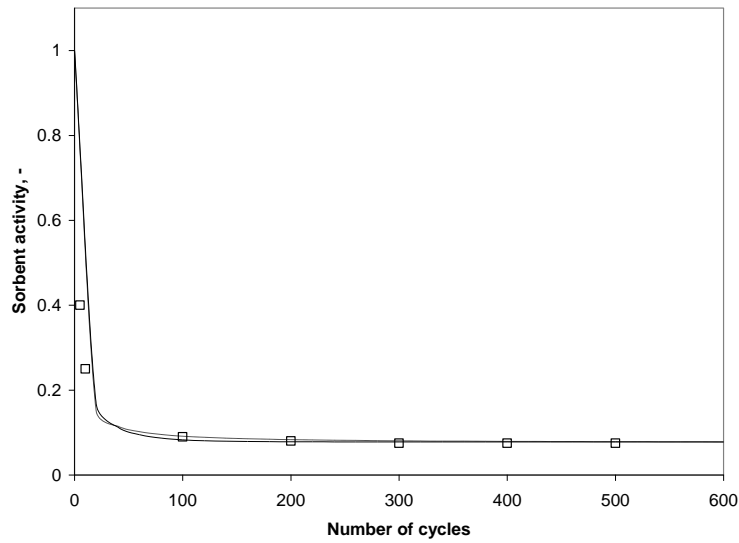


Figure 1: Sorbent activity over large number of carbonation/calcination cycles. The symbol represents data obtained by Grasa and Abanades (2006). The dashed and solid lines represent the description by Equations 4 and 5, respectively.

2. Relation Between Duration of Sintering and Number of Cycles

Sintering reduces surface area and number of active sites on catalysts. The degree of sintering increases with increasing temperature and duration, as is well known for catalysts. However, for CO_2 sorbents and cyclic carbonation/calcination operations, the effect of sintering is still under investigation. By noting the analogy of the activity decay with sintering-caused catalyst deactivation, the following two expressions for the dependence of sorbent activity on the number of carbonation/calcination cycles have been proposed respectively (Grasa and Abanades, 2006; Wang and Anthony, 2007):

$$a_N = \frac{1}{\frac{1}{1 - a_\infty} + kN} + a_\infty \quad (4)$$

$$a_N = \frac{a_\infty}{1 - (1 - a_\infty)e^{-ka_\infty N}} \quad (5)$$

where a_N is the activity at cycle N ; a_∞ is the asymptotic activity or residual activity as N becomes infinitely large. k is a coefficient for the rate of the decay. The two equations give essentially the same description of the data, as represented by the curves in Figure 1. However, to evaluate the residual activity a_∞ , hundreds to thousands of carbonation/calcination cycles are required. As this value can be important for process design and optimization, it is desirable to determine it in a quick and less laborious way. Further studies suggest sintering only occurs in calcination, and the degree of sintering is dependent on the duration of sintering. The duration dependence of the sintering can be measured in continuous experiments, i.e. without the need of repeated cycles of carbonation and calcination. We have thus proposed a way to largely reduce the work for determination of the residual activity, and verified the concept experimentally.

3. Experimental Results and Discussion

Experiments were carried out to evaluate the dependence of carbonation activity on the duration of calcination. Samples of a typical limestone was calcined for varied durations and then tested for carbonation activity. The carbonation conversion, which is a measure of the activity, is shown in Figure 2. The conversion level at several moments of carbonation are shown in Figure 3 as a function of calcination duration. Clearly, with increasing duration of calcination, the carbonation capacity decreases. In particular, the calcination-duration dependence of carbonation conversion (Figure 3) is quite similar to the previously discussed cycle-number dependence of sorbent activity.

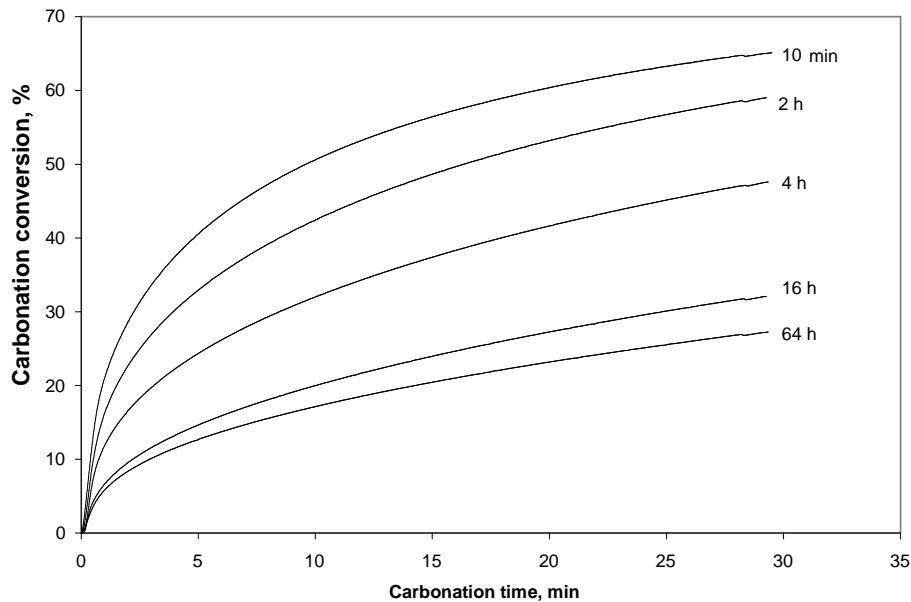


Figure 2: Carbonation conversion for limestone samples calcined for different durations

If the cycle number dependence can be represented by the calcination-duration dependence, the residual activity can be evaluated by a single carbonation measurement following a single, long calcination run. In Figure 4 experimental results are presented to verify the correspondence between the carbonation levels after multiple carbonation/calcination cycles and after single calcination runs. Figure 4a shows multicycle data up to 400 cycles where the calcination and carbonation durations were each of 10 minutes. In Figure 4b the cycle number is converted to total calcination time and the carbonation levels are compared with that of the single-calcination samples. As can be seen, after a short initial period the carbonation levels of the single-calcination data and multicycle data become quite close. It is interesting to note that in the long (single) calcination experiments the the temperature was higher (by 200°C) — a condition expected to cause more pronounced sintering — yet the carbonation levels from the single calcination/carbonation runs after long calcination time are only slightly lower. Apparently, the carbonation conversion level after a single, sufficiently long period of calcination can provide a good estimate of the residual activity.

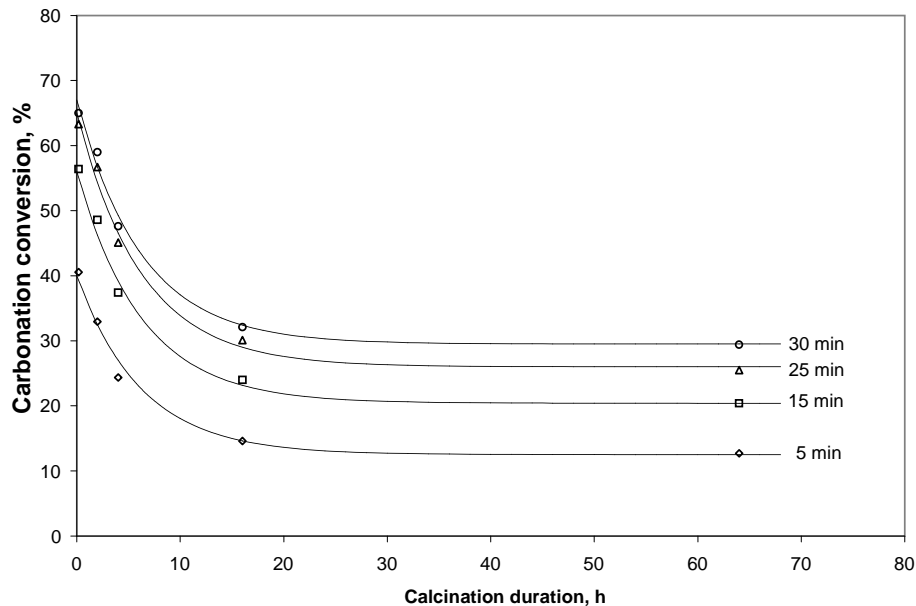


Figure. 3: Carbonation conversion at different moments during the carbonation course, as a function of calcination duration.

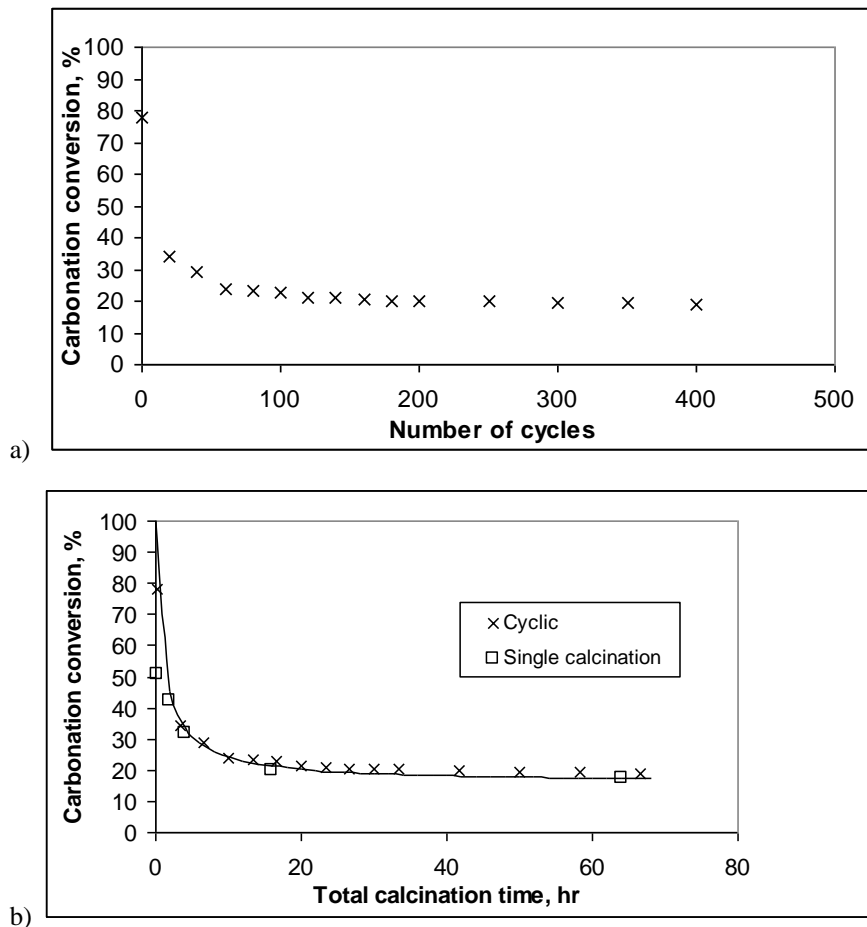


Figure 4: Comparison of carbonation conversion in multicycle and long-calcination tests of limestone samples. a) carbonation conversion in 400 carbonation/calcination cycles; b) carbonation conversion as a function of total calcination duration in multicycle and long-calcination tests.

4. Application to synthetic sorbents

The above results are also useful for development of synthetic sorbents with a target life of thousands of cycles and higher long-term activity. Synthetic sorbents show similar patterns of activity decay to those of natural limestones, as can be seen from the data in Figure 5. Using the approach of this work, the evaluation of long-term activity can be greatly simplified. This would be particularly efficient when multiple sorbents are to be tested or compared, as only a few measurements are needed. In contrast to the need for many thousands of cyclic experiments, the advantage of this approach is obvious. Another application is in screening starting materials (limestone, for example) for sorbent synthesis. Materials that show higher activity after prolonged sintering

treatment would be promising candidates. Hence, measurement of carbonation activity after prolonged sintering would be an effective and efficient method of material screening.

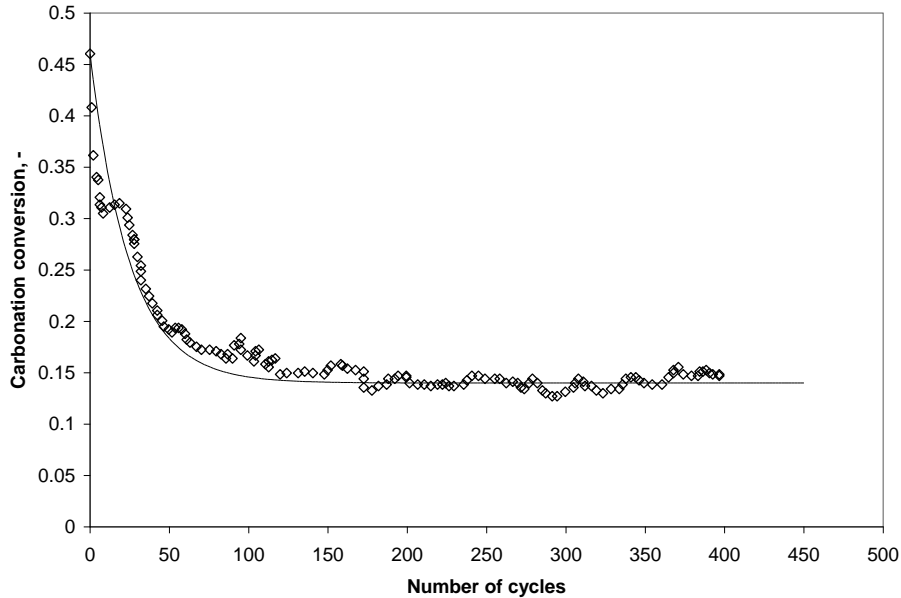


Figure 5: Carbonation conversion of a synthetic sorbent reported by Stevens *et al.* (2007).

5. Conclusions

The observed dependence of sorbent activity on the cycle number can be viewed as the dependence on the duration of sorbent regeneration. The residual activity of the sorbent after a large number of cycles may be simply determined with single calcination and carbonation test runs. This can greatly reduce the amount of work for evaluation of long-term sorbent activity, and for screening materials for sorbent synthesis.

References

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