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Solid Looping Cycles: A New Technology for Coal Conversion

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This article examines both oxygen looping cycles (otherwise known as chemical looping combustion), and lime-based CO₂ looping cycles, where calcined limestone is used for in situ CO₂ capture. There has been a rapid rise in the amount of research carried out recently, and both technologies are likely to see practical application in the near future. However, these technologies urgently require demonstration at the large pilot-plant level – in the case of chemical looping cycles for use with high-pressure syngas of the type likely to be produced by current coal gasification technologies and in the case of CO₂ looping cycles both for combustion and gasification applications with coal. Both approaches have potential for application in schemes for H₂ production, but these have not been considered here, although such applications will also inevitably follow in the medium to long term.

Introduction

The need to reduce anthropogenic greenhouse gas emissions represents a major driving force to reconsider the technologies being used for coal combustion and gasification.^{1,2} Current estimates of CO₂ production³ from fossil fuels are of the order of 5.4 Gt/a and it is clear that, if fossil fuel use is to continue, CO₂ sequestration in deep geological formations must be employed as a final sink for the CO₂ produced.⁴ Unfortunately, alternative approaches such as mineral carbonation of naturally occurring serpentine rocks, are not particularly promising as they require very fine particle sizes (5 μm), and the reaction occurs in slurries at high pressures (10–15 MPa).^{5,6} Natural weathering of carbonate rock can also potentially represent a sink as can carbonation of artificial materials containing CaO and/or MgO, such as steel slags⁷ or FBC solids, which can be carbonated fairly easily.⁸ Unfortunately, none of these is sufficiently abundant to make a significant impact on CO₂ emissions.

At present, most research and development is directed to improving boiler efficiencies via supercritical cycles, along with the possible deployment of amine scrubbing;⁹ for gasification work it is primarily directed to reducing the cost and improving the reliability of the technology. Zero-emissions technologies, which essentially allow a pure stream of CO₂ to be produced from a combustion or gasification process employing hydrocarbons, are now of considerable interest,¹⁰ because the bulk of the costs of CO₂ avoided (80%) is for the CO₂ capture and compression stages.⁹ Oxy-firing combustion represents a possible new direction, allowing more- or less-conventional boiler technology to be employed without the penalties introduced by amine scrubbing;¹¹ however, oxygen production is itself expensive and methods that either avoid using pure oxygen, or minimize its use, almost certainly have a window of opportunity in the next several decades.

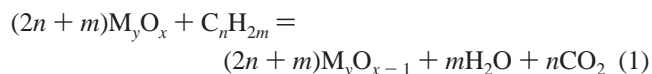
It is in this context that looping cycles represent an important new class of technologies, which can be deployed for direct combustion as well as being used with the gases produced by gasification systems.¹² Here, the definition of a looping cycle is one that employs a solid carrier to bring oxygen to the fuel gas, or takes CO₂ out of the combustion or gasification gases so that it can be subsequently released as a pure CO₂ stream suitable for use or more likely sequestration, with subsequent regeneration of the O₂ or CO₂ carrier. Chemical looping combustion is a new class of processes involving indirect combustion, where the active gas separation needed in post-combustion, oxycombustion, and precombustion can be avoided. Whereas CO₂ looping cycles offer CO₂ scrubbing either during the combustion process or downstream, here we will concentrate only on calcium looping, which offers hot scrubbing of CO₂.

This article will not consider cycles using liquids, although such systems are being developed, and amine scrubbing itself could be regarded as an example. In the interests of space, neither will cycles that involve H₂ production be examined here, although these well may represent potentially important opportunities for looping cycles in the future.

The use of solids also means that, in many cases, fluidized bed systems will represent an optimal method of allowing large quantities of solids to be transferred from one chemical environment to another.¹³ The added advantage here is that large (>350 MWe) atmospheric and pressurized systems exist^{14,15} that could be adapted for use in a number of possible looping cycle schemes.

O₂ Looping Cycles

These cycles typically involve a metal oxide that is used to oxidize a gaseous hydrocarbon, following the global reaction scheme:



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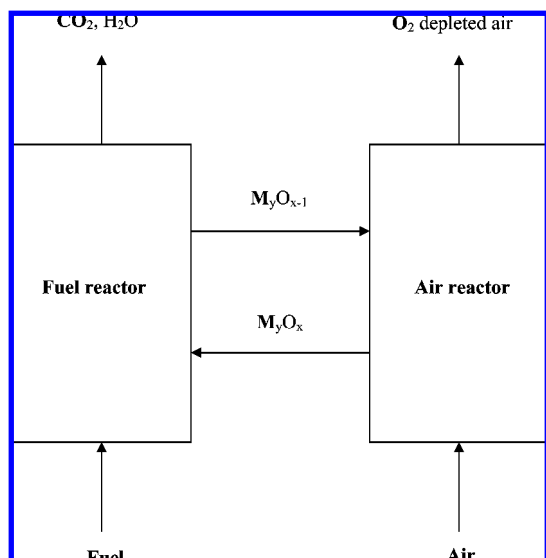


Figure 1. Typical metal-oxide looping cycle.

After the water produced from the hydrocarbon is removed, the flue gas stream contains an effectively pure stream of CO_2 suitable for sequestration. The metal oxide is then returned to its higher oxidation state (regenerated) in a separate reactor by reaction with air (reaction 2), and the regenerated solid can be transferred back for further reaction with the fuel gas (Figure 1).



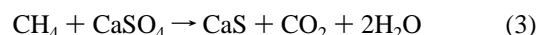
Typically, the oxidation reaction is strongly exothermic and the reduction step is not¹⁶ (an exception is the CuO/Cu cycle¹⁷), so that overall the system yields the heating value of the fuel. Such a cycle represents an elegant way of oxidizing a fuel gas by effectively achieving air separation, without using cryogenic or membrane technology, while avoiding or minimizing the formation of fuel NO_x . In practice these cycles typically operate at temperatures in the range of 800–1000 °C, which normally ensures that the reactions occur at a sufficient rate to be compatible with a fluidized bed system and to ensure that agglomeration and sintering are minimized. It should also be noted that reaction 1 is idealized because many metals can exist in multiple oxidation states, and it is not necessary that complete conversion of the oxide occur in either reaction 1 or 2 to ensure effective use.¹⁶

Although these cycles are usually referred to as chemical looping combustion,¹⁰ they are also a form of chemical looping cycles. In consequence, the term O_2 looping cycles will be used here for cycles in which the solid carries oxygen to the fuel gas, and CO_2 looping cycles for cycles in which CO_2 is carried away from the flue gas, to indicate the common features of both approaches.

The O_2 looping concept was proposed by Richter and Knoche,¹⁸ and early work using nickel-based carriers was carried out by Ishida and co-workers,^{19,20} with experimental studies being conducted in a thermogravimetric analyzer (TGA). Subsequently, this work was extended to fixed-bed studies using nickel-based carriers, which again demonstrated that the reaction was fast enough to be employed in practice and that soot formation or carbon deposition on the particles did not appear to be a major problem if the oxidation reaction was carried out at a high enough temperature.²¹ Subsequent work by Ishida and his colleagues using a TGA looked at improving the binding material (in this case NiAl_2O_3) and determined that, with a

suitable $\text{H}_2\text{O}/\text{CH}_4$ ratio, carbon deposition could be avoided altogether.²² These workers also studied other possible systems including CoO/Co and $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$.

There are a very large number of potential or theoretical material choices for such cycles. Important considerations are the cost of such materials, and their oxygen carrying capacity (usually defined as the mass of oxygen carried per unit mass of the carrier in its oxidized state), with values ranging from 0.03 for the $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$ to 0.21 for the NiO/Ni and CoO/Co systems.¹² Higher values are also possible in principle. We have explored the following reaction for gasification:



With subsequent regeneration of the CaS (one must ensure that the CaS is selectively oxidized to CaSO_4 , rather than CaO), its carrying capacity is exceptionally high at 0.47.²³ It is important to remember that normally the active agent will be distributed on some kind of porous media, such as porous alumina particles, so the oxygen carrying capacity should not be confused with the oxygen transport capacity of the actual particles, which can be significantly lower. Thus, for instance, Abad et al.²⁴ give figures for three oxygen carriers based on copper, iron, and nickel and the actual carrying capacities are 0.02, 0.013, and 0.084. Finally, something should be said about density of these particles, which can range²⁵ from about 1.5 to 4.5 kg/dm^3 . The higher densities are not typical of materials utilizable in standard FBCs used for combustion. Thus, typical bubbling and circulating FBC designs are unlikely to be easily adapted for large-scale units with the heavier oxygen carrying particles, and there will be several design issues, including the effects of vibration, which must first be resolved if this technology is to be adapted for use with pressurized coal syngas. One should perhaps note that this issue has recently been addressed in an article by Abad et al.²⁴ This looks at the inventories and solid circulation rates that would be required for pressurized systems, and this is an important first step in the type of considerations that need to be addressed for application with pressurized coal syngas. However, little else has been published on such matters, and we will not consider these issues further here.

At the beginning of the decade, significant work on O_2 looping cycles began outside of Japan, most notably in Sweden with the Lyngfelt group at Chalmers University, and the interested reader is recommended to look at the link describing the work being done by this group and their collaborators, which lists more than 60 publications.²⁵ Another very prolific source of publications in this area is the Spanish Research Council.²⁶ At the time of writing, Lyngfelt reports over 500 h of operation of a dual fluidized bed looping cycle.²⁷

In 2001, the Chalmers group¹⁶ reported the first experiments on the iron oxide system using CH_4 in a small fixed-bed reactor and indicated that this could be used in a practical fluidized bed dual-reactor system. Subsequent work continued as described in the extensive publication list,²⁵ but arguably the most significant development to date was the construction of a small 10 kW chemical looping combustor (Figure 2) by Chalmers University, CSIC/ICB, the Technical University of Vienna, and Alstom, which first operated in August 2003.²⁸ Initial results from the first 100 h of operation indicated that fuel conversion efficiencies were high (99.5%), with only 0.5% CO , 1% H_2 , and 0.1% CH_4 in the gas exit stream, and no leaks were detected from the reactor. A very low rate of attrition was also determined from the bed particles (0.0023%/h), which was translated into a cost of 1 euros/t of CO_2 captured for an anticipated particle

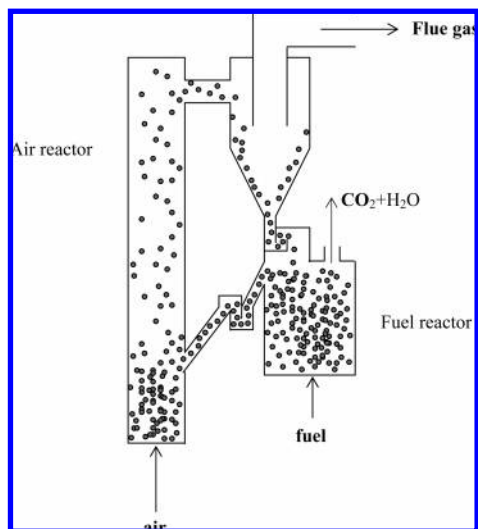


Figure 2. Schematic of grace 10 kW chemical looping reactor.

lifetime of 4000 h (corresponding to a loss of 10% of the bed mass). Subsequently, a second 10 kW unit was built by CSIC/ICB and this has been run for a number of trials, most notably including a 200 h demonstration of the CuO/Cu cycle.^{17,29} For this system, these workers suggested a practical lifetime for the copper-impregnated particles might be 2400 h, and overall the results indicated excellent performance.

Recently, there have been numerous studies done, in particular with the NiO/Ni and CuO/Cu systems, looking at parameters such as the stability of the particles produced, redistribution and/or loss of the active metal component in the synthetic particle, formation of soot or carbon deposits on the particles, and loss of activity due to sintering.^{30,31} Other issues include possible interactions between particular types of substrate and the active metal and their implications for falloff in activity or introduction of mechanical weakness in the carrier particles.³² These articles indicate that there are no important technical limitations to the realization of this concept. Caveats include: the fact that the CuO/Cu system must be operated at 850 °C or below because of the low melting point of the active components, and the iron system is somewhat less effective than expected as an oxygen carrier because of the formation of a variety of compounds. However, none of these types of issues are likely to provide major limitations if the concept is to be employed with natural gas, with operation at typical FBC temperatures (800–1000 °C) depending on the carrier employed.

In this context, it is interesting to look at the conclusions of Tan et al.¹² in their overview article concerning this concept. Positively, they note that the concept is flexible and is potentially an attractive candidate for processing gaseous fuels, whose high flexibility means that it could be adapted into a range of options including industrial boilers, gas turbines, and fuel cells. However, they caution that the technology is currently only suitable for gaseous fuels and that the majority of studies have been done using methane, with the number of studies on syngas extremely limited. They also express concern about carryover of char carbon to the air reactor if such a concept is integrated with gasification technology and possible interactions with ash and the oxygen carrier and called for test work with larger (1 MW_{th}) pilot plants to validate the work done in smaller-scale units.

Another very recent evaluation by Kvamsdal et al.³³ looked at nine concepts for natural gas firing. They concluded that the chemical looping concept is promising but requires a long time frame for realization. In addition, they noted that the concept

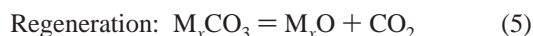
was rate-limited by the maximum temperature in the reactors. Nonetheless, they rated the technology as offering a net plant efficiency of 51%, well ahead of a number of oxyfuel concepts for instance, which must be regarded as a very positive evaluation for this technology if it is used with natural gas. Naqvi et al.³⁴ developed a very positive evaluation for the use of this technology at a partial load with CO₂ capture. At 100% load, an efficiency of 52% (including CO₂ capture) was predicted, and a net plant efficiency drop of only 2.6% was projected when reducing the load to 60%.

For coal on the other hand, it seems likely that such a technology can only be used after a gasification step. In recent work, Abad et al.³⁵ have noted that, in atmospheric tests with iron oxide as the oxygen carrier, better combustion efficiencies were obtained with syngas than natural gas although combustion efficiencies of 99% could be obtained with natural gas if the reaction occurred at higher temperatures (950 °C). They also noted that with this system, no problem is expected from the sulfur component in the syngas stream with the iron system, although there were no sulfur compounds in the synthetic syngas they used. These results are quite reasonable because methane should be more difficult to combust than any other hydrocarbon. However, almost certainly the syngases to be used in such a cycle will be produced via a high-pressure gasification process such as the integrated gasification combined cycle (IGCC). Whereas the benefits of a pressurized cycle in terms of improved efficiency and reduced work to produce a pressurized gas for pipeline transportation are well understood,²⁴ there are very few studies on how well an oxygen looping cycle would perform at high pressures. Further, no test data exist from pilot-scale units as of yet. However, a pressurized thermogravimetric analyzer (PTGA) study carried out with pressures up to 3 MPa showed that increasing total pressure reduces the reaction rate of the oxygen carriers examined, and these workers speculated that increasing pressure might affect the internal structure of the oxygen carrier.³⁶ A significant conclusion of their work was that solid inventories might have to be larger than those initially anticipated for pressurized oxygen looping cycles. In a recent study, Siriwardane et al.³⁷ examined the behavior of a nickel oxide oxygen carrier supported on bentonite, using a high-pressure flow reactor operating from 101 to 690 kPa, and showed rather a more complicated picture for this system, with an improved reaction at the highest pressure. Neither study looked at the effect of sulfur compounds on the performance of the oxygen carriers.

Whereas none of the conclusions of Tan et al.¹² has as yet been invalidated, the overall results of more recent studies seem to be extremely supportive of oxygen looping cycles for natural gas firing with CO₂ capture, whether or not pressurized cycles are shown to be practical. However, it is clear that much more study is needed on the use of this technology for the conversion of synthesis gas if it is to be converted at high pressures typical of IGCC operation. In this respect, it would appear that, whereas oxygen looping cycles might have great potential for natural gas, there is a need for major development and a significant amount of research to confidently deploy them in conjunction with the coal gasification processes. It is also interesting to note that Leion et al.³⁸ have recently reported some success in achieving gasification of petroleum coke using small batches of chemical looping cycle oxygen carriers at 950 °C. However, the implications of this interesting development for coal are far from clear given the ubiquitous presence of relatively high levels of ash in coal but again indicate that oxygen looping cycles continue to offer interesting new possibilities.

CO₂ Looping Cycles

The essential idea of such a cycle is to use a sorbent capable of carbonation to remove CO₂ from a gasification or combustion environment or for reforming.



Whereas it might be argued that the idea of an oxygen looping cycle is implicit in metallurgical operations where a metal oxide is reduced, it can be seen from the earlier discussions that this concept is quite new. Surprisingly, even though the CO₂ looping cycle concept is less well known, it can boast a much older history. Thus, Squires quotes DuMotay, proposing to use lime to promote the shift reaction in 1880.³⁹ The idea was later employed in the CO₂ acceptor gasification project, where lime- or dolomitic-based sorbents were used to remove CO₂ from gases produced in a high-pressure coal gasification process, thus substantially increasing their heating value.⁴⁰ The first industrial demonstration of this concept was achieved in 1974, with a 30 t/d pilot plant that was built and operated in Rapid City, South Dakota. Although the emphasis was on methane production and CO₂ was released to the atmosphere, this plant demonstrated the basic idea implicit in the CO₂ looping concept at the industrial scale.

These ideas were later taken up at the beginning of this decade, in a very ambitious scheme to hydrogasify coal. Here, the hydrogasification step was achieved using conventional technology. However, the H₂ produced was concentrated by the removal of CO₂ using a lime-based sorbent, which served to concentrate the H₂ before it was sent to a solid oxide fuel cell to produce electricity. The final storage of the CO₂ was achieved by the carbonation of serpentine minerals (i.e., mineral carbonation).

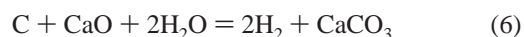
For more detailed analysis of their approach, the interested reader can look at the Zero Emission Coal Alliance work pursued by the ZECA Corporation (documented on a government of Canada website⁴¹). The core of this concept, hydrogasification with CO₂ capture, continues to be developed by Arizona Public Service in a new consortium funded by the USDOE.⁴² In addition, Imperial College (U.K.) and the University of Cambridge (U.K.) are carrying out work on the hydrogasification step and the calcium adsorption cycle, respectively, with the overall goal of demonstrating that combining reforming, shift reaction, and in situ CO₂ capture is feasible at appropriate temperatures and pressures.⁴³

Whereas the fact that 100% capture of CO₂ is not possible for a reaction such as reaction 4, at least not for the CaO/CaCO₃ system, it is interesting to note that Rao and Rubin⁴⁴ have recently questioned the idea that amine scrubbers be operated for 90+% CO₂ removal, and instead suggested that, dependent on plant size, capture efficiencies of less than 90% may be more cost-effective. In addition, it can be remarked that, at 600 °C where the carbonation reaction is still fairly rapid with CaO, the equilibrium partial pressure of CO₂ is only 0.3%, which is practically zero, so this limitation may not be particularly severe as has been suggested by some continuous small pilot-plant experiments exploring this cycle.⁴⁵

Although we will not discuss this concept further here, it is interesting to note that the ASPEN simulation carried out by NEXANT, which showed that such a concept could result in extremely high efficiencies, was supported by other workers⁴⁶ who also suggested simplification of the approach to improve it and reduce the technical challenges of bringing this type of

scheme toward practical application. Another issue that needs to be addressed is the possibility of forming melts with the calcium carrier at high temperatures and pressures; in this context, a study by Paterson et al.⁴⁷ showed that CaCO₃/CaSO₄ could produce eutectic mixtures with melting occurring at approximately 1010 °C and 2 MPa.

For completeness, it should be noted that there is also another interesting concept for hydrogen production using a calcium cycle, in this case the reaction of coal and CaO with H₂O.^{48,49} This process is known as HyPr-Ring (hydrogen production by reaction integrated gasification). Here, the coal is steam gasified, and Ca(OH)₂ is used to absorb CO₂ in a single vessel. The CO₂ is then subsequently released as a pure CO₂ stream by calcining the CaCO₃ in a separate reactor. The overall reaction in the main reactor is



For the gasification reaction to occur at a high enough rate, and for the intermediate formation of Ca(OH)₂ to be possible, temperatures are on the order of 650 °C, and the corresponding pressure is 3 MPa. Again, such a system has the problem of potential melts with the CaO–Ca(OH)₂–CaCO₃ system, and separating the ash from the recycled CO₂ carrier is a potential obstacle.

In 1995, Silaban and Harrison⁵⁰ again suggested that the CO₂ looping cycle approach might have considerable potential for CO₂ removal in IGCC and other processes. Their work was conducted using a PTGA; however, the steady falloff in CO₂-carrying capacity of the sorbent with calcination/carbonation for five cycles stressed the importance of operating the calcination cycles under as mild conditions as possible, to maintain the CO₂-carrying capacity or reversibility of the sorbent at high levels. They also noted that the carbonation process occurred in two stages – a fast one occupying many minutes (typically up to 10 min) and a much slower one, occurring over minutes to hours; and their results were essentially the same as those obtained by Barker,⁵¹ who carried out TGA work on CaCO₃ samples for up to 40 cycles. The fast carbonation stage is clearly the one that is of practical importance in any power generation cycle. Subsequently, Silaban et al.⁵² demonstrated, using a TGA reactor, that dolomitic sorbent retained its reversibility significantly better than did a calcitic one, which they attributed to the extra pore volume due to the calcination of the magnesium component in dolomite.

Later, Shimizu and his co-workers explored the possibility of a twin fluid bed reactor for the removal of CO₂ from combustion processes.^{53,54} In their proposed system, capture occurred at 600 °C and regeneration was done at 950 °C, using fuel burned in pure oxygen. This system could be fitted with any coal-fired power plant, but their calculations were made for a 100 MW power station burning bituminous coal. An interesting conclusion of the second article⁵⁴ was that the net efficiency of this type of process was somewhat better than a comparable oxy-fired scheme.

In 2003, Abanades and co-workers proposed a pressurized scheme⁵⁵ whereby coal combustion and CO₂ capture were achieved in a single reactor, and regeneration occurred in a separate reactor. In Figure 3, E_{CO_2} is the overall CO₂ capture efficiency, and F_{gas} is the flow rate of all other gases, except CO₂, from the combustor (kmol/s); F_{CO_2} is the flow rate of CO₂ produced by combustion (kmol/s); F_0 is the makeup flow rate of fresh limestone (kmol/s), equivalent to the CO₂ produced from this limestone (kmol/s); and F_R is the flow rate of recycled sorbent (kmol/s), excluding fresh makeup.

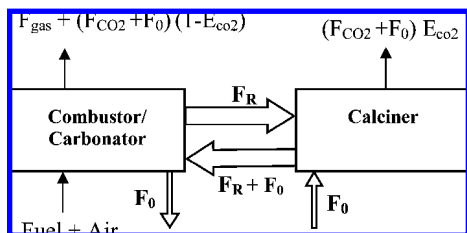


Figure 3. Schematic of lime carbonation/calcination cycle to separate CO₂ from flue gases.

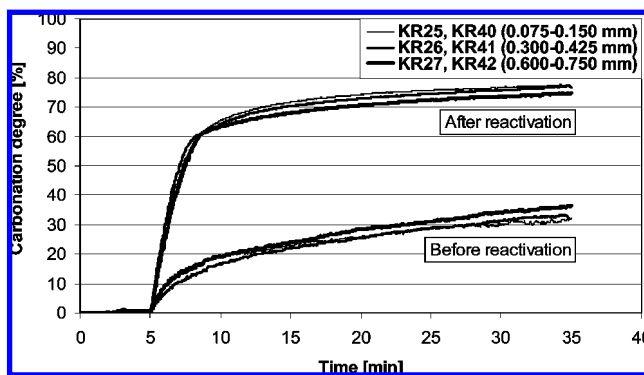


Figure 4. Comparison of (i) spent sample carbonation after 20 CO₂ cycles in tube furnace (before reactivation) and (ii) carbonation of same samples after steam reactivation (after reactivation).

They noted that such a scheme could be operated under a number of different pressure and temperature regimes, depending on the combustion characteristics and the desired degree of CO₂ removal. These workers also suggested that such a system could be deployed for any low-ash, high-combustible fuel, and that spent sorbent might even be used to help improve the economics of such an approach.

These workers and others have also looked at reactivating sorbents to reduce the falloff in activity or CO₂-carrying capacity of the sorbent. Methods included the traditional ones for improving sulfur capture with spent limestone-based sorbents such as the use of hydration and the addition of salts.⁵⁶ Steam reactivation was particularly effective,⁵⁷ but in the pilot-plant environment salt and sodium carbonate addition actually caused the sorbent to lose activity.⁵⁸ Figure 4 shows some results obtained for samples produced in a tube furnace.⁵⁹

Fennell and his co-workers⁶⁰ have also reported that even moist air was sufficient to return up to 55% of the activity or CO₂-carrying capacity of the sintered limestone sorbent.

The capture of CO₂ from combustion gases in a fluidized bed of CaO was also confirmed using a small pilot plant (100 mm diameter × 5 m tall). This work confirmed that the fast reaction period was sufficiently rapid to ensure very high captures in a fluidized bed system at temperatures around 650 °C and that even after 11 cycles the sorbent still had sufficient activity in the fast regime to ensure good capture.⁶¹ In a subsequent study, these authors looked at a range of processes for a nominal 100 MW thermal power station, delivering CO₂ compressed to 10 MPa suitable for storage in a geological formation.⁶² What they found was that, in all cases, processes could be developed with high net power generation efficiencies in the range of 37.7 to 40% depending on the cycle considered, which compared favorably with a conventional O₂/CO₂ system. Further, they noted that additional CO₂ credits could be claimed: if the spent lime was used in some other process such as cement manufacture, thus displacing lime manufactured specifically for that process; and/or if biomass were co-fired (a

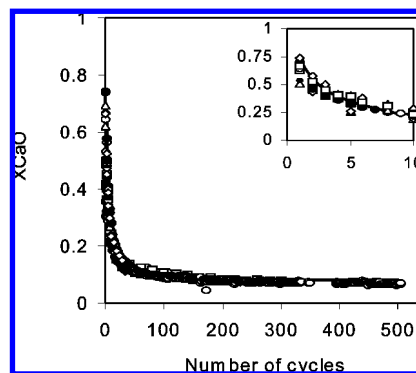


Figure 5. Long series of carbonation/calcination cycles (Grasa and Abanades⁶⁹) and data from earlier work, compiled in Abanades.⁶²

number of these cycles are compatible with co-firing of biomass), which potentially allows one to claim very high CO₂ credits.

A new finding that captured SO₂ not only deactivated the sorbent for CO₂ capture but also actively reduced the performance and reversibility of CO₂ capture under combustion conditions,⁶³ suggested that direct capture in the combustion chamber for most coals would not be practical, although interestingly enough, CaS formation such as would occur in a gasification environment had no such limits.⁶⁴ This finding has led the author and his collaborators to look at different possible cycles where SO₂ is scrubbed prior to CO₂ capture. This study found that options where the spent sorbent was sent to either an atmospheric or pressurized fluidized bed combustor to carry out deep removal of the SO₂ appeared to be promising.⁶⁵ It is also interesting to note that a separate economic evaluation of a pressurized system with the co-capture of SO₂ and CO₂ continued to support the idea that such a cycle would be economically competitive with amine scrubbing.⁶⁶ Finally, in other studies where CO₂ sorbents were generated after 10 to 20 cycles, work on reactivation with steam suggested that the decay in small pores (<200 nm), suitable for fast carbonation, produced sorbents that showed remarkably superior performance in terms of SO₂ capture (i.e., greater than 80% utilization was possible).^{59,67} If these findings are found to be general, then this may also suggest an option in which CO₂ capture is done with reactivated calcined sorbent, with subsequent SO₂ capture using the spent sorbent after it has developed superior sulfur capture behavior.

The decay of activity in limestone sorbents was first modeled in terms of a two-parameter model, relating the degree of conversion to the number of carbonation/calcination cycles:

$$X_N = f_m^N (1 - f_w) + f_w \quad (7)$$

where f_m and f_w are fitting constants taking values of $f_m = 0.77$ and $f_w = 0.17$, N is the number of cycles, and X_N is the degree of conversion to carbonate at each cycle (see Figure 5).⁶¹ These fitting constant values have been shown to vary significantly; for example, Fennell et al.⁶⁸ reported values for f_m ranging from 0.22 to 0.82 and for f_w ranging from 0.13 to 0.35. However, significant efforts have proceeded to find better versions of the equation used to describe the degree of conversion. Thus, for instance, Wang and Anthony⁶⁹ offered an even simpler equation, which suggested that the decay in activity would continue indefinitely. This was plausible because hitherto most tests had been done for 50 or fewer cycles. In a long series of carbonations/calcinations of up to 500 cycles, Grasa and Abanades⁷⁰ have confirmed a residual activity of about 7–8%

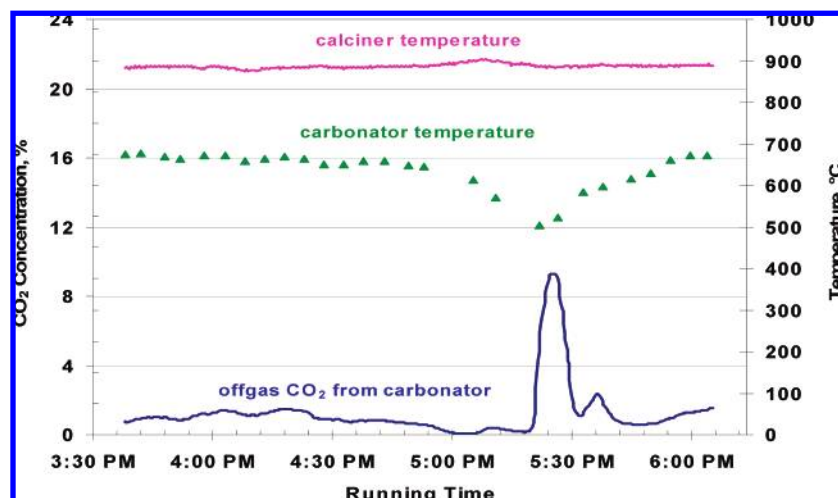


Figure 6. Operation of a pilot-scale FBC lime-based CO₂ looping cycle.

from 50 to 500 cycles (Figure 5). These findings have been confirmed by some recent work at the University of British Columbia, which has taken this process up to 1000 cycles and reports very similar results.⁷¹ For all practical purposes, one can thus count on indefinite activity, albeit a low one, for a limestone-based sorbent, because reasonably one can expect that for much higher numbers of cycles material loss due to attrition phenomena will dominate. Also interesting is evidence suggesting that the residual activity caused by sintering over many carbonation/calcination cycles is due to the formation of an interconnected CaO network, which acts as a refractory support and determines the sorption performance.⁷² A final comment on such residual activity is that a situation in which only 7–8% of the sorbent is active is not essentially different from the case in which one has a good carrier supported on an inert substrate (as is the situation with chemical looping combustion), albeit that one carrier takes oxygen to the combustion zone, and the other removes CO₂ from the combustion region.

Development of a process for CO₂ removal based on residual capacity was suggested by the Abanades group⁷³ on the basis that, even at this level, the carrying capacity of lime at 60 mg/g of sorbent is quite respectable, comparing well with other proposed CO₂ removal sorbents.⁷⁴

The issue of mechanical losses due to attrition has not as yet been properly explored for these cycles but some preliminary work has suggested that the mechanical stability of these sorbents may be enhanced by very slight sulfation (1–2% conversion).⁷⁵ Fennell and his colleagues⁶⁸ noted that most of the limestones they tested lost less than 10% of their mass due to attrition over the course of a typical 8 h test when using a small bubbling bed, and their results are in reasonable agreement with those from tests carried out in a larger (100 mm diameter) CFBC pilot plant operated in a batch mode⁷⁵ using one of the limestones tested by Fennell and his colleagues. However, this is an area requiring urgent attention as soon as the first practical pilot-plant systems become available. Should attrition be shown to be a major problem, various other solutions may also be employed, such as pelletization of the fines escaping the primary reaction loop, to allow these materials to be used in the cycle in a fluidized bed environment, and possibly heat treatment to improve the mechanical stability of the particles. Any such treatment will increase the costs of a calcium looping process, and the implications for the economic viability of the calcium looping cycle concept will need to be re-evaluated for any such approach.

Finally, it should be noted that this discussion has been restricted to natural sorbents. In part, this is because a simple economic analysis indicates that some of the more expensive options may require testing for tens of thousands of sorption/desorption cycles before they can be considered as viable options for CO₂ capture for power plants.⁷⁶ This also suggests that a certain amount of care needs to be taken in terms of extrapolating results from TGA and other systems if small numbers of cycles (<20) are examined because sorbents in real systems will have to stand up to many cycles, with the number increasing as the sorbent or carrier becomes more expensive, if they are to be considered economically viable alternatives to amine scrubbing. The same caveat would obviously apply to oxygen looping cycles, although the pilot-plant work done to date suggests that some of these oxygen carriers at least are remarkably stable.

In the author's own laboratory, the calcium looping cycle concept has been recently demonstrated on a continuous basis at atmospheric pressure. This has been done at the small pilot-plant level (whose design is described elsewhere⁷⁶) for several hours at a time, with over 90% CO₂ removal from the carbonator and delivery of up to 80% CO₂ in the calciner when it was run in the oxy-fuel mode, firing biomass, or coal. It should be noted that biomass firing offers the interesting possibility of a net reduction in anthropogenic CO₂ emissions, assuming that biomass firing is regarded as CO₂ neutral.⁴⁵ Figure 6 shows some results from these tests. Here, the CO₂ emissions remain below 2% providing the carbonator temperature is kept above 650 °C; when the carbonator temperature is allowed to fall below 600 °C, CO₂ emissions quickly rise, but rapidly recover if the temperature is brought back above 600 °C.

Whereas these test results are quite preliminary, they are encouraging and suggest that this technology can also be brought quickly to the market providing the issue of attrition can be dealt with.

Conclusions

Two types of chemical looping have been presented here. The oxygen looping cycle or chemical looping combustion is clearly the more developed of the two technologies. Currently, tests have been carried out for up to 200 h with various metal/metal oxide systems, and the results with methane or natural gas have been extremely good. It is also clear that atmospheric pressure syngas would perform as well or better. Whereas there

is a serious need for these systems to be examined at the large pilot scale, there seems very little doubt that chemical looping combustion can be brought to the market for natural gas with considerable confidence in its expected performance. However, this is not the case for syngas produced under pressure, in a typical IGCC system for example, and much work will be needed to allow this technology to make the transition to dealing with gas from IGCC or similar systems. Nonetheless, given the remarkable success to date, significant progress can be expected in resolving these problems in the near future.

CO₂ looping technology, despite having been demonstrated at the full industrial scale several decades ago, is still in its early stages. However, at least for crushed limestone, that is, natural sorbents, it shows considerable potential for application with coal-based systems. In gasification systems, it seems likely that it could be quickly deployed if economic incentives for avoided CO₂ were provided. However, it is in the area of coal combustion where it appears to have the potential advantages over chemical looping cycles because such sorbents are intrinsically cheap and are unlikely to be significantly affected by the presence of fairly high degrees of contaminants such as ash or acid gases. Like chemical looping for high-pressure syngas, this type of technology needs to be demonstrated at the large pilot scale before it can be seriously considered for practical deployment. However, such demonstrations are likely to be soon underway, and there is every hope that this technology will quickly make the jump to practical application.

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