

The Class and Home Problems section is intended to present novel and innovative scenarios that can enhance the teaching of chemical engineering topics. Submissions must have clear learning objectives, outcomes, or similar statements. The fit within a typical chemical engineering (or closely related) curriculum should be clear. Problems may represent a new application of fundamental principles, substantive adaptations which enable effective pedagogical approaches, or new non-proprietary applications of software. Manuscripts should follow the same general guidelines as other CEE submissions, but should be submitted directly to Dr. David Silverstein (david.silverstein@uky.edu). The column was formerly edited by Dr. Daina Briedis, who oversaw the contribution below.

CARBON DIOXIDE (CO₂) CAPTURE

From Coal-Fired Power Plants

Using Calcium Looping

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Atmospheric carbon dioxide (CO₂) levels have risen from about 280 to 390 ppm following the industrial revolution and rapid progress since then. This increase along with changing weather patterns has caused some alarm and subsequent thrust in research activities in the fields exploring the role of CO₂ in climate change as well as strategies to reverse the increasing trend in atmospheric CO₂ concentration. Global energy demand is predicted to increase by about 50% in the next 20 years and carbon-intensive fossil fuels (such as coal, oil, and natural gas) will continue to supply the majority of this energy. Consequently, CO₂ emissions are also predicted to rise considerably, and thus, it is necessary to develop effective and economical methods of controlling the same.

Although several sources (*e.g.*, transportation sector and chemical manufacturing) make contributions to the atmospheric CO₂, it is important to target large and stationary point sources when developing CO₂ control technologies. The heavily fossil fuel-dependent electricity generation sector presents such a source. Today, coal combustion provides approximately 40% of all the electricity generated in the world and accounts for about 41% of the total CO₂ emissions.^[1] In the United States, coal-fired power plants produce roughly half of the total electricity and emit one-third of the CO₂. Therefore, several ongoing research efforts have been

dedicated to the development of CO₂ control technologies for fossil fuel-based electricity systems in general and coal-fired power plants in particular.^[2]

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In a typical coal-fired power plant, coal is first combusted in a boiler to produce hot combustion gas. This gas is heat-exchanged to generate steam, which is then used in steam turbines to produce electricity. The combustion flue gas is then sent through several gas clean-up units to remove pollutants such as SO_x , NO_x , and particulates, before venting through the stack. As legislation mandating CO_2 control is only recently coming into effect, most existing plants do not have any CO_2 control system installed. When CO_2 removal is desired, the flue gas will be sent through an additional gas clean-up unit/reactor— CO_2 absorber. In this absorber, the CO_2 removal can be affected using liquid solvent, solid sorbents, etc. To regenerate the solvent/sorbent, another reactor—regenerator—will be necessary. The regenerator will provide a pure CO_2 stream for sequestration (or storage) and the regenerated solvent/sorbent which can be recycled back to the absorber.

The calcium oxide (CaO)-calcium carbonate (CaCO_3) cycle is among the most widely studied cycles for large-scale CO_2

control.^[3,4] The reversibility of the CaO-CO_2 reaction enables this solid sorbent to be used repeatedly, and the cycling between two reactors completes a closed loop of the solids, thus the name, calcium looping. In this article, we examine this technology using the example of a coal-fired power plant.

INTRODUCTION TO CALCIUM LOOPING

Calcium looping is a CO_2 capture technique using a solid sorbent, and is based on the following reversible reaction:



CaO reacts with CO_2 from a mixture of gases to effectively separate it to a desirable degree. The sorbent converts into its carbonate form— CaCO_3 . In a separate reactor, this carbonate so formed can be decomposed to regenerate the CaO and release pure CO_2 . In this way, CO_2 is removed from a mixture of gases, by “fixing” it in the solid metal carbonate form and separating it in its gaseous form at another location. The regenerated sorbent (CaO) can then be re-introduced in the gas stream containing CO_2 , completing the solids loop. The simplified schematic of the process is given in Figure 1. Here the carbonator is the CO_2 absorber and the calciner is the regenerator.

The thermodynamic equilibrium curve of Reaction (1) is shown in Figure 2. The forward reaction of capturing CO_2 is called “carbonation,” and the reverse reaction is termed as “calcination.” If the temperature and the CO_2 partial pressure in the reactive atmosphere are below the equilibrium curve, calcination is the thermodynamically favored reaction. If the reaction conditions are above the equilibrium curve, carbonation occurs. This reversibility of the reaction is the key concept of the calcium looping process. The information provided in Figure 2 can be used to determine the operating conditions of the carbonator and the calciner. For example, flue gas produced from coal combustion typically contains 10% (by vol.) CO_2 and is available at atmospheric pressure, which corresponds to a partial pressure of 0.1 atm. To reduce this CO_2 by 90% [which is a target specified by the U.S. Department of Energy (DOE) for all CO_2 control technologies^[2]], the carbonator needs to operate at 650 °C or lower. Since the kinetics of the reaction will be favored at higher temperature, it will be advantageous to operate the carbonator at 650 °C. Similarly, from Figure 2 it can be concluded that the calciner will operate at or above 890 °C, so that a pure stream of CO_2 can be produced for sequestration.

One of the key aspects that make calcium looping economically attractive is the raw material that can be used to produce the sorbent (CaO)—limestone (CaCO_3). Limestone is a naturally occurring, abundantly available, and inexpensive resource. Theoretically, 1 mole CaO can react with 1 mole CO_2 , giving an extremely high capture capacity of 0.79 g CO_2 /g CaO sorbent (although complete conversions are never

achieved due to mass transfer limitations). However, it has been observed that the capacity decreases (see Figure 3) as the sorbent is cycled. This is an imminent hurdle in the further development of this technology. The reason for this decrease is “sintering”—a phenomenon that occurs at high temperatures used during calcination. The effect is that the sorbent loses

reactivity toward CO_2 . Current research efforts are focused on finding a suitable method of averting or reversing sintering.

To address this issue, a unique three-step calcium looping process was proposed and developed at The Ohio State University (OSU), which incorporates an intermediate sorbent reactivation step.^[3,5] The reactivation is conducted by hydrating CaO every cycle. The process schematic is shown in Figure 4. The hydration reaction is known to reverse the deactivation due to sintering and restore sorbent reactivity. The sorbent undergoes the reverse reaction *viz.* dehydration, prior to reacting with CO_2 in the carbonator.

PROCESS DESCRIPTION

The simplified process flowsheet is shown in Figure 5. It consists of the coal-combustion boiler and the three calcium looping reactors—carbonator, calciner, and hydrator.

About 204 tons per hour (tph) of coal is combusted in the boiler, which produces the hot combustion gas and ash. The combustion gas is heat-exchanged to produce steam, which is used in the steam turbine cycle of the plant to produce electricity. This gas (henceforth referred to as “flue gas”) is then sent to the carbonator. The flue gas (stream 1) contains nitrogen (N_2), CO_2 , steam (H_2O), O_2 , sulfur dioxide (SO_2), and flyash (particulates). The given coal input to the boiler is equivalent to a 500 MWe plant, which is the generation capacity of a typical coal-fired power plant. The output from the boiler (in terms of mass flow rates of the components) is provided in Table 1 (next page).

From the boiler, the flue gas is sent to the carbonator. The calcium sorbent (stream 12) enters the carbonator in the form of Ca(OH)_2 supplied by the hydrator. In the carbonator, the following reactions occur



The calcium sorbent loading in the carbonator is maintained such that 90% CO_2 capture is achieved. It should be noted that although steam enters the carbonator, the operating conditions of the carbonator are such that instantaneous decomposition of Ca(OH)_2 will be favored, and CaO hydration [reverse of Reaction (2)] will not occur. Due to the above reactions, the gas at the exit of the carbonator is lean in CO_2 and SO_2 , and the solids mainly contain CaCO_3 along with smaller quantities of CaO and CaSO_4 . The unreacted CaO is due to the use of excess calcium sorbent than is stoichiometrically necessary. The gas-solid mixture coming out from the carbonator (stream 2) is separated in a particle capture device (*e.g.*, cyclone)—PCD1. The clean gas (stream 3) is vented out of the plant or used for further heat-exchange downstream, and the solids (stream 4) are sent to the calciner.

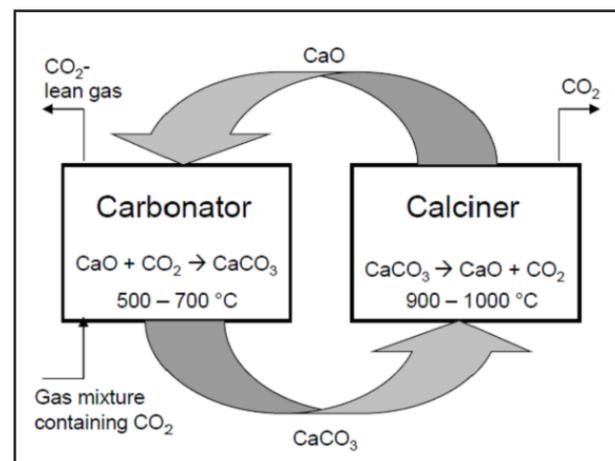


Figure 1. Simplified schematic of the calcium looping process.

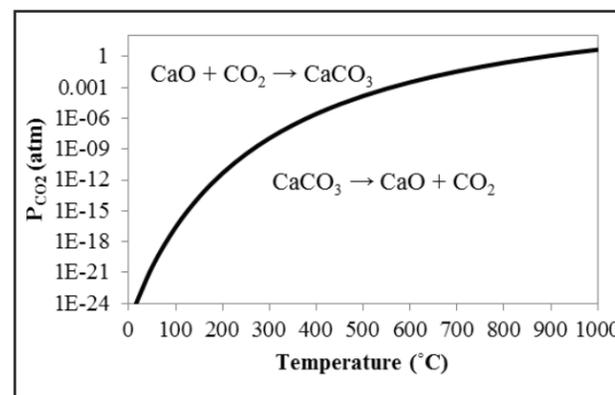


Figure 2. Thermodynamic equilibrium curve for the reversible reaction between CaO and CO_2 .

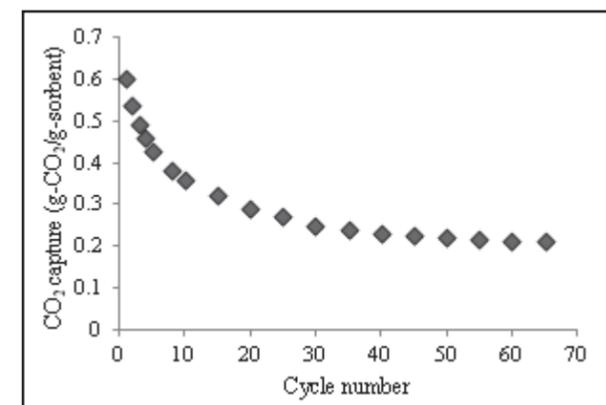


Figure 3. CO_2 capture capacity of limestone-derived CaO over multiple cycles.

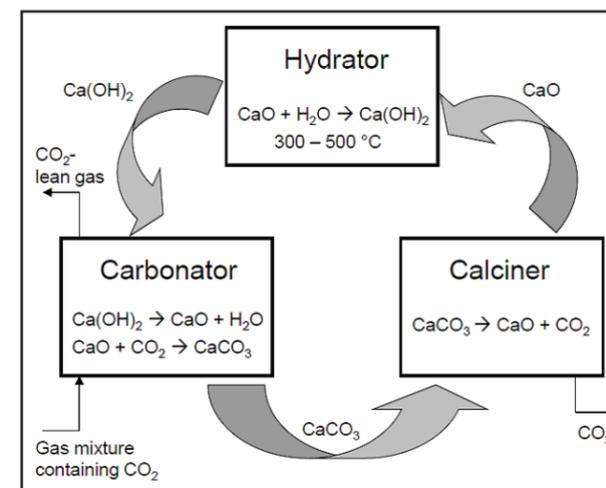


Figure 4. Simplified schematic of the three-step calcium looping process developed at OSU.

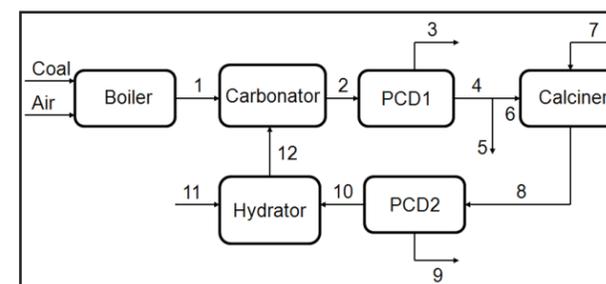
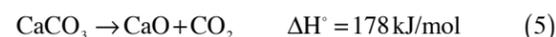


Figure 5. Process flowsheet for calcium looping process for CO_2 capture from coal-combustion flue gas.

Component	Mass flow rate (tph)
N ₂	1782.94
CO ₂	525.05
H ₂ O	98.61
O ₂	89.82
SO ₂	8.89
Ash (solid)	0.264

In the calciner, the CaCO₃ is decomposed to form CaO, and CO₂ is released as per the following reaction



At the operating conditions of the calciner, the CaSO₄ does not decompose. Thus, the sulfur capture reaction is irreversible with respect to the calcium looping process. To avoid the buildup of CaSO₄, ash, and other inerts in the solids loop, a purge stream (stream 5) is maintained prior to the calciner, and sufficient make-up sorbent (stream 7) is supplied to the calciner. Again, a particle capture device—PCD2—is used to separate the gas-solid mixture at the exit of the calciner. The CO₂ (stream 9) is sent for sequestration and the solids (stream 10) are sent to the hydrator.

In the hydrator, steam (stream 11) is supplied to hydrate the CaO and form Ca(OH)₂ according to the following reaction



From the hydrator, the Ca(OH)₂ is supplied to the carbonator completing the solids loop.

PROBLEMS FOR PRACTICE

This process can be used to illustrate basic chemical engineering functions such as mass and energy balance calculations. Some examples are provided in this section. The study of this system offers the students a glimpse of the research conducted on climate change, as well as an opportunity to handle problems involving solid reactants. (The solutions can be obtained by contacting the corresponding author.) The following is suggested as an assignment for students:

Problem 1

Using the information given in the Process Description section, perform a detailed material balance across each unit in Figure 5. Make the following assumptions to simplify the material balance calculations:

1. A calcium to carbon mol ratio (Ca:C) of 1.33 is sufficient to capture 90% CO₂ and 100% SO₂ in the carbonator.
2. All particle capture devices operate at 100% efficiency.
3. Purge rate is 5% (by mass) and the solids are removed

from the loop prior to the calciner as shown in Figure 5.

4. The make-up stream supplied to the calciner is in the form of pure CaCO₃. The make-up should equal the amount of calcium (in moles equivalent) exiting the system through the purge.

5. Extent of calcination in the calciner is 98%.

6. The hydrator operates at a steam-to-calcium mol ratio (S:CaO) of 1. Further, 98% hydration occurs in the hydrator.

Problem 2

The solid circulation rates among the three calcium looping reactors depend mainly on the Ca:C ratio used in the carbonator. A Ca:C of 1.33 was used in Problem 1, which has been experimentally identified by OSU as sufficient to achieve desired gas cleanup.^[5] Such a low Ca:C is possible only when using an intermediate hydration step. If the traditional calcium looping process (as shown in Figure 1) is used, a Ca:C of 5 to 20 may be necessary.^[6]

Compare the solid circulation rates (tph) in the carbonator for the two cases. Is there any existing commercial process in the chemical industry, which employs similar circulation rates?

Problem 3

As discussed earlier, a purge is maintained in the process to avoid the accumulation of inerts like CaSO₄, ash, etc. In a real process the solids purge will also occur due to the inefficiencies of the PCDs (PCDs were assumed to be 100% efficient in Problem 1). Theoretically, the purge stream can be maintained anywhere in the process—upstream or downstream of the carbonator, calciner, or hydrator. Sometimes the selection of the purge location can also provide additional advantages—for example, if the purge is located after the calciner, then the solid mixture (which is purged out) will mainly contain CaO and minor quantities of CaCO₃, CaSO₄, and flyash. Such a mixture can become useful in cement manufacture.^[4] Generally, cement manufacture involves calcination of limestone which also releases CO₂; thus the use of calcium looping purge material in making cement can potentially decarbonize two major industries.

Assuming that approximately 0.65 kg CaO is required for manufacturing 1 kg of cement, estimate what fraction of the coal-fired power plants in the United States should be retrofitted with the calcium looping technology so that all the CaO demand is satisfied by the calcium looping purge material. Assume that the 5% (by mass) purge is withdrawn from stream 10 in Figure 5. If this technology is used in all the coal plants worldwide, will it lead to an overabundance of the raw material?

Problem 4

Most coal-fired power plants currently under operation have an SO₂ removal (flue gas desulfurization) system because SO₂ is one of the criteria pollutants. Since the calcium looping

process enables simultaneous removal of CO₂ and SO₂, an independent SO₂ scrubber will not be needed. Alternately, calcium looping can be placed after the existing desulfurization units so that only CO₂ capture occurs in the carbonator. This will minimize the amount of CaSO₄ circulating in the loop. While each configuration has its own advantages and disadvantages, final decision will be driven by the economics.

Perform a material balance for a case where an independent unit for sulfur removal exists. Assume that this unit removes all the SO₂ and is placed upstream of the calcium looping process (*i.e.*, stream 1 in Figure 5 does not contain any SO₂).

Problem 5

Calcium looping is a high-temperature process and the energy requirement of the process is mainly in operating the calciner. If the carbonator is assumed to operate at 600 °C and the calciner is assumed to operate at 1000 °C, then heat will be needed in the calciner to heat the solids to the operating temperature (1000 °C) and to drive the highly endothermic calcination reaction.^[6]

Neglecting temperature dependence of heats of reaction and assuming a specific heat capacity of 0.08 kJ/mol °C for the solids, calculate the energy (in MWth) that needs to be supplied to the calciner. Compare this energy requirement to the energy (in the form of coal) supplied to the coal boiler, assuming an overall plant efficiency of 35% (*i.e.*, for each unit of heat supplied by combusting coal, only 0.35 unit is converted to electricity).

Problem 6

The energy required in the calciner is supplied by firing additional fuel (such as coal or natural gas) in the calciner.

For the energy requirement calculated in Problem 5, estimate the amount (tph) of fuel necessary if coal is used. Make the same estimation if natural gas is used. Which fuel would you recommend and why? Assume the higher heating value (HHV) of coal and natural gas to be 12,000 BTU/lb and 20,000 BTU/lb, respectively.

Problem 7

It is interesting to note that if the calciner fuel is combusted in air, it will produce another flue gas (different from stream 1). This flue gas will also contain a mixture similar to the one given in Table 1 and will come out in stream 9. This presents a problem because the plant will fail to produce a pure CO₂ stream for sequestration. Hence, in a commercial calcium looping process it is envisaged that the calciner fuel will be combusted using pure O₂ and not air. This mode of fuel combustion is termed as oxy-combustion.

When coal is used as a fuel in the calciner, how much additional CO₂ (tph) will be produced in the calciner itself? How does this compare with the CO₂ produced by the boiler? Assume that coal contains 70% carbon (by wt.) and complete coal combustion occurs in the calciner.

Problem 8

The U.S. Environmental Protection Agency has released emission standards under the new Clean Power Plan.^[7]

To limit the CO₂ emissions from coal-fired power plants to 1000 lb/MW-h, how much CO₂ (in %) should be removed from stream 1 (in Figure 5)? If the calcium looping process is used for the same, what is the Ca:C that you would use in the carbonator for achieving this CO₂ reduction? Assume that the following relation is true:

$$y = 57.283 \ln(x) + 76.926$$

where y = % CO₂ removal required and x = Ca:C.

CALCIUM LOOPING AS A DESIGN PROJECT

The questions discussed in the Problems section are examples of simple material and energy balance problems based on calcium looping. Further in-depth analysis of a calcium looping system is also possible, by treating it as a design problem. At OSU, such a project for pre-combustion CO₂ capture application has been integrated into a senior-level undergraduate design course taught in an 11-week quarter by one of the authors (L.-S. Fan) for the last 10 years. The principles explained in the article are used extensively in this project, using the two-stage calcium looping system applied to a coal-to-hydrogen plant with integrated CO₂ capture. In this project, the students design a plant for production of hydrogen (H₂) from coal. The students learn that using calcium looping for pre-combustion CO₂ capture has a number of advantages, including an increase in the efficiency of the coal-to-hydrogen conversion, and production of a sequestration-ready pure CO₂ stream. The design problem is discussed in further detail in Appendix A.

COMPLIANCE WITH ABET STUDENT OUTCOMES

The problems described in this paper directly map out to various student outcomes defined by the ABET engineering criteria.^[8] This is an opportunity for students to delve into the problem of climate change, through the example of calcium looping. Through this study, students will come to appreciate the importance of offering engineering solutions in a global environmental context, while also meeting the societal demands for energy through economic means. Although this study does not require conducting experiments, students have to rely on engineering assumptions and available experimental evidence when theoretical knowledge falls short. In so doing, they enhance their ability to analyze and interpret data. Through the design project exercise, students also acquire the ability to design specific units as well as the entire process. Climate change is an important and pressing contemporary issue, which the students learn to tackle with the help of modern engineering tools such as design and computational softwares. Systems thinking is instilled into

students with the help of concepts such as overall process efficiency, heat recovery and integration, and so forth.

CONCLUDING REMARKS

Development of carbon capture and sequestration (CCS) methods has been identified as one of the “grand challenges for engineering” and has been the focus of several recent research efforts.⁹¹ Chemical engineers are expected to play a crucial role in this development, which will affect the energy industry in particular and society in general. This article is, therefore, intended to engage the next generation of chemical engineers by providing them an insight to this field. Using material and energy balances—core to any chemical engineering evaluation—this exercise highlights one of the most promising CCS technologies: calcium looping. Besides providing an interesting case study, this article intends to inform and inspire future chemical engineers to tackle similar problems.

ACKNOWLEDGMENTS

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