



To what extent will factors such as types of sorbent attritions, carbonation temperatures and gas humidity influence the capability of carbon capture using CaO?

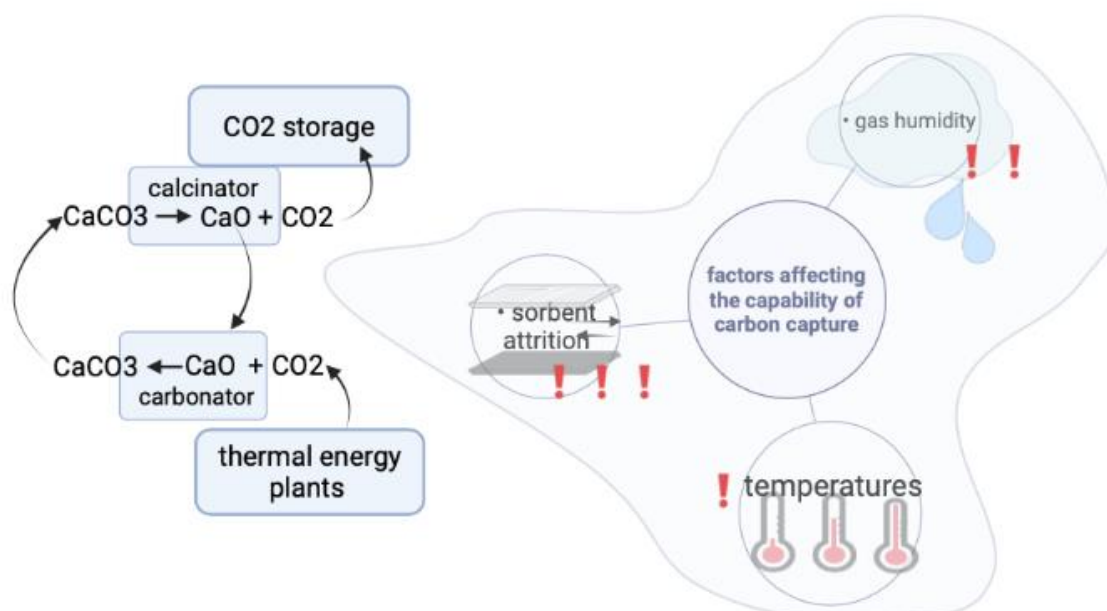
By Harrison Xu

Table of Contents

Abstract	1
1.Introduction	2
2.How does the calcium looping carbon capture work?	3
3.What is the importance of calcium looping carbon capture to the environment?	4
4.Factors that affect the capability of the calcium looping carbon capture	5
a.Sorbent attrition	5
b.Temperatures	5
c. Gas humidity	7
5.What are the extent to which these factors affect the carbon capture industry?	7
6.Conclusions	8
7.Abbreviations	8
8.Bibliography	8

Abstract

The greenhouse effect caused mainly by the increasing carbon emissions are getting more serious, and hence the scientific research in alleviating it is carried out, which is important. It is found one of the most suitable technologies is the calcium-looping carbon capture including the separation of the compound gases, transformation, and storage of the carbon dioxide. This typical carbon capture operates with two functional reactors within a circuit, with carbonation and calcination of calcium oxide which are responsible for the absorption and transformation of carbon dioxide. High efficiency, relatively low oxygen-demanding, facilitation of electricity output and regeneration of the sorbent are found to contribute largely to the importance of calcium-looping carbon capture. Also, factors influencing the capacities are investigated. The experiment on how the sorbent attritions caused by SO₂ are mainly discussed, which the results showed that SO₂ has a significant effect on the sorbent deactivation but only a disappointing small amount of influence on the capability of the carbon capture. Besides, there are favoured temperature ranges and both going below or above the ranges are found having a negative effect on the capability. At last but not the least, gas humidity has, for some reactions, the ability to increase the capability of the carbon capture since it can enhance the reactivities of the reactors, but also, with some exceptions. Finally, the extent of influences on the industrial carbon capture that three factors have been compared, with sorbent attrition being the most influential to the capability of the carbon capture, whereas temperature the least. At the end of the review, some future directions for research are suggested.

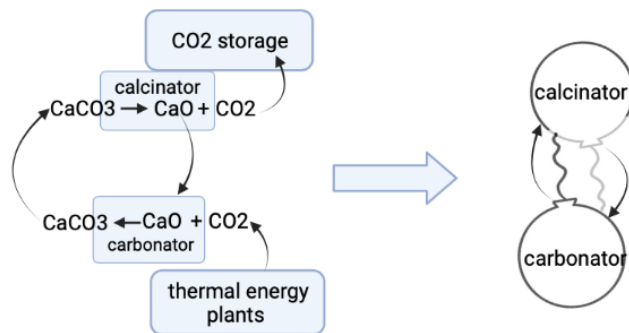




1. Introduction

As humanity is developing, this has led to deforestation, large scale agriculture along with industrialization, as a result, large amounts of greenhouse gases are hence released and accumulated in the atmosphere which has reached the criteria never seen before. This accumulation seriously affects climate change, and according to the UN, which is listed as one of the global issues that humans are facing. It is noted as well that approximately two-thirds of the greenhouse gases are contributed by carbon dioxide produced from burning fossil fuels (United Nations). Hence, the further, intensive researches in sustainable greenhouse gases reduction are encouraged (Pimenidou *et al.*, 2010). Here we will be evaluating the use of a well-developed technology in reducing CO₂--the carbon capture (CC) and investigating the factors that could influence its capability. CC includes several technologies absorbing CO₂ from the processes such as factory-scale thermal power plants, cement manufacture and iron and steel calcination which in general produce a large amount of carbon dioxide. For these industries, in fact, carbon capture is one of only a few remaining technologies which is suitable to reduce the carbon dioxide released considering the efficiency (Boot-Handford *et al.*, 2014). The application of carbon capture and storage (CCS) in plants involves mainly three stages, including: the separation of the CO₂ from released gases, transportation of captured gases to the other plants and finally, the storage of CO₂. During the CC, particular substances are used to capture carbon dioxide as the sorbent, and a lab-scale experiment suggested that compared with an amine solvent system, a solid adsorbent system could significantly reduce the energy penalty while the whole capturing system is working (Drage *et al.*, 2012). As a result, this review focuses on the solid adsorbent system, to be more specifically, the Calcium looping (CaL) CC.

As the carbon capture process is being better developed, the CaL process is becoming a very important technology available based on the idea of post-combustion CO₂ capture with fossil fuel fired power plants. CaL can reach a high efficiency using the common materials in earth--limestone as the sorbent for CO₂, and with the conversion of CaO and CaCO₃, the sustainability is ensured. As the technology tends to be applied worldwide, the factors which influence the capacity of the CC must be discovered and experimented so that we can achieve the maximum capacity. Those factors include but are not limited to: (i) sorbent attritions; (ii) temperatures; (iii) gas humidity. (i) Within the circuit of the conversion of CaO and CaCO₃, there are some resistances here called the sorbent attritions, which will decrease the capability of the CC. Many factors are related to the deactivation of the sorbent (Coppola *et al.*, 2012b). In this review, only the presence of sulphur dioxide is discussed. (ii) Temperature, which is closely signified as the particle kinetic, can also be a great dominating factor to the efficiency. As some research has shown, the different plants have neither the same temperature nor the extent when responding to the temperature change, and furthermore, the temperature fluctuation exceeding a certain extent could also have a negative effect on the capability of CC. (iii) Opposing the sorbent attrition, results show that steam can surprisingly offer extended potential for the operation of CC, so the extent is investigated by scientists. The aim of the review is not only reviewing and discussing CaL process, as well as the extent of the affection of three factors listed previously on CaL CC, but also compare those factors to reach a conclusion that which one is the most dominating in influencing the capacity of CaL CC process.



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2. How does the calcium looping carbon capture work?

There are basically two main steps in CaL CC, including the carbonations and calcinations. Limestone (CaCO_3), which is commonly found in the earth, is used in the CaL process as the raw material to produce lime through a single reaction ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$) at a

temperature above 850°C . This is known as the calcination of CaCO_3 . The produced CaO in the system reacts with CO_2 at a temperature over 600°C ($\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$), and that is the main process contributing to the absorption of CO_2 used in the carbon capture. The two processes mentioned above are operated in a circuit of two fluidized bed reactors: carbonator for CO_2 capture and regenerator as the place for sorbent calcination, which are connected with transport pipes in between.

As illustrated in Fig. 1 (Created with BioRender.com), compound gases generated while producing energies such as electricity in the thermal energy plants are blown into the carbonator. In the carbonator, CO_2 gas involved in the compound is absorbed by the carbonation of CaO and hence is separated and transferred into the calcinator in the form of limestone. The remaining gases which are CO_2 -free in the carbonator are safely released to the atmosphere. Back in Calcinator, where limestone arrives, is thermally decomposed, regenerating CaO and releasing a pure CO_2 stream. The CaO regenerated in the calcinator is transported back to the carbonator by pipes, whilst the released CO_2 gas is purified, compressed and is stored with some alternative methods which is not necessarily

Fig. 1: the circulation of two reactors and the analogy of this process. In the carbonator, CO_2 is absorbed by the carbonation of CaO and is separated and transferred into calcinator. Then in calcinator the limestone thermally decompose, giving out the CO_2 and the CaO . Regenerated CaO is then transported back to the carbonator, where the process repeats. The two processes operated in a circuit with two functional reactors resembles to a connection of two balloons together, as shown. (Created with BioRender.com)

discussed here. The circular chain reactions are designed to keep propagating.

Just as an analogy, the two processes operated in a circuit with two functional reactors resembles to a connection of two balloons together: the gas (which signifies the CaO) is treated with other different-compound gas (CaCO_3) and then is treated to give back the original gas (The treatments are basically separating, absorbing and releasing). And finally, the gas is blown back to the initial balloon where the steps mentioned above are kept repeating, in order to, in reality, capture CO_2 from the compound gases.



3. What is the importance of calcium looping carbon capture to the environment?

As the carbon capture process is being better developed, the calcium looping (CaL) process is becoming a very important technology based on the idea of post-combustion CO₂ capture with fossil fuel fired power plants. One of the reasons why it is important is that the efficiency of operating is above 90% in comparison to the 6% waste which is relatively low. Also, compared with the oxy-fuel combustion CC, the oxygen required can be relatively low when it comes to the CaL process. That is because they are based on different ways of capturing CO₂: oxy-fuel combustion utilises pure oxygen and hence produces pure CO₂ which is then stored directly (Wilberforce *et al.*, 2021), while the original gases in CaL CC is not pure CO₂. This difference largely alleviated the cost of producing pure O₂ and saved a lot of energy. Furthermore, there is an approximately 40-50% increment of the net output of electricity compared to the original thermal power system without the capture (Dieter *et al.*, 2013), evidences also support that it is the usage of the high temperature streams that significantly reduces the efficiency penalty of the CaL CC (Perejón *et al.*, 2016). At last but not the least, the CaL CC is one of the most effective ways of reducing greenhouse gases in the long term, since the raw materials are regenerated and there is just a small proportion of deactivation.

Overall, CaL is a promising, efficient carbon capture technology that may greatly aid in the reduction of greenhouse gases if adopted by industries.

4. Factors that affect the capability of the calcium looping carbon capture

a. Sorbent attrition

According to (Dieter *et al.*, 2013), limestone can be more easily corroded than other materials in the CaL CC due to its relatively high porosity and the low hardness. The two main reasons for attrition may be attributed to the thermal stress of the calcination and the mechanical stress in the reactor. SO₂, which is found as a main contributor to the calcium deactivation, is being studied about its effects on CO₂ capture capacity (Coppola *et al.*, 2012b). In the experiment carried out by (Coppola *et al.*, 2012b), five calcination/carbonation cycles were carried out in bubbling fluidized bed reactors, with the same amount of similar sized limestone. The SO₂ concentrations in which representing the pre-desulphurized flue gas were given initially 110 and 1800 ppmv respectively in different sets of experiments and the concentrations were measured which represent the extent of the conversion of calcium to its sulphate. The measuring of the CO₂ concentrations at the exhaust port showed the degree of both the calcination and the carbonation at different stages of the reaction. To give the results, the capacity of CC was given by the ratio of total amount of CO₂ absorbed (by mass) to the initial amount of limestone, shown below.

$$\text{capacity} = \frac{\text{total amount of CO}_2 \text{ absorbed (by mass)}}{\text{initial amount of limestone (by mass)}}$$

The results show that the percentages of Ca converted to sulphate is found to be 27% with 1800 ppm of SO₂, whilst the data is 1.5% with 110 ppm SO₂. The huge, significant incline claims that SO₂ is clearly a consequence of deactivating the sorbent. However, comparing



the time of the reaction, which means the other factors are the same, performing for 45 min instead of 15 min shows surprisingly a 13% decrease of the conversion. It can be briefly explained that the time is long enough to absorb almost all the CO₂ and SO₂ (Coppola *et al.*, 2012b). It is then thought to be better for further potential research to focus on the different performing times with same sulphur fractions so that a clear pattern presenting the decreased tendency is obtained and the theory explaining the consequences could be proved. Talking about the influence on capability, experiment with no SO₂ used shows the maximum capability, which is 0.098 g/g. Although with disappointing small amount, it shows that the higher the concentration, the lower the capabilities that results in, from 0.044 g/g with 110 ppm SO₂, to 0.036 g/g with 1800 ppm SO₂, which may be interpreted by the existence of calcium sulphate shell formed on the surface of the sorbent. Besides SO₂, there are many other factors that may worsen the sorbent attrition, such as the particle size measurements (Malvern Mastersizer) (Dieter *et al.*, 2013) and number of cycles that the fluid goes (Coppola *et al.*, 2012a)(Coppola *et al.*, 2012b).

The significant deactivation of the capture sorbent suggests that sorbent attrition can influence the capability of the CC and further research with pilot scale facilities are suggested to focus on how to alleviate the drawback of those attrition.

b. Temperatures

Temperature may have the potential to determine the capabilities of CC as the calcination and carbonation processes are endothermic and exothermic respectively. Research experiments which are carried out with a bubbling fluidized bed reactor (Coppola *et al.*, 2012a) proved the predictions. The conditions the separate three experiments used are listed as table 1 below: the conditions set for the carbonation were not changed, with 15 minutes' reaction time, 700 Degree Celsius and the inlet CO₂ concentrations reaching 16 %v/v in balanced air. Differently, the time operating varied from 15min to 35min, temperature was set at 850 and 900 separately, and the inlet concentrations of CO₂ changed from 0 to 44 %v/v.

Calcination/carbonation	Condition 1		Condition 2		Condition 3	
Duration [min]	15	15	35	15	20	15
Temperature [degree]	850	700	850	700	900	700
Inlet CO ₂ [%v/v]	0	16	20	16	44	16

Table 1: the conditions used for separate experiments: note that the carbonation conditions are not changed, but for calcination.
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It is found that the capture capability of conditions 1 and 2 are, to a high extent, similar, which is decreased from about 0.27 to 0.17 and from 0.26 to 0.11 g/g respectively according to the increase of number of cycles. However, the experiment with 900 Degree Celsius calcination-temperature shows significant decline even at each cycle compared with the previous two, with the capability ranges of 0.155 to 0.06 g/g. This large difference may be interpreted by an enhancement of sintering at higher temperature (Coppola *et al.*, 2012a) (Borgwardt, 1989). The higher the temperature, the greater extent a decrease of sorbent capability will show. Although the results do not match that of the experiment demonstrated by (Dieter *et al.*, 2013), it is the type of the CC which altered and resulted in the differences.

However, when it comes to the low temperature zones, the situation seems to disobey the results we have found. Fig. 2 is plotted whereby CO₂ gas percentage concentration (y-axis) against time of the operation (x-axis).

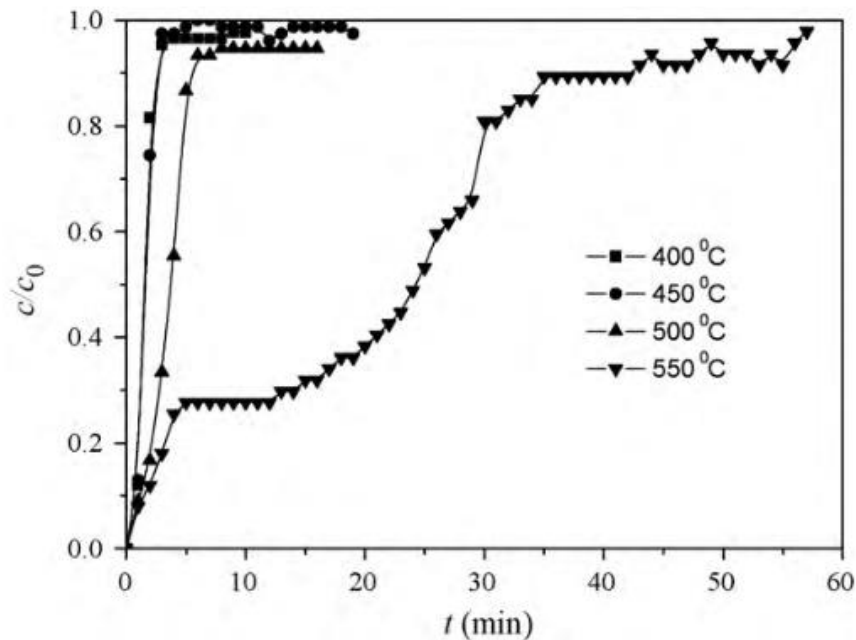


Fig. 2: It is plotted whereby CO₂ gas percentage concentration (y-axis) against time of the operation (x-axis) It shows with the more sufficient temperature (550 °C), about 70% of the CO₂ is captured at 550. ADDIN CSL_CITATION {"citationItems":{"id":"ITEM-1","itemData":{"ISSN":"0304-

The results show that when temperatures vary around 400-500 °C, the CO₂ concentrations increase significantly to 100% within 5 minutes, which represents that the capability of CC is fairly low. But when the temperature is 550 °C, the concentrations can be maintained at around 0.3 in the capture plant for 13 minutes, which means about 70% of the CO₂ is captured at 550.

In general, the temperature used cannot be either high or low, to result in a fairly capable CC. It still needs to be further investigated to find out in what temperature range is the most suitable for the highest efficient CC.

c. Gas humidity

The details of the experiment on the effect of gas humidity are considered below:



	Calcination	Carbonation
<i>dry</i>		
Temperature	940 °C	650 °C
Test duration	20 min	15 min
Fluidisation superficial velocity	0.7 m s ⁻¹	0.6 m s ⁻¹
Fluidising gas flow rate (at 25 °C)	826 L h ⁻¹	930 L h ⁻¹
Fluidising gas composition (vol.)	70% CO ₂ + 30% air	15% CO ₂ + 85% air
<i>ste_cal</i>		
Fluidising gas composition (vol.)	10% steam + 70% CO ₂ + 20% air	15% CO ₂ + 85% air
<i>ste_car</i>		
Fluidising gas composition (vol.)	70% CO ₂ + 30% air	10% steam + 15% CO ₂ + 75% air
<i>ste_cal_car</i>		
Fluidising gas composition (vol.)	10% steam + 70% CO ₂ + 20% air	10% steam + 15% CO ₂ + 75% air

Table 2: the conditions designed for Coppola *et al.*'s experiment. Note that the addition of steam in separate reactions are indicated by *ste_reaction*. E.g., *ste_cal_car* indicates that 10% steam is added to both calcination and carbonation parts.

The main process conditions are summarised in Table 2 above (Coppola *et al.*, 2017). Note that the addition of steam in separate reactions is indicated by *ste_reaction*. E.g., *ste_cal_car* indicates that 10% steam is added to both calcination and carbonation parts. The outcomes shows that capture capacities of CO₂ are in the range: 0.179–0.093 (*ste_cal_car*), 0.178–0.070 (*ste_car*), 0.158–0.040 (*dry*) and 0.153–0.038 (*ste_cal*) g/g (Coppola *et al.*, 2017). Generally, the addition of the steam has significantly enhanced the capacity of the CC, as the capacities shown in the reaction *ste_cal_car* and *ste_car* were fairly greater than that when dry gases are used. That may be explained by adding steam actually enhance the sorbent reactivities, and hence the capability is facilitated (Coppola *et al.*, 2017). This idea seems to reach an agreement with (Dieter *et al.*, 2013), whereas the latter stated that water vapour increased the conservation of CaCO₃, which slightly compensated for the deactivation of the sorbent. However, results also showed that increasing only the gas humidity in the calcination reactor has decreased the capability, although with a small amount. As a result, it is important to realise that different combinations of reactors that steam is added in will result in different capability of CC.

5. What are the extent to which these factors affect the carbon capture industry?

From previous experiments we have seen that those three factors (sorbent attrition, temperature and gas humidity) influence the capability in the different ways: SO₂ can deactivate the sorbent by forming a layer of sulphate, preventing the reaction of CaO with CO₂, hence decrease the capability; both going below or above a certain temperature range can have a negative effect but the adding of certain gas humidity to certain reactors will have increased the capability. Among them, SO₂ sorbent attrition are considered the most influential because it can greatly deactivate the sorbent which will not capture CO₂ anymore, and that is why it is crucial to remove SO₂ and other impure gases before the



compound get into the CC (Coppola *et al.*, 2012b). On the other hand, the temperature seems to have a relatively smaller effect. Please note that, the temperature is considered having small influence here not because while going to high or low temperature, there will still be a passable capability, but as it is fairly easy for temperature to be well-controlled in the industry, since the temperature/capability graph is plotted after further research.

6. Conclusions

The CaL CC includes the carbonation and calcination reactions in a circular chain reaction, which is responsible to solve climate change, basically to alleviate the effect of greenhouse gases. Factors influencing the capabilities of the CC are discussed and we found that SO₂ has a significant effect on the sorbent deactivation but only a disappointing small amount of influence on the capability. Besides, there are favoured temperature ranges and both going below or above the ranges are found having a negative effect on the capability. Gas humidity has, for some reactions, the ability to increase the capability of the carbon capture since it can enhance the reactivities of the reactors, but also with some exceptions. A comparison of three influences on the industrial carbon capture has led us to conclude that sorbent attrition is the most influential factor affecting the industrial capability and temperature the weakest factor.

To minimise the energy penalty of CaL CC in the industry, further research is suggested to focus on both how to separate the SO₂ gas from the raw gases to prevent the sorbent attrition and the most suitable temperature contributed to highest capability of CC.

7. Abbreviations

CC--carbon capture

CCS--carbon capture and storage

CaL--Calcium looping

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