Carbon Capture and Storage technology's role in CO_2 emissions reduction and the energy cost

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Abstract: The energy and material use associated with carbon capture and storage in the industrial sector are studied, specifically in the cement and petrochemical sectors. A 6.8% increase in energy consumption in the industrial sector would be needed to make the cement industry carbon neutral, and a 2.9% increase would be necessary for the petrochemical industry. A 6.5% increase in limestone mining would be needed to fulfill the material requirements in the cement industry. Additionally, the emissions associated with the transportation of the captured carbon to a storage site are calculated and determined to be minor compared with the capture stage.

I. Introduction

The Intergovernmental Panel on Climate Change (IPCC) recommends to limit global warming to 1.5°C to avoid significant harm to the climate [1]. The carbon budget that remains in order to stay below this threshold is 510 Gt CO_2 and our current annual emissions are of 56 Gt CO_2eq/year, which corresponds to approximately a decade to reduce emissions to zero. Given that this is unlikely to happen under current policies, many Integrated Assessment Models (IAMs) rely on carbon capture and storage (CCS), and other Negative Emissions Technologies (NET) to reach the established carbon emission goals [15]. IAMs are a type of model which study the interaction between socioeconomic factors and the environment, and are used to develop climate policy. As a result, current climate policies rely heavily on the use of these technologies. CCS refers to the process of separating carbon from other gases in industrial processes or energy generation, and transporting it to a location where it can be stored long term, usually injected into aquifers or stored at the bottom of the ocean. NET is a more general term referring to processes in which there is a net removal of carbon from the atmosphere.

One of the most studied types of NETs are bio-energy carbon capture and storage (BECCS) [15]. BECCS consist in capturing CO_2 as it is emitted at a bioenergy thermal plant, and storing it. Assuming that the energy costs of raising the crops, operating the power-plant and transportation does not exceed the carbon captured by the energy crops, net emissions will be negative. This type of NET has the advantage of being a source of clean energy, which could offset the energy required for carbon capture. However, the exact lifetime emissions of a BECCS plant are very system-dependent, and factors including the type of crop, how the biomass is processed and the type of sorbent used can affect the carbon balance of the process [10]. This means that wide implementation of BECCS would be challenging, as it would be necessary to carry out an analysis of each plant individually, and there is a risk of their net emissions being positive. It must also be noted that land is a limited resource, and there is a limit to how much of it can be destined to grow energy crops without infringing on land for food crops. A literature review estimated that BECCS's potential for negative emissions were 0.5-5 $GtCO_2$/year [15]. Another study that investigated the potential of retrofitting all point sources of biogenic CO_2 in Europe with BECCS found that in doing so, 5% of European emissions could be mitigated [16]. On its own, BECCS cannot account for the negative emissions that are necessary to meet climate goals.

Another form of NETs are direct air carbon capture and storage (DACCS), which involve capturing carbon directly from the atmosphere through the use of sorbents. They have the advantage of capturing emissions that are not from point sources, such as those from transportation. They can also be placed on land that is not needed for other purposes, and are fairly efficient, with capture rates of 85.4 - 93.1% [9]. The technology is still immature, and they require an energy input to operate, so the net negative emissions per plant are small, in the order of 0.5-5 $GtCO_2$/year [15]. One study estimated that to capture 1% of emissions in 2019, 3683 DACCS plants would have been needed [9]. This technology is also fairly expensive, which makes it even less likely that it will be deployed at the necessary scale.

It is often more effective to apply CCS to power plants, or other point sources where there are large amounts of concentrated emissions. These types of plants are categorized by capture method into post-combustion, pre-combustion, and oxy-fuel combustion [17]. Post-combustion capture entails separating CO_2 from flue gases using chemical sorbents. This method has the advantage that it is easy to retrofit into existing thermal plants, but there is often a significant energy toll associated with heating the flue gas and the most common sorbent can become corrosive. In pre-combustion carbon capture, syngas, a mix of hydrogen and CO, is produced using methane. CO reacts with water to produce CO_2, which is then captured and the hydrogen is used as fuel. Oxy-fuel carbon capture involves burning the fuel in pure oxygen, which means the flue gas will only contain CO_2 and water, rather than nitrogen, which is cooled to condense the water so that the now-isolated CO_2 can be compressed.

While sectors such as transportation and energy for home use could become carbon neutral through electrification and the use of renewable energy sources, there are several industrial processes that, because of the chemical reactions involved in their production, cannot be decarbonized [14]. This fact, in addition to the emissions being localized at a few large point sources, makes the industrial sector a good candidate for CCS. The largest industrial sources of emissions are iron and steel (31%), cement (27%), and petroleum refineries (10%) [14].

While the iron and steel industry accounts for a significant portion of industrial emissions, these emissions are spread across many small mills rather than being concentrated in a few large ones. The industrial process is also more complex and involves multiple stages where carbon would be produced. These factors make it a less suitable candidate for CCS [11, 14]. This leaves the cement and petrochemical industries as possible candidates for carbon capture.

The objective of this work is to calculate the energy and material costs associated with carbon capture in both the cement and petrochemical industry, in order to evaluate their feasibility. The emissions associated with the transportation of the captured carbon in these industries to a storage site will also be studied. The present work is structured as follows: section II discusses the theoretical background necessary to understand the functioning of the industries discussed; section III describes the methods used to determine the energy and material efficiency, and the transportation emissions associated with carbon capture in these industries and section IV presents and discusses the results.

II. Theoretical Background

A. Cement industry

In the production of cement, limestone ($CaCO_3$) and other raw materials are heated in a kiln where a series of chemical reactions take place to produce clinker and CO_2. This process accounts for 95% of the emissions associated with the cement industry. Of these, 60% are due to the calcination reactions, and 40% from the energy necessary to raise the kiln to an adequate temperature [2, 11, 14].

The calcium looping cycle is a method of post-combustion carbon capture. It involves a succession of calcination and carbonation reactions, which isolate CO_2 from the rest of the flue gas so that it can be compressed and stored.

The primary chemical reaction involved in the process is:

$$CaCO_3(s) \rightleftharpoons CaO\ (s)\ + CO_2\ (g) \tag{1}$$

The forward reaction is called calcination, and is endothermic. The backwards reaction is called carbonation and is exothermic. One can shift the reaction rate to favor carbonation or calcination by modifying the CO_2 partial pressure [8]. Since the equilibrium partial pressure depends on the temperature, the calcium looping cycle functions by transporting the flue gas mix from the carbonator, at relatively lower temperatures of 650-700°C, where the CO_2 binds to CaO, to the calciner, at temperatures of 900-950°C, where the now isolated CO_2 is released [8].

The entirety of the CO_2 present will not be captured after a single cycle; this process requires repeated cycling of the flue gas between the two chambers.

The calcination-carbonation reaction is only partially reversible. The reactivity of CaO decreases over time due to exposure to high temperatures. This results in a permanent change to the material's shape, making it less porous. Consequently, there is less surface available for the CO_2 to react with. This process is known as sintering, and is correlated most strongly with number of carbonation-calcination cycles undergone, although other factors, such as calcination temperatures exceeding 950°C and CO_2 partial pressure may also play a small role.[8]

The following semi-empirical equation (Eq. 2) describes the evolution of the amount of CO_2 captured, where a_N represents the fraction of active sorbent during the Nth cycle, $a_m = 0.77$ is an empirically-determined decay constant, and $a_\infty = 0.17$ is the residual reactivity after many cycles. All these values are adimensional [5].

$$a_N = a_m^N(1 - a_\infty) + a_\infty \tag{2}$$

CaO cannot be mined directly, and is instead obtained through the calcination of limestone, emitting one mole of CO_2 per mole of sorbent used.

B. Petrochemical Industry

The petrochemical industry creates materials derived from petroleum. It accounts for 17% of industrial emissions. Because this is a very diverse industry, there exists a wide array of plant designs, meaning CCS cannot be applied in a "one size fits all" manner. The primary emission sources are flaring, which consists of burning off gases to release pressure, in oxidation reactions, and in burning fuel for heating. Only about 20% of emissions are high-purity, and as such have CO_2 concentrations suitable for CCS [11].

The most studied form of carbon capture for this sector involves retrofitting plants with post-combustion capture using monoethanolamines (MEA), since it is cheap and has a relatively high capture rate of 50-75% [14]. Like the calcium-looping cycle, this process involves cycling the flue gas between the absorber at temperatures of about 160ºC, which binds CO_2 to the MEA in an exothermic reaction, and the stripper at 400°C, which regenerates the sorbent[18].

III. Methods

In order to study the energy and material efficiencies of carbon capture in these industries, a bibliographical re-

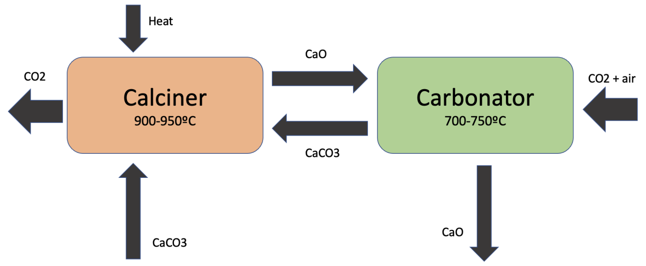

FIG. 1: Diagram showing energy and mass flows of calcium looping cycle

view was carried out. Suitable equations from the literature were adapted to fit a model that is proposed to simulate the capture process.

In the case of the cement industry, the mass and energy fluxes associated with each cycle of operation of the capture plant can be analyzed. There are energy costs associated with both adding fresh sorbent with an increased reactivity and cycling the same carbon many times. Calculating the energy efficiency implies finding an equilibrium between these two factors.

We will propose a hypothetical capture plant where each cycle, fuel gas containing 1000 moles of CO_2 enters the carbonator, where the same number of moles of CaO will be initially present. After each cycle, some amount of $CaCO_3$ (N_{out} in Eq. 5) will be transported to the calciner. This amount is equal to the amount of captured carbon, and will depend on the amount of active CaO during that cycle. In the calciner, heat will be supplied to carry out the endothermic calcination reaction ($\Delta H = 165 kJ/mol$) [8]. At the end of each cycle, some amount of CaO, N_{in} will be removed, and replaced with fresh $CaCO_3$. The CaO removed will contain both active and inactive sorbent.

The flows of energy and materials are represented in Figure 1.

In addition to the activation energy for calcination, the primary energy contributions are to raise the temperature of $CaCO_3$ as it is transported from the carbonator, at 700°C, to the calciner at 900°C, and to raise new $CaCO_3$ to replace the used up sorbent, which is heated from atmospheric temperature (20°C) to 900°C. Eq. 3, which is adapted from [8], shows the energy required for one cycle.

$$E = \Delta H N_{in} + N_{in} C \Delta T_1 + N_{out} C \Delta T_2 \tag{3}$$

C refers to the molar specific heat capacity of $CaCO_3$ (J/mol/K), and the increases in temperature are $\Delta T_1 = 200°C$ and $\Delta T_2 = 880°C$.

The specific heat capacity of $CaCO_3$ at high temperatures (in J/mol/K) is [13]:

$$C_p(T) = -184 + 0.32T - 368T^{-2} - (1.30 \times 10^4)T^2 + 3880T^{-1/2} \tag{4}$$

We deduce that the value of N_{out} (mol) for the model proposed in this work is:

$$N_{out} = N_{in} + a_N (N_{max})^{N-2} (N_{max} - N_{in})^{N+1} + \sum_{i=0}^{N-1} N_{in} (\frac{N_{max} - N_{in}}{N_max})^{i+1} \tag{5}$$

Here, $N_{max} = 1000$ is the maximum amount of CO_2 that can be captured in a given cycle, and a_N is the reactivity, calculated using equation 2.

By integrating to find the specific heat capacity, and substituting the above equation for the moles of active CaO, one can determine the energy per cycle as a function of the cycle number and amount of new $CaCO_3$ added each cycle.

In the case of the petrochemical industry, the structure of the plants is more complex and there is less literature discussing the specifics of how they function. Bibliographical results for energy efficiency will be cited in order to compare them with those of the cement industry.

To determine the emissions associated with transportation, the distances between cement mills, petrochemical plants, and potential storage locations in Spain were compared.

The location of carbon capture plants were taken to be the latitude and longitude of Spanish cities where the industrial plants are located, according to [3] and [7]. The locations of injection sites were taken from the report ”Assessing European Capacity for Geological Storage of Carbon Dioxide”, which conducted geological surveys in the regions surrounding the largest Spanish rivers, and analyzed their suitability for CCS storage. The coordinates were taken to be those from the nearest town to the locations mentioned in the survey.

The geometric distance between all coordinates were calculated, and the smallest distances between each cement mill location and an injection site were averaged.

IV. Results and Discussion

A. Energy and Material Use

Figure 2 and 3 show the evolution of the energy requirements (J) and captured carbon (mol) as a function of cycle number for different values of N_{in}. We can observe that in the initial cycles, there is some variation, before it reaches an asymptotic value for energy and capture efficiency.

Figure 4 shows the limit capture rate as a function of the limit energy use. Each point corresponds to a different value of N_{in}. We can observe that the capture rate increases approximately linearly with energy until it reaches a maximum, at E = 195456 kJ, Captured CO_2 = 907.9 mol and N_{in} = 73 mol.

This means that, for this model, the ideal energy efficiency is 215 kJ/mol CO_2, or 4892 kJ/kg CO_2, and the material efficiency is 0.080 mol $CaCO_3$/mol CO_2.

The capture efficiency per cycle is of 90.79%, which is in line with real capture efficiency of pilot plants using this method of 80-90% [8].

Total worldwide emissions due to the cement industry were 3.915Gt CO_2 in 2015 [14]. If we wanted to reduce these by 60%, which as mentioned previously corresponds to the emissions in this sector that cannot be abated, 11.4 EJ of energy would be required. The global energy consumption of the industrial sector in 2021 was of 169 EJ[12], so this would imply a 6.8% increase to reduce emissions of the cement industry only. For the sector to become carbon neutral, renewable energy would also need to cover the remaining 40% of the energy necessary for the rest of the cement production process.

Worldwide renewable energy production in 2021 was of 26.8EJ [12], so the energy needed to reduce the emissions associated with chemical reactions in the cement industry correspond to over 40% of current renewable energy production. To make the cement industry carbon neutral, we would need to dramatically increase our renewable energy output, improve plant design to make them more energy efficient, and consider reducing our cement consumption. This is in line with the existing research, which indicates that deployment of NETs at the necessary scale is unfeasible [15].

To accomplish the previously mentioned reduction in emissions, 0.429Gt of limestone would be necessary to use as sorbent. The worldwide limestone mined is estimated to be 6.6 Gt [6], so this would correspond to 6.5%. Although limestone is a very common mineral and there would not be shortage issues, implementing this would cause damage to ecosystems and additional emissions associated with mining and transportation to the cement plants, which might outweigh the amount of carbon captured.

A study which investigated the limestone extraction that would be necessary for another NET which is also based on carbonation, stated in its conclusions that an increase in limestone mining of a few gigatons would only be "a limited upscale of the current production" [6]. It also suggested life-cycle analyses would be needed to study the full impacts.

With regards to the petrochemical industry, Nan et al. studied the energy requirements for MEA applied to a thermal plant, which had similar temperatures and CO_2 concentrations to a typical refinery, so their results are applicable[18]. They found that the energy consumption was of 2.848 kWh/kgCO_2 (1.0252×10^{-8} EJ/ tonne CO_2).

Worldwide emissions in the petrochemical industry are of 2.465 Gt CO_2[11, 14]. If we want to reduce this by the 20% that corresponds to high-concentration sources, we would need 5.05 EJ of energy, which represents a 2.9% increase in energy consumption in the industrial sector.

The energy efficiency cited is greater than that of the calcium-looping cycle. However, the study did not consider the energy costs associated with sorbent decay. It also did not consider the emissions associated with cre-

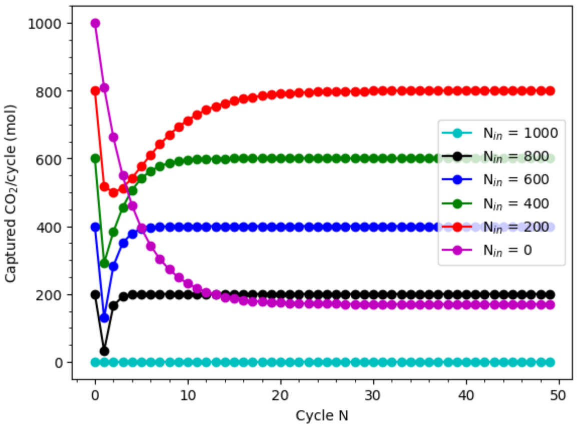

FIG. 2: Captured carbon per cycle (mol) as a function of the carbonation-calcination cycle, N, for a range of values of new sorbent added per cycle, calculated with Eq. 5.

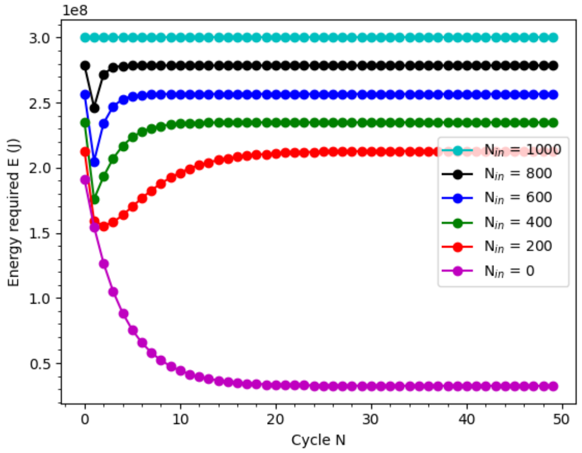

FIG. 3: Energy required per cycle (J), as a function of the carbonation-calcination cycle, N, for a range of values of new sorbent added per cycle, calculated with Eq. 5 and 3.

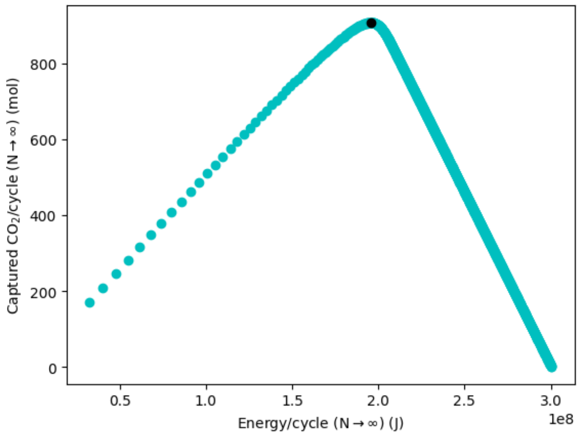

FIG. 4: Carbon captured per cycle (mol) as a function of energy required per cycle (J). The point that corresponds to the maximum is represented in black.

ating MEA. To produce amines, one needs ammonia and ethylene oxide, which are themselves products of the petrochemical industry.[18].

Although the total energy needed is a more reasonable amount compared to the cement industry, the total emissions that can be abated using CCS in the petrochemical industry are also significantly reduced, potentially making the investment necessary to construct the infrastructure not be worth it.

B. Transport

The average distance between cement and petrochemical plants to storage sites were found to be $d_{cement} = (110 \pm 20)$ km and $d_{petro} = (130 \pm 40)$ km, where the uncertainty was taken to be $\sigma/\sqrt{N}$. This does not take into account the existence of roads, rail-tracks or other methods for transport, and a such, this is a very conservative estimate. According to the European Automobile Manufacturer Association, the average CO_2 emissions per km traveled are 73.46 gCO_2/km [4]. Assuming every truck carries 25 tonnes (the legal weight limit), emissions associated with the transportation process will be 0.382 gCO_2 emitted / gCO_2captured in the case of petrochemicals, and 0.323 g/gCO_2 in the case of cement. These values are comparatively small but illustrate that the logistics of the transport phase are complex.

V. Conclusion

In this work, the energy requirements associated with making the industrial energy carbon neutral through the use of carbon capture were calculated. We found that the worldwide yearly energy necessary to make the cement and petrochemical sectors carbon neutral through the use of carbon capture are 11.4 EJ and 5.05 EJ respectively, which correspond to around 40% and 20% of current renewable energy production. It would be unfeasible to apply CCS at the scale necessary to reach emission goals. In the case of cement, the raw materials necessary would be significant and unsustainable in the long term. Although the energy requirements for the petrochemical industry are more reasonable, due to the heterogeneity of the sector and the structure of most plants, even if all of the carbon from sources that are suitable for CCS were captured, this would not make a great difference in moving towards zero emissions.

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