Use of Full Oxy-Fuel Combustion and Accelerated Carbonation Curing for Carbon Capture and Storage in Concrete Manufacturing

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SECTION 1: SUMMARY

Concrete's ubiquitous impact on the world will not change any time soon. It is a world leader regarding its levels of production, consumption, and contribution to carbon dioxide (CO_2) emissions. Given that CO_2 is a significant greenhouse gas, concrete manufacturing should be considered one of the most critical fronts in the fight against anthropogenic climate change. The primary objective of this report is to demonstrate that the dramatic reduction in the carbon footprint of concrete manufacturing is readily possible. To do so, the team proposes a reimagining of the concrete manufacturing process that adds full oxy-fuel combustion and accelerated carbonation curing to the traditional method to transform the process into a carbon capture and storage (CCS) system. Concrete is a natural carbon sink, so this revamped process capitalizes on an organic mechanism. Theoretically, concrete can capture permanently half its mass of CO_2. This figure is unattainable practically due to diffusion limitations within the cement structure and undesirable due to its effect on the structural integrity of the concrete. Therefore, the team designed the proposed system to capture approximately 30% of CO_2 by mass, which is about 82% of the CO_2 generated in the process.

In this report, the team will outline a brand new factory that uses the CCS process to manufacture concrete masonry units (CMUs). The team recognizes that it is possible to retrofit the same methods into an existing factory, and proposes that this is something for consideration in future work. The factory, which contains on-site both the firing and casting processes, is specified to operate at a capacity of 3,000 metric tons of clinker per year. This capacity is pilot-sized, much smaller than a standard cement factory that may operate at a rate of 3,000 metric tons of clinker per day. The plant detailed in this report will manufacture 324,495 CMUs each year, produce 1,720,668.1 kg carbon dioxide per year, and capture 82% of that amount in the

CMUs. The remainder of the CO_2 can be stored or otherwise used to diminish emissions further. The team plans to sell the remaining CO_2.

The team's primary intention with the creation of this process is to reduce the typical carbon footprint of concrete manufacturing by implementing an entire CCS process within the process design; however, the green concrete manufacturing process will indirectly accomplish other positive environmental impacts. In addition to being an excellent form of carbon capture that yields a high purity CO_2 stream, oxy-fuel combustion removes many of the environmental hazards associated with cement manufacturing, such as the production of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) emissions. The use of natural gas as fuel adds to the plant's environmental friendliness as well.

Currently, this process as designed is not economically viable due to high operating costs versus revenue. This disparity comes from the small production scale of the plant. Nonetheless, it has great potential, which is made clear by the results of the research. The highest recurring costs come from labor costs. Increasing the load on the kiln and curing systems will not necessitate a significant increase in labor costs or equipment costs. However, it will bring significant increases in profit due to the additional CMUs produced. Only a slight increase of about twofold makes the operation a profitable one. Increasing the scale to that of a small concrete manufacturing plant of about 3,000 metric tons of clinker per day increases the profit drastically from negative to $21,592,969 per year. This profit margin quickly diminishes the $3,591,712 price tag of capital costs and equipment costs.

Overall, the plant in this report is not desirable or practical (exactly as designed), but it can be. There exist many avenues for future research that will result in favorable results and, perhaps, an actual factory built using the design proposed.

SECTION 2: BACKGROUND AND MOTIVATION

Concrete is the most widely created and used human-made material in existence. In terms of human consumption, it is second only to water (Rodgers, 2018). Thirty billion metric tons of concrete are used annually in construction alone (Jacoby, 2020). Cement is the principal component and binder of concrete. Since the beginnings of human civilization, populations have used crude cements to forge concrete materials and construct societies (Gromicko & Shepard, n.d.). For example, the Nabataea and Bedouin peoples built concrete structures in and around the 6500s BCE (Gromicko & Shepard, n.d.). Almost nothing in the recipe to make the most common cement, ordinary Portland cement (OPC), has changed in the 200 years it has existed (Jacoby, 2020). OPC concrete makes up 70% of all building and construction materials (Qian et al., 2018).

Unfortunately, the production of cement leads to massive CO_2 emissions. It is estimated that one ton of cement produced through traditional methods releases an equal amount of CO_2 (El-Hassan, 2020). In fact, cement manufacturing releases approximately 2.2 billion tons of CO_2 per year, making up 8% of all global carbon emissions (Rodgers, 2018). This amount represents the second-largest single industrial process emitter after iron and steel production (Harvey, 2018). Cement manufacturing should be considered a major sector in the fight against anthropogenic climate change due to these figures. To put in perspective the impact cement manufacturing has on the environment, the average energy input required to make one ton of cement is 4.4 million Btu, or 389 pounds of coal (Portland Cement Association, 2019). The cement industry is a promising opportunity for industrial sustainability, due to its scope and worth. Approximately, one cubic meter of cement is produced per capita. With the rising human population and rising demand for infrastructure and superstructures, the overall demand for cement increases each year (El-Hassan, 2020). Global per capita consumption of concrete has nearly tripled in the past four decades (Jacoby, 2020). This growth is driven by new developments in Africa and Asia and aging infrastructure in Europe and the Americas (Jacoby, 2020). Market projections suggest that the cement market value will grow from $312.5B in 2018 to be worth $682.3B by 2025 (Grand View Research, 2018).

This report will propose modifications to the cement manufacturing process to transform the process into a CCS technology through the implementation of an alternative combustion process, called oxy-fuel combustion, and accelerated carbonation curing. This approach tackles the carbon footprint by addressing the most emission heavy parts of cement manufacturing. The de-carbonation of limestone in the kiln produces about 525 kg CO_2 per ton of clinker, an intermediary product in cement manufacturing, and fuel combustion produces about 335 kg CO_2 per ton of cement (Bosoaga et al., 2009).

To meet the standards outlined in the 2015 Paris Agreement, global carbon emissions associated with cement production must drop 16% by 2030 (Rodgers, 2018). Over the last few decades, many advances have been made with regards to kiln and feedstock design in order to make the process more environmentally-friendly. Some tactics for the reduced carbon footprint of cement production are supplementary cementitious materials (SCMs), improved energy efficiency, and alternative fuels. These methods are insufficient. Only recent studies have explored the possibility of CCS and cement’s role in this environmentally-sustainable technology. Additionally, the resulting designs of these studies face adverse market conditions. An economical design will be necessary to garner the support needed to make a substantial shift toward sustainable cement production.

SECTION 3: LITERATURE REVIEW

This thesis provides an overview and design for a cement clinker production process using both oxy-fuel combustion and accelerated carbonation curing to reduce the environmental impact of the process via carbon dioxide emissions. These topics represent the two key points of this process and will be the focus of this literature review. For oxy-fuel combustion, the group selected two studies to determine scale and scope of this process. The group's efforts on accelerated carbonation curing modeling come from Sormeh Kashef-Haghighi et al. This study provided a mathematical model for accelerated carbonation curing in precast cement. This literature review will summarize and synthesize these major studies. The review will also serve to provide insight as to why these studies were chosen, what limitations were found, and other sources used in this thesis.

First, the oxy-fuel combustion section of the process will be discussed. Two studies were the basis for the team's effort. The first study was by Zeman. This study introduced the idea of a reduced emission oxygen kiln. This study was beneficial in creating the team's process flow diagram. The study provided process schematics and unit operations necessary for both a new plant and outfitting an older plant. The study also provided energy usage data that was beneficial in solving the team's energy balance and completing the carbon inventory. The group slightly deviated from this study as natural gas was determined to be the ideal fuel of choice, over coal. This choice reduces emissions in the form of sulfur oxides, and removes the need for flue gas recycling. The Zeman study utilized flue gas recycling to dilute the oxygen stream, as the flame temperature from coal combustion with pure oxygen was too high for the process. Zeman's study is significant for the team's purposes, as reduced emission oxygen kilns are relatively new. Not many large data sets are available for production using this technology. For reference, Zeman's first study into this technology occurred in 2009. This is the earliest mention of this technology. Zeman was the first researcher to propose the use of carbon capture and sequestration technology in the cement industry.

The second major oxy-fuel combustion study referenced was Ditaranto and Bakken's 2019 paper on a full scale rotary kiln. This study provided the group with the first large-scale implementation of oxy-fuel combustion in a cement plant. This study is where the basis of 3,000 metric tons per year originates. The group chose this study as the design basis for its large dataset. The goal of this project is to model and improve an existing process, rather than create a novel process. The work of Ditaranto and Bakken allowed the team to better understand the scale of the process and model in Aspen using a preexisting basis. This study also provided economic analysis of outfitting an existing plant. This information allows the group to better price the process and make accurate recommendations with regard to the financial viability of the overall process. Furthermore, this study also provided the group with the first full process flow diagram of oxy-fuel combustion in cement production. This process flow diagram was used as the basis for the process flow diagram and Aspen Plus model. While a major focus of this paper was on a computational fluid dynamics simulation for the flame within the kiln, the study still provided adequate background and introduction for the technology and a strong production basis. Like the Zeman study, a major shortfall of this study was the fuel source again being coal. Also, the cement plant in this study was retrofitted for oxy-fuel combustion, rather than being a newly built plant. While the group is open to upgrading current plants, the process outlined in this thesis is unique to a newly built cement plant.

While these two studies provided the bulk of the background and basis for the oxy-fuel combustion side of the process, another study made a major impact on this process and design solution. One major hurdle the team came across was settling and solving the energy balance. Using a traditional method of accounting for all stream enthalpies and heats of reaction, was almost impossible using readily available data. For example, the enthalpy of freezing for most cement components is not relatively available. To solve this dilemma, the group researched heat transfer in cement kilns. In this research, a study by Mastorakos et al. provided a general specific energy usage of clinker formation of 3.2 MJ/kg of clinker produced. This value was then used to complete the energy balance and fuel needs of this process.

The other major component of the process was accelerated carbonation curing. The various studies by Kashef-Haghighi and Ghoshal provided both background information on accelerated carbonation curing and a mathematical model for carbon uptake via this process. These studies provided values for carbon uptake, a process flow diagram for designing an accelerated carbonation curing process, and finally experimental data on accelerated carbonation curing systems and their performance. From these studies, the team created a model to simulate the carbon uptake in the process. Much like oxy-fuel combustion, this is a new technology in the field of carbon capture and sequestration. The field of carbon capture and sequestration is relatively small in the cement industry. Kashef-Haghighi and Goshal's work represents the most thorough and extensive research into this topic. Other studies focus on carbon uptake via concrete, but the studies of Kashef-Haghighi and Goshal focus only on production. These other studies focus on existing concrete and demolition. The focus of this project is in production. This thesis aims to build on the work of Kashef-Haghighi and Goshal and to add this technology to oxy-fuel combustion, as outlined by Zeman, Ditaranto and Bakken, in the klin.

SECTION 4: DISCUSSION

4.1 THE DESIGN

First and foremost, this report details the creation and operation of a new concrete manufacturing plant that has the ability to capture the CO_2 it produces and store the majority of it in the product produced. The proposed design incorporates the aforementioned research in order to create a pilot concrete production plant as opposed to a large-scale operation. This was decided in order to remain closely in line with the numerical values of studies such as Ditaranto and Bakken which provided the team with the production parameter of 3,000 tons per year of clinker, and, as the process of using oxy-fuel combustion in conjunction with accelerated carbonation curing is fairly novel, to focus on process design while accounting for future scalability (2019).

4.1.1 Process Flow Diagram

The team has developed a process flow diagram, based on studies from Ditaranto and Bakken (2019), as well as Zeman (2009). The process flow diagram is shown in Figure 1 on the next page, split into two photographs for readability.

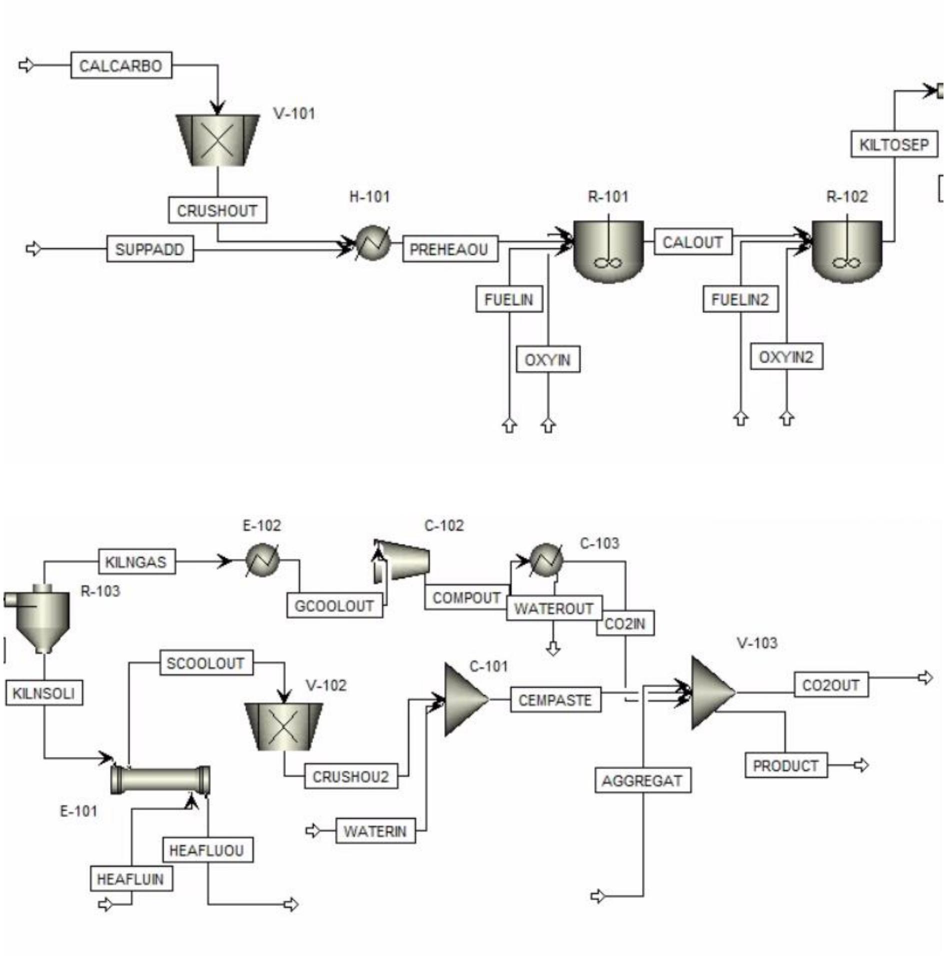


Figure 1: Process Flow Diagram: Process flow diagram for entire oxy-fuel combustion and accelerated carbonation curing (ACC) process. The first photograph represents the process from start up to the kiln (the last component being the CSTR, R-102), while the second photograph shows the process from kiln (cyclone, R-103, component) to finish.

The process flow diagram at its core, features a series of components to develop a Reduced Oxygen Emission (REO) kiln design. This design allows for efficient calcination and clinker production, as well as near 100% conversion of oxygen feed to carbon dioxide. This will allow the team to easily separate and utilize the CO_2 in the process in an environmentally-friendly manner. The design involves the definition of the calciner, kiln, cooler, and preheater components.

The calciner is designed with an oxygen stream feed (OXYIN) to kick-start the calcination process, as well as a natural gas feed to supply fuel/heat to the process at this stage (FUELIN). The material feed is supplied by stream PREHEAOU, which contains crushed limestone and clay, composed of iron and shale, from the preheater. The materials stream CALOUT contains reacted and unreacted material which feeds directly to the kiln. The team was able to find a suitable calciner design (i.e., composed of materials conforming to desired temperatures) made of stainless steel and with dimensions of 9 m long, 3 m tall, and 2 m wide, showing in part that this design is feasible (Aaron Equipment Company, *Used - Rotary Calciner / Calcining Furnace*, 2021).

The rotary kiln in this process is split into two components, as Aspen is incapable of modeling a rotary kiln in one, inclusive element. The two components are a continuous stirred-tank reactor (CSTR), and a cyclone. A CSTR, specifically, was used because this simulates the constant stirring that rotation in a rotary kiln would provide. The cyclone also builds upon the rotation of the kiln, but in this component, there is no reaction occurring, only gas-solid separation. The cyclone accounts for rotation as well as the effect that the length of the kiln would have on the material within. In a typical rotary kiln, the material is exposed to uneven heating, which leads to different rates of reaction along the kiln. The cyclone in this model allows the material to leave the reactor/deviate from the constant reaction rate within the CSTR. Equivalent rates of reactivity are not experienced along the length of the kiln so the cyclone factors in the low rate of reaction at the end of the concurrent flow kiln. The kiln also has an oxygen feed (OXYIN2) as well as a fuel/natural gas stream (FUELIN2). As previously mentioned, material is transferred from the calciner to the kiln (CSTR component) via the CALOUT stream. The KILNTOSEP stream transfers molten clinker, formed in the CSTR, to the cyclone component. The process flow diagram assumes separation; therefore, no joint take-off stream is present leaving the cyclone. Alternatively, the gases and solid materials are shown to leave the cyclone via the KILNGAS and KILNSOLI streams respectively. The kiln in an REO set-up must be maintained at approximately 1450^{o}C, generating a copious amount of waste heat (Zeman, 2009). A natural gas take-off stream allows for excess fuel from the CALOUT stream from the calciner and KILNTOSEP stream from the rotary kiln to leave the system in the CSTR. The kiln is modeled as two components, but the team will be following the dimensions of 60 m long with an inner diameter of 3.76 m to conform with the Ditaranto and Bakken study (2019).

There are two coolers in this process: a gas cooler and a solids cooler. The material to the gas cooler is fed by the KILNGAS stream and exits via the GCOOLOUT stream, which feeds to a process intended to isolate produced CO_2. The solids cooler is more complex. A heat exchanger with higher-temperature solids collection encapsulated in a lower-temperature heat transfer fluid shell, allows for conductive heat transfer. The team has modeled one cooler; however, multiple coolers may be necessary and dependent on further modeling due to the high temperature difference between the molten clinker (1450^{o}C) and the cooler exit temperature (approximately 300-400^{o}C) (Zeman, 2009; White, et al., 2009). The team has determined a manufacturer, Solex Thermal Science, is capable of producing a plate heat exchanger that can handle input temperatures of up to 2000^{o}C, while simultaneously maximizing efficiency (n.d.). If this process is adapted, this technology and similar iterations may be crucial in future design.

The REO kiln design consists of specifications for the calciner, kiln, and cooler. However, the pre-heater has been partially designed to accommodate for REO kiln design. The CRUSHOUT stream contains limestone that has been crushed to a fine powder. The SUPPADD stream contains the clay. The CRUSHOUT and SUPPADD streams supply material to the pre-heater at lower temperatures than the heater. Material and gases produced from the heating process leave the pre-heater through the PREHEAOU stream. The temperature of the pre-heater is assumed to be approximately 300-400ºC, based on the exhaust gas temperature from the pre-heater component (Zeman, 2009; White, et al., 2009).

The REO kiln design is only a fraction of the overall process, however. For example, there is a crusher component to integrate the limestone, clay, shale, and iron components prior to the pre-heater; fed by the CALCARBO stream (gaining its name from the more abundant material in the stream, calcium carbonate), and relieved by the CRUSHOUT stream.

Additionally, there is a cooling system for the CO_2 gas that leaves the kiln, to treat it before being reintroduced to the concrete. The KILNGAS stream, containing CO_2 and water vapor from combustion, feeds to an initial cooler. This brings down the temperature of the components from extremely superheated levels. The GCOOLOUT stream takes the cooled components and feeds them to a compressor, which increases the pressure of the components to approximately 128.3 atm (Ditaranto & Bakken, 2019). The COMPOUT stream feeds this compressed material to the condenser, which separates the water from the CO_2 resulting in a CO2IN stream of pure CO_2 introduced to the concrete for curing.

To elaborate on the solids cooling and concrete production process beyond the SCOOLER unit, the cooled material in the SCOOLOUT stream is fed to a second crusher unit, to create a more powder-like substance rather than clinker-shaped spheres. The CRUSHOU2 stream is then fed to a mixer with water from the WATERIN stream to create cement paste. This leaves the mixer in the CEMPASTE stream and is introduced to the CO2IN stream in a blackboxed accelerated carbonation curing process represented by the V-103 unit. The excess CO_2 leaves the system via the CO2OUT stream. The concrete product is represented by the PRODUCT stream.

4.1.2 Design Basis and Scale

Due to concrete's vast scale of consumption and production needs, one goal of this project is industrial scale. To make a true dent in the carbon emissions of cement production, the scale of this project must be comparable to current industrial capabilities. A study on oxy-fuel combustion by Ditaranto and Bakken, which utilizes a scale of 3,000 metric tons of clinker production per year and a kiln of 60 m long with an inner diameter of 3.76 m, will be used (2019). The mass of the concrete produced is equal to the clinker produced plus the additives that are added to the cement mill. As a result, the scale used for this project will be an output of 3,000 metric tons of clinker per year. This is extremely small for cement plants, but this scale will allow the team to utilize the study by Ditaranto and Bakken effectively.

To complete the material balance, the team split the process into two parts, because the process specification was in the middle of the process. The aim is to make 3,000 metric tons per year of clinker. The kiln serves as the splitting point. The first half of the process was from the start of the process to the rotary kiln, and the second half was from the kiln to the end of the process. The initial approach to completing the material balance for the first half was using a known amount and composition of clinker produced from the kiln, and subsequently solving for the composition of the inputs by working backwards.

The team ran into several issues at first and the material balance would not close. The team was fairly confident that it was due to the chosen input materials, and neglecting trace materials in this process for simplicity. The sources examined offered varying chemical compositions for the materials in the process. For example, limestone can have a variety of compositions, and some sources considered limestone to be pure calcium carbonate, while others used a mixed composition of calcium carbonate, magnesium carbonate, and other components. Whether or not the material balance would close was dependent on the materials chosen. Additionally, the team did not initially account for all the reactions occurring in the rotary kiln. Though the main reaction in the kiln is the decomposition of calcium carbonate to calcium oxide and carbon dioxide, there are seven other reactions that were not factored in. This issue was coupled with the input material issue mentioned earlier, since all of the materials engage in various reactions in the kiln.

To finally get the finished material balance, the team decided to work from the start of the process to the kiln, instead of working backwards. The team set a dry basis of 100 kg/day of input materials, and used accepted compositions of inputs from literature, and solved for the composition of the clinker. The team then evaluated this clinker composition to make sure that it was consistent with traditional clinker composition. Finally, the process was scaled up to achieve the target amount of 3,000 metric tons of clinker per year.

The chosen input composition was 85% limestone and 15% clay, which includes shale and iron. The limestone consisted primarily of calcium carbonate, but also included trace amounts of silica, alumina, magnesium carbonate, and iron (III) oxide (see Table I on the next page for a detailed breakdown). The clay consisted mostly of silica and alumina, but also contained small amounts of calcium carbonate, magnesium carbonate, and iron (III) oxide (see Table II below).

Table I
Composition of limestone by weight percent

Component	SiO_2	Al_2O_3	$CaCO_3$	Fe_2O_3	$MgCO_3$	Inert
Wt %	1.88	1.2	94.45	0.57	1.95	0

Table II
Composition of clay by weight percent

Component	SiO_2	Al_2O_3	$CaCO_3$	Fe_2O_3	$MgCO_3$	Inert
Wt %	70.69	14.91	4.5	6	1.5	2.4

These feed compositions were then used to solve for the amount of clinker and exhaust gases produced. As mentioned earlier, there are eight reactions occurring in the kiln to create the clinker. The reactions are shown below in Table III.

Table III
Kiln reactions

$CaCO_3$ -------------- $CaO + CO_2$	3.1
$MgCO_3$ ------------- $MgO + CO_2$	3.2
$CaO + Al_2O_3$ ------------- $CaO.Al_2O_3$	3.3
$4CaO + 2Al_2O_3 + CaO.Al_2O_3$ ----------------- $5CaO.3Al_2O_3$	3.4
$2CaO + SiO_2$ -------------- $2CaO.SiO_2$	3.5
$4CaO + 5CaO.3Al_2O_3$ -------------- $3(3CaO.Al_2O_3)$	3.6

$CaO + 2CaO.SiO_2$ -------------- $3CaO.SiO$	3.7
$4CaO + Al_2O_3 + Fe_2O_3$ -------------- $4CaO.Al_2O_3.Fe_2O_3$	3.8

Similarly, the streams in the second half of the process could be solved with the calculated values for the first half, since the second half contained mostly heating and cooling processes. However, at the end of the process is also where ACC occurs. The process for solving the material balance for the ACC was similar to the kiln except that there were nine reactions occurring. The reactions occurring in the ACC are shown in Table IV below. Note that in reactions 4.5 and 4.6, there is an unspecified *n* value. For simplicity in calculations, the value of 1 for *n* was used.

Commented [1]: Can we elaborate on what the n value represents?

Table IV **Reactions involved in the accelerated carbonation curing process**	
$2(3CaO.SiO_2) + 6H_2O$ -------------- $3CaO.2SiO_2.3H_2O + 3Ca(OH)_2$	4.1
$2(2CaO.SiO_2) + 4H_2O$ -------------- $3CaO.2SiO_2.3H_2O + Ca(OH)_2$	4.2
$3CaO.Al_2O_3 + 3CaSO_4.2H_2O + 26H_2O$ --------------- $3CaO.Al_2O_3.3CaSO_4.32H_2O$	4.3
$4CaO.Al_2O_3.Fe_2O_3 + 2Ca(OH)_2 + 18H_2O$ -------------- $6CaO.Al_2O_3.Fe_2O_3.2CaSO_4.24H_2O$	4.4
$3CaO.SiO_2 + 3CO_2 + nH_2O$------------ $SiO_2.nH_2O + 3CaCO_3$	4.5
$2CaO.SiO_2 + 2CO_2 + nH_2O$------------ $SiO_2.nH_2O + 2CaCO_3$	4.6
$3CaO.2SiO_2.3H_2O + 3CO_2$ ------------ $3CaCO_3.2SiO_2.3H_2O$	4.7
$Ca(OH)_2 + CO_2$ -------------- $CaCO_3 + H_2O$	4.8
$3CaO.Al_2O_3.3CaSO_4.32H_2O + 3CO_2$ -------------- $3CaCO_3 + 3CaSO_4.2H_2O + 2Al(OH)_3 + 9H_2O$	4.9

As a result of the material balance calculations, it was determined that the CO_2 uptake was about 64.6%. This is a much higher value than desired. Although a higher CO_2 uptake is environmentally beneficial, the structural integrity of the cement suffers with such a high CO_2 uptake. The team will therefore manually limit the uptake of the concrete to less than 64.6%, which will be described in later sections. The total amount of cement produced from the design basis is 4,703,882.7 kg/year. The total amount of CO_2 produced at the end of the process after ACC is 608,347.8 kg/year. A stream table containing the major streams in the process are shown in Table A.1 in Appendix A.

The energy balance for this process was solved using the data presented in the Mastorakos et al. 1999 study. This study used a basis of 3.2 MJ/kg of clinker produced. For this process, this equates 9.6 million MJ/year of energy input needed. Because clinker formation is highly endothermic, this energy is provided using a natural gas flame in the reduced oxygen emission kiln. The fuel needed for this is further explained in the carbon inventory.

4.1.3 Schedule

The production goal of 3,000 metric tons per year is based on the production basis from Ditaranto and Bakken (2019). However, this goal can be manipulated to meet customer demand and must be increased in order to make the operation a profitable one. The capacity of the plant is constrained by the time needed to measure, dispense, and mix ingredients necessary for clinker production. These processes are generally computerized, thus very efficient.

The team’s concrete process focuses on precast concrete, rather than ready-mix concrete. This distinction alleviates many scheduling concerns. To expand upon these concerns, the concrete is cast at the site of production, versus trucked to a construction site. This eliminates demand issues at the construction site and logistical issues connecting production and distribution of concrete. The biggest logistical concern of ready-mix concrete production is cold jointing (hardening) of the concrete before placement. This concern is all but eliminated in a precast plant. The greatest obstacle in precast production is demand variability. However, the goal of this project is to design a chemical process, rather than create an efficient factory simulator, to model scheduling and consumer demand.

The current precast production schedule is as follows: assemble mold, place parts, cast concrete, cure concrete, strip mold, and finish products. This schedule nests into this process after the cooling of the clinker. The later formed cement will be cast into premade molds for curing. The curing process is explained in-depth within the accelerated carbonation curing section (see section 4.2.2). Casting and curing represent the most time-intensive steps of the process, lasting between 28 and 30 days. This time span is typical for any precast process. Production surges can lead to incomplete curing and casting of concrete. This creates a brittle product and eliminates the competitive advantage of carbon sequestration in this process. To avoid an overwhelming production surge, plant operators can implement a lead time estimation model, as proposed by Ko (2004). This model produced a 33% increase in lead time estimation accuracy over current projections.

4.1.4 End Product

The team intends to expand on the typical cement manufacturing practices using OPC. OPC is widely used due to the easy sourceability of its components and low price. OPC concrete also makes up 70% of all building and construction materials (Qian et al., 2018). The team’s goal is to demonstrate that common concrete products can be manufactured in an economically attainable and practical fashion, while still accomplishing the mission of driving down global carbon emissions. Theoretically, the aforementioned modifications would be applied by retrofitting an already existing cement factory. After all, full oxy-fuel combustion for CCS is retrofit-friendly. Nonetheless, in the interest of the team's research, the pilot factory will be designed as if the factory were brand new and originally built to utilize oxy-fuel combustion and accelerated carbonation curing, as the research objective is testing the design's feasibility as a stand-alone variable first and foremost. The factory will externally source the raw materials, and carry out the rest of the manufacturing in house. That is to say, the clinker will be formed in the team's factory design, and the commercial concrete products will be cast and molded in the factory as well.

Another objective of the design is producing structurally sound and viable commercial products. For this reason, the team is avoiding producing reinforced concrete products as carbonation, natural and accelerated, lowers the pH of the concrete to levels that can destroy the protective oxide film on the surface of the steel, trigger reinforcement corrosion, and cause cracking of the concrete cover due to rust buildup (Zhang et al., 2020). This decision limits the types of concrete products the factory can manufacture as most of the precast industry is reinforced (Zhang et al., 2017). The factory must produce precast concrete products as it is the only way to implement accelerated carbonation curing.

The team considered several common precast concrete products to investigate: slabs, blocks, and pipes. Originally, the team had hoped to explore each one, including scaling each product; however, due to time constraints and lack of published material this was not achieved. The first product considered was 24x24x4 in. solid concrete slab. These slabs are good for residential concrete floor slabs as they could withstand heavy loads, such as motorhomes or garbage trucks and meet the compressive strength requirements of 3,000 pounds per square inch

(Vanderwerf, 2007). The flooring slabs would start at 24x24x4 inches and could be scaled up to 5 and 6 inches in depth, which are common thicknesses used in solid flooring slabs. This would increase the weight load for which the flooring could be used. The second product considered was concrete masonry units (CMUs), also known as cinder blocks, with the standard dimensions of 16x8x8 inches wide. CMUs are good for concrete columns and tie beams in concrete block structure construction, and they are also used in American houses for concrete foundations and fire-rated partition walls (“Typical Sizes and Shapes of Concrete Masonry Units”, 2019). The concrete blocks are a standardized unit, so scale up is not as practical for this particular product, although slight variations in weight, size, and shape can be found. They are not commercially common. The final product considered was concrete circular pipes. Each pipe segment would have dimensions of 24 in. inner diameter, 60 in. length and a wall thickness of 3 in. (“Reinforced concrete pipe, n.d.). These pipe segments can be used for storm sewers, sanitary sewers, low pressure pipelines, and culverts (“Concrete pipe”, n.d.). The concrete piping could be scaled up to 48, 60, and 96 inches in diameter with respective wall thicknesses of 5”, 6”, and 9”, respectively. In the end, CMUs were chosen as the product due to limited data the team was able to find. The other products and their scale up should be considered in future research.

4.2 THE PROCESS

4.2.1 Carbon Capture through Full Oxy-Fuel Combustion

The team intends to modify the general OPC production process by adding two additional steps. The first step is full oxy-fuel combustion. Oxy-fuel combustion is a carbon capture and sequestration technology. The following paragraph describes the oxy-fuel combustion process as it is described in “Oxy-fuel combustion systems” (n.d.).

The process begins with an air separator, which produces a pure oxygen (O_2) feed to the combustion process. The oxygen is then fed, in conjunction with a hydrocarbon fuel, to the boiler which facilitates combustion. CO_2 and H_2O are the main products of this process and are taken off as flue gas. The stream then splits into two, one which recycles part of the flue gas back into the boiler, and one which leads to cooling, compressing, and dehydrating the stream to produce pure CO_2. Figure 2 below provides a visual representation of how this process is integrated into cement manufacturing:

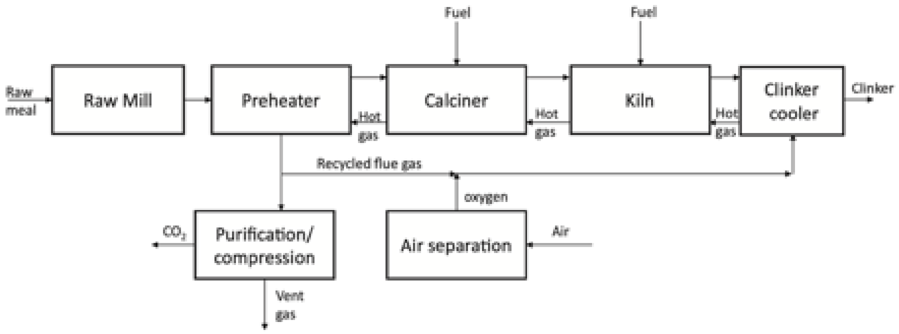


Figure 2: Basic layout of full oxy-fuel configuration: modifications to the OPC process to achieve the full oxy-fuel configuration; for the purposes of this design, the recycled flue gas from the preheater to the cooler will be neglected (Carrasco-Maldonado et al., 2016).

Part of what sets oxy-fuel combustion apart from other carbon capture and sequestration technologies is that the process utilizes a pure O_2 stream and recycles flue gas back into the combustion process. This is as opposed to feeding air into the process, which presents inert nitrogen that dilutes the O_2 to a set level of approximately 20% in the boiler. Using a separate inert gas to dilute a pure oxygen stream instead allows for higher variability and concentration of O_2 (Zeman, 2009).

4.2.2 Carbon Storage through Accelerated Carbonation Curing

Accelerated carbonation curing (ACC) is a technique that utilizes the natural process of carbonation to cure precast concrete with CO_2 instead of steam or water. The intentional introduction of CO_2 and silicates in concrete leads to an increase in CO_2 storage capacity, as well as increased durability and strength of concrete (Ahmad, 2018). Two main challenges to industrial-scale production are (1) current lab results demonstrate CO_2 sequestration at only 20-50% of the theoretically possible amounts due to limitations occurring in the CO_2 diffusion into the cement matrix during ACC and (2) there are unclear effects of ACC on the durability of cement-based composites due to unknown mechanisms, especially for alkali-silica reaction, corrosion, and sulfate attack (Liu & Meng, 2021). However, ACC is sustainable and renewable, and requires less energy than steam curing, making it a valuable technology (Goyal & Sharma, 2020; Shi & Wang, 2017).

There are some important differences in the mechanisms between passive and accelerated carbonation that allow ACC to be a beneficial process whereas passive carbonation is considered detrimental to concrete (Goyal & Sharma, 2020). One difference is that because accelerated carbonation occurs at an early age, it allows for the CO_2 to react with the unhydrated cement phases as well as the hydrated products creating more structurally strong concrete (Goyal & Sharma, 2020). Another difference is that CO_2 acts as a reactant in ACC while in passive carbonation it acts more as a catalyst (Zhang et al., 2017). Additionally, for passive carbonation the diffusion of CO_2 into the pores is considered the rate-controlling process; however, for ACC, the diffusion is chemically-limited by the detachment of calcium ions (Cui et al., 2015).

The reaction mechanism of ACC will be discussed in the following sections as will the experimental set up and conditions. ACC occurs in a three-stage approach: preconditioning, carbonation, and post-conditioning.

4.2.2.1 Preconditioning

The first stage is preconditioning, consisting of in-mold and de-mold curing. In-mold curing is only necessary for wet-mix concrete, which is what the team is using as pressure-compacted, dry-mix, precast, concrete has lower carbon uptake capacity (Goyal & Sharma, 2020). During de-molding, the shell is removed from around each sample, which exposes more surface area. HIgh-pressure gas can be used to accelerate the process of drying. The objective of preconditioning is to optimize the amount of water before carbonation. The water-cement ratio (w/c) is extremely important as it dictates the structural fluidity of the concrete and possible degree of carbonation; these two characteristics change inversely with each other (Li et al., 2019). Both the in-mold and de-mold processes typically occur in an ambient environment at 20-25°C and relative humidity (RH) of 40-60% (Liu & Meng, 2021). In-mold curing lasts for ~5 hours while de-mold curing lasts 5-6 hours (Zhang & Shao, 2016). Overall, the preconditioning process can last as little as two hours and as long as 24 hours (El-Hassan, 2020). In in-mold curing, the cement-based composite begins early setting. Once hardened, the products are de-molded. The de-molding increases the surface area available for evaporation of the free water inside (Goyal & Sharma, 2020). The removal of this water increases CO_2 diffusivity in micro-pore solution in the carbonation stage by a factor of 10,000 (Liu & Meng, 2021). About 40-45% of mixing water should be removed to bring the w/c to ~0.2, an ideal level for carbonation (Zhang & Shao, 2016; Li et al., 2019). Li et al. (2019) uses wind at a speed of 1±0.2 m/s. Additionally, the samples can be turned over to ensure uniform water dispersion loss. Equations 1-3 represent the hydration reactions that occur primarily during this stage. A hydration degree of around 20-30% can be reached during this stage after approximately 24 hrs (Liu & Meng, 2021).

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \tag{1}$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \tag{2}$$

$$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{3}$$

From Table A.1 in Appendix A, the PRODUCT stream is equal to 4,703,882.7 kg/year of concrete. This roughly translates to 45 CMUs per hour. The ACC system must be able to handle this load. For that reason, a mold with the capacity of 500-750 CMUs per hour was chosen, as it was the smallest mold available. This large size will however be beneficial for scale-up, which will be discussed later in this report. The room that the preconditioning takes place in does not have to be special as it all occurs at ambient pressure and temperature. Several fans can be added to aid the process. Once an hour, the molds will be filled. This number is chosen out of practicality. It limits the burden on the rest of the ACC process, especially carbonation. After five hours, the molds will be removed. After another three hours, the specimens will be flipped. Three hours later they will be moved to the carbonation chamber. Due to the process conditions and the size of the mold chosen, the team does not fear bottlenecking at this point of the process.

4.2.2.2 Carbonation

The second stage of ACC is carbonation which consists of exposure of the precast concrete to a CO_2 environment for 2-24 hours, generally at ambient temperatures. Studies show that the degree of carbonation reaches its maximum value at 100℃ for short carbonation periods; however, the team will be using a 12 hour period to follow the studies from which the team has adapted this system (Wang et al., 2019). Two styles of chambers can be used for this process: closed and flowable. Most research has been conducted in closed chambers due to the ability to operate at higher pressures which leads to higher carbonation rate and degree. The flowable chamber can sustain a high flow rate of CO_2 at atmospheric pressure, and requires less energy input than the closed chamber. The team will be using a closed chamber as the goal is to maximize carbon uptake and the studies which the system is modeled after utilize closed chambers. The closed chamber used in carbonation tends to be maintained as a vacuum at the beginning of the process to maximize the space to be occupied by CO_2 gas only (Goyal & Sharma, 2020).

The mechanism for carbonation is as follows: (1) the transportation and dissolution of CO_2 releases carbonate ions, (2) the Ca^{2+} species is released in the pore solution by cement and cement hydration products, and (3) Ca^{2+} and carbonate ions react and precipitate calcium carbonate (Liu & Meng, 2021). This is shown in Figure 3 below.

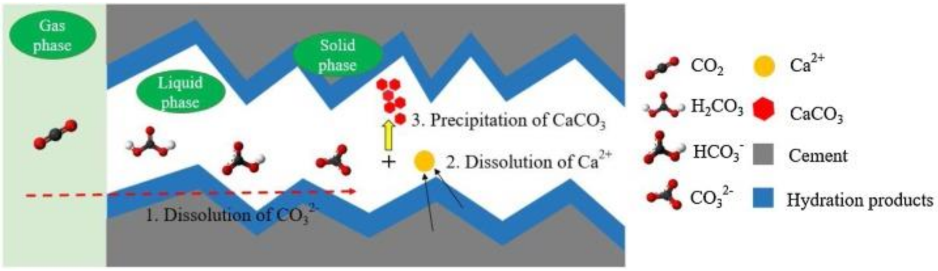


Figure 3: Mechanism of carbonation: Step-by-step breakdown of how carbonation works in cementitious material (Liu and Meng, 2021).

This process forms H^+ ions, which decreases the pH of the concrete (Zhang & Shao, 2016). Three polymorphs of calcium carbonate are formed in the process as well: aragonite, vaterite, and calcite (El-Hassan, 2020). The first two polymorphs form from the carbonation of

C-S-H, while calcite forms from the carbonation of calcium silicates (El-Hassan, 2020). Calcite is by far the predominant product in ACC and the most desired (El-Hassan, 2020).

Equations 4 and 5 show how the dehydrated calcium silicates alite ($3CaO \cdot SiO_2$ or C_3S) and belite ($2CaO \cdot SiO_2$ or C_2S) react with CO_2 in the presence of water to form calcium silicate hydrate (C-S-H) and calcium carbonate ($CaCO_3$). These reactions are exothermic, and their reaction rates limited by CO_2 diffusion, which depends on CO_2 concentration and pressure (El-Hassan, 2020).

$$3(3CaO \cdot SiO_2) + (3 - x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_2 \cdot yH_2O + (3 - x)CaCO_3 \tag{4}$$

$$2(2CaO \cdot SiO_2) + (2 - x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_2 \cdot yH_2O + (2 - x)CaCO_3 \tag{5}$$

C_3A and C_4AF are not significantly reactive with CO_2. Adding too much CO_2 to concrete decreases the concrete's integrity by removing calcium hydroxide from the product, replacing it with calcium carbonate, thereby decreasing the concrete's volume while increasing its porosity (Hanson, 2015).

Some hydration products are reactive with CO_2. Equations 6-9 show these reactions. C-S-H and CH react with CO_2 at the same time. Decalcified C-S-H reacts under extensive exposure to CO_2 to become silica gel, a higher density compound. Ettringite, a hydrous calcium aluminium sulfate mineral, decomposes under exposure to CO_2 to make multiple compounds.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{6}$$

$$xCaO \cdot SiO_2 \cdot yH_2O + zCO_2 \rightarrow zCaCO_3 + (x - z)CaO \cdot SiO_2 \cdot yH_2O\ (decalcified) \tag{7}$$

$$xCaO \cdot ySiO_2 \cdot zH_2O + xCO_2 \rightarrow xCaCO_3 + y(SiO_2 \cdot tH_2O) + (z - yt)H_2O \tag{8}$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \rightarrow Al_2O_3 \cdot xH_2O + 3CaCO_3 + 3(CaSO_4 \cdot H_2O + (26 - x)H_2O \tag{9}$$

Carbonation is going to be the limiting step in the ACC process. As it takes 12 hours, there will be 12 chambers so as to not bottleneck the system. The chambers chosen will be able to handle the 45 CMUs per hour laid and some, which is beneficial for scale-up. For the team's design, ambient temperature will be used. The carbonation chambers will first be vacuumed to remove any air present before being pumped with CO_2 at 1 bar from the KILNGAS stream. The leftover CO_2 from this process will come out as the CO2OUT stream. The theoretical values of these streams can be found in Table A.1 in Appendix A. After the 12 hours are up, operators will move the CMUs from the carbonation chamber to a moisture room where post-conditioning will occur. The leftover CO_2 will be stored for alternative use.

4.2.2.3 Post-Conditioning

The third stage is post-conditioning, which utilizes the conventional curing technique. A significant amount of water is evaporated during the exothermic carbonation period (Goyal and Sharma, 2020). As such during the post-conditioning stage, water is added to compensate for water loss and enable further hydration, which promotes denser microstructure and further structural integrity (Liu & Meng, 2021). This is due to the production of C-S-H that occurs during the hydration of cement (Goyal & Sharma, 2020). This stage has reported up to a 45% increase in compressive strength after 3 days (El-Hassan, 2020). While a water spray or immersion can be used, the team will opt to use a moisture room as the studies the experimental set up is modeled after use moisture rooms. Based on recommendations from Zhang and Shao (2016), Li et al. (2019), and Liu and Meng (2021), the subsequent water curing will last 27-28 days at 25℃ and RH of 95%. 28 days is the typical curing age for traditional concrete manufacturing (Zhang et al., 2018).

The designed plant will include five moisture rooms that can handle the capacity of 30,240 CMUs over the course of 28 days. Using five moisture rooms is optimal for the plant because CMUs can be easily organized by length of time in the post-conditioning stage. Once this stage is complete, the process is done, and the CMUs can be packaged and sold.

4.2.2.4 Carbon Uptake

One ton of cement could theoretically capture approximately half a ton of CO_2 based on the relative mass of oxides within the cement (Kashef-Haghighi & Ghoshal, 2009; Shi et al., 2017). The exact value can be calculated using Equation 10. Given the chemical composition of the raw materials listed in Table V, the carbon uptake potential of the team's product is 68.6%. This number is a bit high likely due to the high amount of CaO calculated to be in the raw material. Regardless, the theoretical maximum carbonation should never be reached as it would compromise the strength of the concrete (Qian et al., 2018). Some factors that have an impact on the carbon storage capacity of cement curing using ACC are the weight-percent replacement of cement by SCMs and the surface-area-to-volume ratio (Souto-Martinez et al., 2017). Additionally, carbon uptake depends on the carbonation process design such as the length of carbonation curing, concentration of CO_2, etc. In general, the carbon uptake is calculated experimentally using Equation 11 (Kashef-Haghighi & Ghosahal, 2010).

Table V
Chemical compositions of ordinary Portland cement raw material by component

	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	Inerts
(wt%)	0.073	0.862	0.035	.015	0.010	0.002	0.004

$$X_{CO_2,tot} = 0.785(X_{CaO} - 0.560X_{CaCO_3} - 0.700X_{SO_3}) + 1.091X_{MgO} + 1.420X_{Na_2O} + 0.935X_{K_2O} \qquad (10)$$

$$Carbon\ Uptake\ (\%)\ = \frac{Final\ mass\ -\ initial\ mass\ +\ mass\ of\ water\ lost}{Mass\ of\ CO_2\ reactants} * 100\% \tag{11}$$

The team is going to assume the use of an aggregate to cement ratio of 4, which is average (Kashef-Haghighi & Ghosahal, 2010). With a CMU product, the carbon uptake was found to be 24.63%-25.21% with OPC (El-Hassan & Shao, 2015). However, the mix of OPC used in this study had a theoretical uptake value of 68.65%. Given the OPC mix has a much higher threshold, the team should be able to achieve an uptake value the slightly above level recorded in the El-Hassan and Shao (2015) study at about 30%, this would mean that 1,411 metric tons of CO_2 are sequestered per year. This amount corresponds to approximately 82% of the CO_2 captured from the kiln. Estimations suggest that if all CMUs in the U.S. and Canada were produced with ACC, 1.5 million tons of recovered CO_2 could be sequestered annually (Goyal & Sharma, 2020).

4.3 ENVIRONMENTAL CONCERNS

4.3.1 Carbon Dioxide Inventory

The major carbon capture and sequestration techniques used in this process are oxy-fuel combustion and ACC. Oxy-fuel combustion simplifies capture and storage of carbon dioxide. Because oxy-fuel combustion uses pure oxygen and hydrocarbons, the combustion products are pure water vapor and carbon dioxide. A major cost of oxy-fuel combustion is air separation. The oxygen needed for this process would be separated from atmospheric air. An alternative would be purchase and storage of pure oxygen. This is costly and unfeasible. Carbon dioxide in the flue gas is easily separated by condensing residual water vapor. This resolves any need for carbon scrubbers whether through adsorption, absorption, or membrane filtration. Carbon dioxide is then easily condensed for transportation either through pipeline systems or tanker trucks. The carbon dioxide pipeline system is relatively extensive in the United States with 50 individual pipelines forming a combined length over 4,500 miles (DoE, 2016). Connecting to this pipeline may represent a capital cost of the project, the total cost dependent on the distance from this proposed plant to the existing network. However, the Department of Energy expects that the carbon dioxide pipeline system will vastly expand into 2030 and beyond with a renewed interest into low-carbon emissions and CCS. One process hurdle to using oxy-fuel combustion is flame temperature. Oxy-fuel combustion with natural gas burns at a temperature higher than desired in this process. One strategy to alleviate temperature is to recycle product CO_2 back into the kiln to dilute the oxygen stream.

Commented [2]: source

The vast majority of the CO_2 pipeline system is dedicated to enhanced oil recovery (EOR). While EOR would help to offset some operating costs of this plant, increasing oil production may not be in line with the overarching goal of the project. Other sequestration options include deep geological injection and carbonate storage. Carbonate storage is merely an expansion of the carbonation curing seen in this process, but instead of being sold as a building product, these carbonates are formed as final-use storage solutions.

However, carbon dioxide does not always need to be sequestered. There is a growing demand for carbon dioxide as an industrial product. In Figure 4, from the International Energy Agency, one can see that the total carbon dioxide demand is expected to grow to 272 million tonnes per year (2019). The largest consumers being the fertilizer industry and EOR.

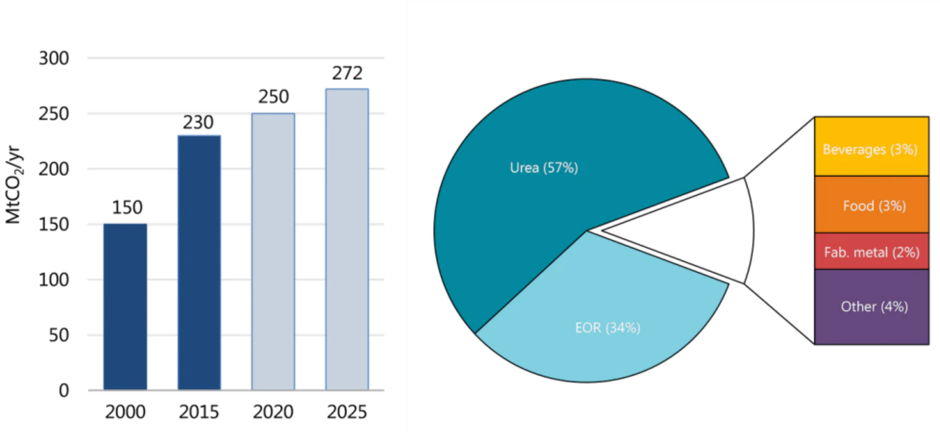


Figure 4: Carbon dioxide demand predictions and industry analysis: Breakdown of where the demand for carbon dioxide will be coming from (International Energy Agency, 2019).

One interesting CO_2 use that the team discovered was as a heat transfer fluid. CO_2 makes for an interesting heat transfer fluid due to its relatively accessible critical point. Some drawbacks to this approach are the high costs of pumps needed to reach the critical point. Also, cheaper, better understood heat transfer fluids exist (steam, oil, air). Furthermore, much of the heat transfer fluid CO_2 used would be recycled, thus other storage solutions would need to be explored for the remaining CO_2.

In total, this system produces CO_2 in two processes. The first being limestone calcination and the second fuel combustion. This model expects calcination to produce just over 1.7 million kilograms of CO_2 per year. For combustion, Mastorakos et al. found that the specific energy use is around 3.2 MJ/kg of clinker manufactured (1999). This corresponds to 9.6 million MJ/year of energy needed. The group has chosen natural gas to fuel the cement kiln. Natural gas is around 95% methane. For the purpose of these calculations, the natural gas source is treated as pure methane and sweetened. Methane’s heat of combustion is 55.50 MJ/kg, thus 0.173

million kg/year of methane is needed. Assuming complete combustion, the CO_2 output is 0.475 million kilograms per year. Bringing the total CO_2 production to 2,175 million kg/year. This ACC model also expects 30% uptake of CO_2, calculating to 82% of CO_2 sequestered thus leaving 392 million kilograms of CO_2 that can be captured and sold per year.

4.3.2 Water Inventory

Water is an extremely important ingredient in concrete controlling many characteristics, such as workability of fresh concrete, and compressive strength, permeability, watertightness, durability, weathering, and potential for cracking in hardened concrete. The cement to water ratio is also extremely important concrete curing and ever more important in ACC. The water to cement ratio is even so important that building codes mandate specific ratios for certain building materials. For most concrete production, potable source water is needed. Some batches even require distilled water. These requirements can be met using simple, commercially available pre-production treatment systems. Per the material balances, 1,200 tonnes of water are needed per year. However, 1,768 tonnes of water are produced via combustion, thus no outside water is needed, only condensed water from other unit operations.

Commented [3]: source

Concrete process water is both highly caustic and basic due to the presence of limestone. Processed water also contains dissolved solids including sulfates and hydroxides from clinker production, derivatives from chemical mixtures, and lubricants from machinery. Environmental regulations prohibit the discharge of highly basic and suspended solids within wastewater. Furthermore, most public sanitation facilities are ill-equipped to handle such caustic wastewaters. The normal threshold for local sanitation is around a pH of 10. Commercial systems exist to both separate the dissolved solids (grit separators and holding tanks) and lower the pH of wastewater streams. One interesting solution to acidification of wastewater is the addition of gaseous carbon dioxide. Typical solutions involve adding sulfuric or hydrochloric acid. Many well-established processes exist for wastewater treatment, and this will not be a large focus within the scope of this project.

Another solution to both wastewater and water usage, in general, would be recycling. After treatment, the treated wastewater could be diverted back to the kiln and curing operation. Condensed water from oxy-fuel combustion can also be used throughout the process. Recycling reduces both the waste output and cost of the overall process, making this process less resource and capital intensive. Recycling wastewater from the CO_2 purification process should be explored in future work.

4.3.3 Other Environmental Considerations

In addition to CO_2, typical cement plants emit sulfur dioxide (SO_2), nitrogen oxides (NO_x), and carbon monoxide (CO) (*Cement Manufacturing Enforcement Initiative*, 2013). These emissions are mitigated due to the use of oxy-fuel combustion, natural gas as fuel, and the team's assumption of complete combustion; however, discussion of the risks of these environmental hazards is still warranted. SO_2 at high levels affects breathing and aggravates existing respiratory and cardiovascular disease, and it causes acid rain (*Cement Manufacturing Enforcement Initiative*, 2013). NO_x contributes to various health problems and negative environmental impacts, such as ground-level ozone, acid rain, global warming, water quality deterioration, lung damage, and visual impairment (*Cement Manufacturing Enforcement Initiative*, 2013). CO inhibits the body's ability to transport oxygen to its organs and tissues, negatively affects the cardiovascular and central nervous systems, and contributes to smog formation (*Cement Manufacturing Enforcement Initiative*, 2013).

SECTION 5: FINAL DESIGN

5.1 EQUIPMENT AND FLOWS

The process begins with a crusher unit, which pulverizes the calcium carbonate and additional input components as detailed by the CALCARBO stream in Table A.1 in the Appendix. All input materials are then fed to a pre-heater unit, which increases the temperature of the input materials in preparation for calcination. The calcination reactions occur in the subsequent calciner unit. The calcination of the input materials continues into the kiln, at which point the maximum temperature of the process is reached: approximately 1450^oC (Zeman, 2009). Kiln gas and molten clinker result from the reactions within the REO kiln, which are separated and undergo separate processing pathways to create CO_2 and concrete ready for accelerated carbonation curing.

The gas processing pathway utilizes a gas cooling unit, compressor, and condenser in that order. The gas cooling unit brings down the temperature of the CO_2, H_2O, and methane (this stream was estimated as pure CO_2 for simplicity of calculation, but there will be a small portion of methane from natural gas use) of the KILNGAS stream from 1450^oC to a manageable temperature around 300-400^oC (Zeman, 2009; White, et al., 2009). The compressor and condenser units act to facilitate the separation of the H_2O and CO_2 in the gas pathway, with H_2O removal occurring in the condenser, resulting in a CO_2 stream with trace amounts of methane. Since methane (CH_4) and CO_2 are chemically similar and only trace amounts exist in the gas stream, separation of these chemicals is not within the scope of this project.

The solids processing pathway uses a solids cooling unit, crusher, and mixer. The solids cooling unit brings the temperature of the molten clinker to approximately 300-400^oC (Zeman, 2009; White, et al., 2009). This clinker is typically cooled into a spherical shape. The clinker is then crushed again to produce smaller grains for introduction to H_2O in a mixing unit, with the aim of creating cement paste. This paste is then combined with aggregate in a ratio of 4:1 aggregate to cement and introduced to the gas stream in the ACC process.

The ACC process proposed is optimized based on various studies and theory discussed in the earlier sections. The entire ACC process will take place in three separate locations. First, the preconditioning stages will occur in open air for a total of 10-11 hours. The operating conditions for these stages and all others can be found in Table VI on the following page. The carbonation stage will occur in a pressure chamber capable of holding 50 CMUs, as the factory will be producing 45 CMUs per hour. There will be twelve of these chambers to manage the production rate given the amount of 12 hours that carbonation takes. Finally, the post-conditioning stage will occur in a moisture room.

Table VI
Breakdown of the design parameters for ACC

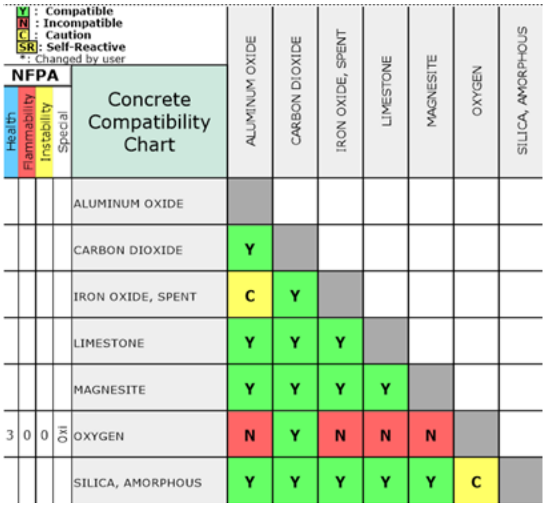
Stage	Temperature (℃)	Pressure (bar)	Time (hr)	Other notes
In-Mold Curing	20-25[1]	1.013[1]	5	RH=40-60%
De-Mold Curing	20-25[1]	1.013[1]	5-6	RH=40-60%, wind=1±0.2 m/s, flip over halfway
Carbonation	20-25[1]	1	12	Closed chamber, vacuumed prior to carbonation
Post-Conditioning	25	1	27-28 days	Moisture room, RH=95%

[1] ambient temperature or pressure

5.2 SAFETY

It is important to note the various hazards associated with the heat and chemicals handled in this process. As combustion is occurring in this process, or the purposeful use of oxygen and fuel to maintain a fire, many associated risks are present. For example, fire is an exothermic oxidation while an explosion is a high energy release. As an explosion can result from a fire, it is important to pay close attention to flame properties within the kiln. Additionally, CO_2, in confined spaces, can displace O_2, and cause asphyxiation to any nearby workers (Praxair, 2016). Superheated water vapor can also cause burns to nearby workers.

The chemical interactions of other materials in the process were analyzed in the Chemical Reactivity Worksheet (CRW) application, developed by the American Institute of Chemical Engineers (AIChE), the National Oceanic and Atmospheric Administration (NOAA), and the U.S. Environmental Protection Agency (EPA). An analysis of compatibility involving all input materials, shown in Figure 5 on the next page, reveals that Fe_2O_3 and Al_2O_3 result in an intensive, potentially explosive reaction, and that SiO_2 and O_2 result in an exothermic reaction when placed in contact. Most input materials are shown to be incompatible with oxygen, due to reactions being extremely exothermic, toxic, and explosive. However, pure O_2 is introduced to the system in the calciner component: after the input materials have been transformed into belite (C_2S), alite (C_3S), and tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF) in the preheater (see cement species nomenclature in Section 10). Therefore, these components never interact in these forms.



Y : Compatible
N : Incompatible
C : Caution
SR: Self-Reactive
*: Changed by user

NFPA Health	NFPA Flammability	NFPA Instability	NFPA Special	Concrete Compatibility Chart	ALUMINUM OXIDE	CARBON DIOXIDE	IRON OXIDE, SPENT	LIMESTONE	MAGNESITE	OXYGEN	SILICA, AMORPHOUS
				ALUMINUM OXIDE							
				CARBON DIOXIDE	Y						
				IRON OXIDE, SPENT	C	Y					
				LIMESTONE	Y	Y	Y				
				MAGNESITE	Y	Y	Y	Y			
3	0	0	OX	OXYGEN	N	Y	N	N	N		
				SILICA, AMORPHOUS	Y	Y	Y	Y	Y	C	

Figure 5: CRW Compatibility Generation: Where the green boxes represent compatible materials, yellow boxes represent materials with potentially dangerous interactions that should be treated with caution, and red boxes represent incompatible materials.

For this process specifically, high temperature and pressure pose serious threats to safety. The kiln in particular is operated at a temperature of 1450^{o}C (Zeman, 2009). Contact with material at this temperature may result in serious damage to equipment and or personnel improperly equipped to handle high temperatures. Therefore, operators must ensure proper temperature regulation, inspections of the structural integrity of high temperature equipment, and use of proper personal protective equipment. High pressure units are also an issue. The compressor unit is operated at approximately 128 atm. High pressure equipment is prone particularly to structural failure, especially when exothermic, explosive processes are at play. Therefore, operators must ensure a proper shutdown and replacement schedule as needed for high pressure equipment.

5.3 SOCIETAL IMPACT

The impacts of this proposed process on society can be felt in the realms of public health, politics, public opinion, and the economy.

First and foremost, the carbon capture technology explored in this design has the potential to prevent large amounts of CO_2 from entering the atmosphere. By decreasing CO_2 levels in the atmosphere, global temperature rise can stagnate, and eventually fall with the operation of further carbon capture technologies. The effects on public health from high levels of CO_2 in the atmosphere, for example, increased frequency and magnitude of natural disasters and sea level rise, will be diminished and lead to greater prosperity and human welfare with the implementation of this technology (NASA, 2021).

Politically, carbon capture technology has faced negative consideration from some factions; especially from groups that support keeping coal miners, and others that work in unsustainable energy generation, in their jobs. This, coupled with adverse public opinion of large carbon capture facilities may lead to difficulty establishing funding and other resources for this technology. However, the technology proposed here would serve to augment concrete production, and not detract from current landscapes nor jobs in the energy sector directly. Therefore, this technology may be a good stepping stone to other sustainable options.

The effect of this technology on the economy will be explored further in the next section. However, considering the novel concept of carbon capture, it may be difficult to find investors for this technology. This should be kept in mind if implementation is attempted.

SECTION 6: ECONOMIC CONSIDERATIONS

6.1 CAPITAL COSTS

The team has chosen Texas as the location for the cement plant. Texas is a state with a large cement capacity, demand, and low energy costs. The plant will not include mining operations, thus limiting land investment and cost of mineral rights. The group has estimated that a plant of the desired capacity will need 100 acres to include all ancillary operations, storage facilities, and buildings. The cost for rural land in Texas just under $3,000 per acre. The cost estimation per ton produced comes from the IEA’s Energy Technology Systems Analysis Programme and provides the construction costs for a plant that includes oxy-fuel combustion. This number includes man-hours, building erection costs, and other construction operations and materials. The total initial investment of the plant is relatively low at 1.62 million dollars without ancillary equipment costs. This low cost can be attributed to the small scale of the process.

Equipment costs are summarized in Table VII on the following page where each cost is broken down by the individual unit operation. The ACC costs are bundled together. The total cost of ancillary equipment adds up to $1,804,660, which brings the total initial investment to build the desired concrete manufacturing plant to $3,427,860.

Table VII
Ancillary equipment cost breakdown

Equipment Item	Estimated Cost (in 2021)
Crusher (Inputs)	$57,500
Preheater	$42,000
ASUs	$3,000
Calciner	$600,000
Kiln	
Cooler (Gas)	$122,000
Compressor	$10,000
Condenser	$42,000
Cooler (Solids)	$173,000
Crusher (Clinker)	$19,000
Mixer	$19,000
ACC (Molds and Chambers)	$25,160
Overflow Storage Equipment	$692,000
TOTAL	**$1,804,660**

The initial crusher unit for reducing input materials is estimated to cost around $57,500. This was found by averaging the prices of a high-capacity crusher made specifically for cement input materials. As the team's project is at the pilot scale, a price between $15,000 (the lower value found), and $57,500 is more practical; however, to remain conservative in this estimate, an average was taken (*High capacity stone crusher machine for coal /clay /limestone/nickel ore/oil shale,* n.d.).The preheater unit price is obtained from the value for an 8-pass heat exchanger made for alcohol production, and therefore solids and liquids manufacture (*Preheater Condenser - 8-pass. 942 Sq Ft. 24" O.d. X 20 Ft Tube Length*, n.d.). The air separation units (ASUs) were estimated to cost approximately $1,500 each (*Oxygen Concentrator Industrial for Ozone or Glass Blowing 8 SCFH, 110V/60Hz,* n.d.). The calciner and kiln components were designed based on a model from Ditaranto and Bakken (2019). However, as this study did not provide pricing details on the pilot scale kiln design cost, the team found a unit that was approximately half of the designed size in Ditaranto and Bakken and doubled that amount (2019; *Best Price New Type Rotary Kiln Calciner*, n.d.).

The cooler systems proved challenging to price-estimate because they are required to withstand high temperatures of approximately 1450^{o}C, and many coolers are composed of stainless steel, copper, and similar materials, which are not capable of operating at these temperatures (Zeman, 2009). The gas cooler price of $122,000 is a value estimated in the Excel Application CAPCOST, designed by Richard Turton for a fixed, shell-and-tube heat exchanger, capable of withstanding temperatures of 1083^{o}C (the melting point of its composition material, copper, at atmospheric pressure) (Alcobra, 2020). A primary method of cooling the kiln gas to 1083^{o}C is necessary, but this equipment is believed to be rare or nonexistent at the moment because the use of oxy-fuel combustion increases the materials outlet temperature; and since the use of oxy-fuel combustion in cement production is novel, the required equipment may not currently exist (Zeman, 2009). A unique solids cooling process, designed by Solex Thermal

Science, was determined by the team to be capable of withstanding the required temperatures of this process with cost estimation completed in CAPCOST using the product specifications (n.d).

Price estimates for the gas compressor and condenser units were found by locating units for sale that satisfy temperature and pressure standards for the process (*350bar Oil Free CO2 Gas Diaphragm Compressor Carbon Dioxide Compressor*, n.d.; *Preheater Condenser - 8-pass. 942 Sq Ft. 24" O.d. X 20 Ft Tube Length*, n.d.). Estimates for the solids crusher and mixer were also located based on current availability in the market for concrete crushers and mixers (*Used 20HP Dual Roller Stainless Steel Clinker Grinder Crusher*, n.d.; *Used 10 cubic yard stationary concrete mixer*, n.d.).

The value listed in Table VIII for “ACC (Molds and Chambers)” is the combined price of one molding unit, twelve carbonation chambers, and five moisture rooms. As detailed in Section 4.2.2.4: ACC Design Review, the ACC process will occur in three stages each in its own location. The mold cost is based on the average price of a split faced concrete production unit, which would mold the concrete blocks but maintain wet concrete (*Split face concrete block splitter machine qt4-28 brick block machine low price*, n.d.). The individual price for each carbonation chamber is based on two different chambers that both retail for $750 each when bought in quantities equal to or greater than ten (*2020 Guangzhou Material Airshower with Two Doors for Electronic Interlocking*, n.d.; *Cleanroom Entrance Class 100 Filtration Air Shower Room*, n.d.). Finally, each moisture room’s cost combines the price of a control panel designed by Gilson Company, inc. specifically for concrete curing that can maintain the environment at proper temperature and relative humidity and two sets of the atomizing spray heads, also produced by Gilson Company, inc. that integrate with the control panel (*Atomizing Spray Head*, n.d.; *Moisture Room Control Panel*, n.d.).

The “Overflow Storage Equipment" heading incompases all storage tanks in the process. The team analyzed the design and determined that it would be pertinent to account for the following tanks: a limestone storage tank, clay storage tank, and gypsum storage tank (each at the beginning of the process); a clinker overflow tank (after the solids cooler unit, indicated as E-101 in Figure 1, Section 4.1.1); a cement overflow tank (sealed as to maintain wet cement paste and located after the mixer unit, C-101); a water input storage tank (feeding to C-101 via stream WATERIN); and a water output storage tank (after the condenser unit, C-103, feed by stream WATEROUT). Each tank is designed to hold one month’s worth of material flow. Cost estimates were found using Richard Turton’s Excel Application, CAPCOST, and all estimates assume fixed roof tank designs accommodating the minimum size requirement for one month’s worth of full material flow to the tank.

6.2 OPERATING CASH FLOW

The overall operating cash flow for this process is not favorable, as the net cash flow is negative. The inflows and outflows for this process are shown on the following page in Table VIII. Labor is by far the largest operating cost at $730,884.00. The labor costs account for fifteen operators and three managers making $15.75/hr and $27.33/hr, respectively. Though the products make a fair amount, they are not close to offsetting the costs of labor.

Building off of the energy balance, the group determined the fuel flows and costs of the process. 121,081 m^3 per year of natural gas are needed, with a basis of $4.04 per 1,000 ft^3 for industrial natural gas gives the total cost per year of $17,274.78 for fuel. The water cost per year is very low at $2,617.21 per year. The basis was from a municipal average in Texas. Finally, electricity will cost $45,205.56 per year, again using an average cost for Texas.

One way to alter the process to make it profitable is to increase the design basis, since labor costs and taxes, the two largest costs, will not increase by as large of a factor. The current design basis is 3,000 metric tons of clinker per year, which corresponds to about 4,700 metric tons of cement product per year. This design basis is much smaller than most cement plant capacities, so it is understandable that it is not profitable. The process the team designed here could be used as a pilot plant before scaling up the process to an industrial scale. In order for the process to be profitable, the design basis should increase to at least 8,086 metric tons per year of cement produced, which is close to double the original design basis. This would result in a profit of $609,980.17 per year from the sale of cement and CO_2. With this larger design basis, the profit from cement and CO_2 sales would offset the large labor costs. Though the original design basis was 3,000 metric tons of clinker produced per year, a design basis of 3,000 metric tons of clinker per day would be closer to the scale of a traditional cement plant. With this traditional basis, the net cash flow would be $21,592,969.00 per year or $59,158.00 per day.

Table VIII
Estimated revenue of factory broken down into individual cash flow streams

Expenses		**Income**	
Category	**Price ($/yr)**	**Category**	**Price ($/yr)**
Limestone	10,515.00	CMUs	324,495.00
Clay	1,390.00	CO_2	30,415.00
Gypsum	1,358.00		
Ambient air	0.00		
Natural gas	17,274.78		
Water	2,617.21		
Electricity	45,205.56		
Labor	730,884.00		
Taxes	100,092.00		
Total	**909,336.55**	**Total**	**354,910.00**
		Net Cash Flow	**-554,426.55**

6.3 PROFITABLE SCENARIO ECONOMICS

Given the massive capacity difference between the pilot plant and the recommended plant, the team estimates that equipment costs and labor costs must both increase by a factor of ten to handle the 3,000 metric tons of clicker per day design basis. Table IX shows all of the multiplier factors assumed in the calculation of the internal rate of return (IRR) of the profitable, full-scale plant. Raw materials and utilities minus electricity are scaled up by 300 as that is the amount of days the factory will operate each year. Assuming that the factory operates at half capacity in its first year, 75% capacity in its second year, and then full capacity its third year on, the internal rate of return was calculated to be 122%. The IRR takes into account the previously presented scenario. This value comes from an initial investment of $32,792,600 and an annual profit return of $62,044,753.83 once the factory begins to operate a full capacity. This value indicates the great potential of a cement plant that uses a similar process to that described in this report. Given this internal rate of return, it would be favorable to invest in the factory of this scale.

Table IX
Multiplying factors assumed in the scale up of the cement plant

Variable	Multiplier
Labor	10
Raw Material	300
Utilities	300
Electricity	10
Equipment	10
Land	5
Installation	10

SECTION 7: CONCLUSION

The team has designed a pilot-scale process combining full oxy-fuel combustion from Zeman with the accelerated carbonation curing process from the various Zhang et al. studies (2009; 2016; 2017; 2018; 2019; 2020). The result is a concrete plant with a capacity of 3,000 metric tons of clinker produced per year that captures around 82% by mass of produced CO_2. While not profitable at the current scale, the plant concept and design present a competitive advantage regarding emissions standards. To further increase this advantage, scale-up is required. The highest operating cost of the process is labor. This number should not significantly increase with an expansion in capacity, as labor costs are estimated per unit operation instead of on a capacity basis. Also, the equipment chosen can handle the increased load. Two products drive the income of the project, carbon dioxide and CMUs. These two flows create $355k of income at the current scale.

Further studies are needed to prove the viability of this process in the current pilot scale. However, this work creates a proof of concept for the combination of processes. As more companies and government organizations focus on sustainability, a green concrete process becomes more viable and desirable. Currently, the concrete industry accounts for the second-largest industrial emitter of CO_2, with over 2.2 billion metric tons produced annually.

Unfortunately, the marketability of the process does not solely depend on environmental, social, corporate governance principles. At the pilot scale, the process is not profitable. As aforementioned, the labor costs are the largest expenditure. Assuming that the labor costs are constant, the group found the breakeven point to be just over 8,000 metric tons of clinker per year. A plausible solution, given that many cement plants operate on the scale of thousands of metric tons per day. However, the design presented in this paper is pilot-sized and must first undergo testing at that scale before scaling up. The group hopes to target a full-sized concrete producer to pursue this project as a research project to prove product viability and safety.

SECTION 8: FINAL RECOMMENDATIONS

One of the biggest priorities of this project was to find a green process for producing concrete. The primary method for this goal was CO_2 emission reduction, which this report showed to be possible to a higher degree than initially hypothesized. The innovative carbon capture and storage process established in this report is a solid step toward achieving the green concrete goal. However, many aspects can be expanded upon to make the process more practical. For one, utilizing materials and heat more efficiently, such as using more recycling streams, would significantly impact the quality of the product and the costs of production. Since several units require very high temperatures, optimizing heat flow throughout the process is crucial for further research. Another aspect to consider is the use of SCMs to reduce the carbon footprint and perhaps enhance the ACC and carbon storage capacity. The manufacture of different geometries of precast products besides CMUs should be pursued as well to investigate the effect on carbon capture and the potential for more diverse and profitable products. Another approach to this research would be investigating retrofitting an existing factory as opposed to building a new one. This tactic could be more viable cost-wise and more environmentally-friendly as new building construction has a major environmental impact.

Ultimately, two of the forefront technologies in the described process, REO kiln design and ACC, are relatively new processes. As a result, further research on these technologies would be beneficial to understand better how to implement them into this process most effectively. Research into the combination of full oxy-fuel combustion and ACC together, in particular, would be helpful as these technologies only exist independently in research currently. Overall, this process is neither optimized nor profitable, but it can be both in the future. That being said, the team does not think the designed process is currently marketable for industrial production. This unfortunate fact is especially prevalent when comparing the proposed green process to the current, established, and profitable method of concrete manufacturing. To optimize the overall process, future researchers should consider using a larger design basis of at least 3,000 metric tons of clinker per day to make this product.

SECTION 9: ACKNOWLEDGEMENTS

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SECTION 10: NOMENCLATURE

Cement species:
AFt: ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$ (s))
C-S-H: silicate hydrate gel ($3CaO.2SiO_2.3H_2O$ or C–S–H)
C_2S: dicalcium silicate or belite ($2CaO.SiO_2$)
C_3A: tricalcium aluminate ($3CaO.Al_2O_3$)
C_3S: tricalcium silicate or alite ($3CaO.SiO_2$)
C_4AF: tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$)
CH: dissolved calcium hydroxide ($Ca(OH)_2$)
CH (s): solid calcium hydroxide ($Ca(OH)_2$ (s))

Other Species:
Al_2O_3: aluminium oxide
$CaCO_3$: calcium carbonate
CaO: calcium oxide
CO: carbon monoxide
CO_2: carbon dioxide
Fe_2O_3: iron (III) oxide
$MgCO_3$: magnesium carbonate
MgO: magnesium oxide
NO_x: nitrogen oxides
O_2: oxygen gas
SiO_2: silica; silicon dioxide
SO_x: sulfate oxides

Terms:
ACC: accelerated carbonation curing
ASUs: air separation unit
CCS: carbon capture and storage
CMUs: concrete masonry units
CRW: chemical reactivity worksheet
CSTR: continuous stirred-tank reactor
EOR: enhanced oil recovery
GHG: greenhouse gas
OPC: ordinary Portland cement
SCMs: supplementary cementitious materials
REO: reduced oxygen emission
RH: relative humidity
w/c: water to cement ratio

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SECTION 12: APPENDIX

APPENDIX A: SUPPLEMENTARY INFORMATION

Table A.1
Stream table of mass flows in kg/year for the entire process starting from raw material inputs to carbonated concrete output

	Stream Name							
Component	CALCARBO	SUPPADD	KILNSOLI	KILNGAS	CEMPASTE	AGGREGAT	PRODUCT	CO2OUT
SiO_2	75,168.0	498,776.2	0.0	0.0	0.0	0.0	0.0	0.0
Al_2O_3	47,979.6	105,202.3	0.0	0.0	0.0	0.0	0.0	0.0
$CaCO_3$	3,776,394.6	31,751.2	0.0	0.0	0.0	0.0	1,865,247.4	0.0
Fe_2O_3	22,790.3	42,334.9	0.0	0.0	0.0	0.0	0.0	0.0
$MgCO_3$	77,966.9	10,583.7	0.0	0.0	0.0	0.0	0.0	0.0
Inert	0.0	16,933.9	474,000.0	0.0	474,000.0	0.0	55,568.6	0.0
C_2S	0.0	0.0	519,000.0	0.0	519,000.0	0.0	0.0	0.0
C_3S	0.0	0.0	1,512,000.0	0.0	1,512,000.0	0.0	0.0	0.0
C_3A	0.0	0.0	300,000.0	0.0	300,000.0	0.0	0.0	0.0
C_4AF	0.0	0.0	198,000.0	0.0	198,000.0	0.0	0.0	0.0
CO_2	0.0	0.0	0.0	1,720,668.1	0.0	0.0	0.0	608,347.8
H_2O	0.0	0.0	0.0	0.0	1,200,000.0	0.0	299,545.6	0.0
$CaSO_4$	0.0	0.0	0.0	0.0	0.0	157,894.7	0.0	0.0
$6CaO.Al_2O_3.Fe_2O_3.2CaSO_4.24H_2O$	0.0	0.0	0.0	0.0	0.0	0.0	531,018.8	0.0
$SiO_2.nH_2O$	0.0	0.0	0.0	0.0	0.0	0.0	248,460.7	0.0
$3CaCO_3.2SiO_2.3H_2O$	0.0	0.0	0.0	0.0	0.0	0.0	1,047,150.1	0.0

$3CaSO_4.2H_2O$	0.0	0.0	0.0	0.0	0.0	0.0	486,099.7	0.0
$Al(OH)_3$	0.0	0.0	0.0	0.0	0.0	0.0	170,791.8	0.0
Total flow rate	3,998,300.3	705,582.4	3,000,000.0	1,720,668.1	4,200,000.0	157,894.7	4,703,882.7	608,347.8