SUSTAINABLE CEMENT PRODUCTION TECHNOLOGY

Group Design Project

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SUSTAINABLE CEMENT PRODUCTION TECHNOLOGY

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Abstract

This research discusses the ongoing environmental difficulties shown by conventional cement production, which makes up roughly 8% of worldwide CO_2 emissions. The report stresses the crucial responsibility of cement in construction and facility developments while emphasizing the industry's energy-consuming practice and its major affiliation with air pollution. A detailed literature review showcases the feasibility of sustainable methods, including enhancing energy deficiency and using novel technologies, such as carbon capture technology to capture CO_2 emissions from cement plants. The report overviews the cement manufacture procedure, differentiating between dry and wet techniques as well as addressing the significance of implementing sustainable applications in terms of economic feasibility and environmental effects in addition to reviewing hazard and operability study and choosing best location for plant based on environmental and economic factors using all required tables and figures. The report reviews the chosen equipment's sizing and specifications as well. In addition, a project timeline is presented to develop a sustainable cement manufacturing process, attempting to mitigate toxic emissions and decrease the expenditure of fresh raw materials. Studies demonstrate that deploying environmentally friendly procedures decreases CO_2 emissions in addition to promoting a circular economy by harnessing commercial by-products. Future research pathways suggest optimizing carbon capture technologies, studying novel binding agents, and examining the prolonged sustainability of substitute cement specifications, stressing the requirement for industry engagement to attain a greener future. This report provides a base for additional studies intended for corresponding environmental obligation and economic growth in the cement industry. Finally, this report showed the possibility of extracting NH_4CL from a cement plant in addition to regenerate the raw material through closed loop of CO_2 and CO_2 capturing. The selected site for the proposed plant is Alexandria, Egypt due to different reasons will be mentioned through out the report.

Key words: sustainability, Carbon Capture, carbon capture and storage, Fly Ash, Emissions, Cement Kiln Dust, Pollution, Global warming, Climate change, carbonate looping technologies

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Chapter one

Introduction

Overview About Cement and Cement Industry

Cement is an essential component in construction, functioning as a primary binding agent of concrete, a common building material. However, its manufacture accounts for 5-10% of CO_2 emissions worldwide[1], as this production has resulted in increased pollution and contributes significantly to environmental degradation by depleting resources, consuming energy, and producing trash. This industry is an energy-intensive production that emits CO_2, NO_X, SO_X, VOCs, and particulate matter[2].

Additionally, cement becomes required in masonry, serving as a binding agent in mortar for stone and brick construction. Its strength and durability are essential in infrastructure projects such as roads, airports, and dams. Moreover, the most prevalent construction material, concrete, is made from basic elements such as limestone, chalk, shale, clay, and sand. Calcination is followed by calcination in very elevated temperatures that makes calcium oxide, silica, alumina, and ferrous oxide to produce clinker, it is subsequently ground and crushed into cement. Furthermore, precast items, overlays, and ornamental concrete are all produced with cement. As Its significance goes beyond its physical features, it contributes to economic growth by creating jobs and supporting associated businesses. Advances in cement technology enhance sustainability by resolving those environmental concerns while also promoting urbanization and infrastructure development.

Emissions from cement production plants vary depending on the analyzed part. By considering the crushing parts, Particulate matters (PMs) and dusts are emitted. In calcination and rotary kiln part there are two main sources of emissions such which are the fuel burnt to operate the kiln, which means NO_X, SO_X, VOC_S and CO_2 [2]besides to the calcination process products which large part of it consists of CO_2[3]. In addition to the indirect emissions produced by electricity generated to satisfy different requirements in the factory.

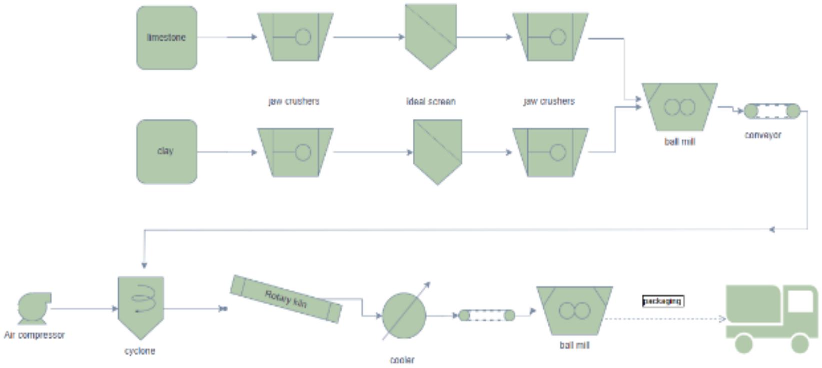


Figure 1: cement production process

CO_2 is one of the greenhouse gases that contributes strongly to the global warming phenomena[4]. The carbon capture technologies aim to reduce the emissions and pollution caused by industries, support sustainable development approaches and enable reusing wasted CO_2. One of the important methods of capturing CO_2 is carbon mineralization. Mineral carbonation aims to store CO_2 in the form of calcium and magnesium carbonates[5]. Such a technology has dual benefits for the cement industry which are: capturing the polluting CO_2 produced by the process and regenerating the raw material from the waste. For applying this method in cement industry and to create better imagination for carbon mineralization, $CaCl_2/NH_4OH$ system is employed. In $CaCl_2/NH_4OH$ systems depend of reacting calcium ions with hydroxide ions to precipitate calcium-based compounds such as calcium carbonate in presence of the captured CO_2 from the carbon mineralization process[6].

The proposed modification of cement production process seeks routes to decrease the carbon dioxide amounts emitted to the atmosphere by capturing it and reusing it to regenerate the raw material. And as a second aim, as mentioned, decrease the amount of raw material (calcium carbonate) extracted from quarries to decrease both emissions and costs.

Problem statement

The increasing population all over the world required increasing facilities construction power, as a result, the amount of required cement massively increased. Cement production occupies 5-10% of total CO_2 production on the earth [1]noting that CO_2 is a main contributor in global warming phenomena and its consequences such as climate change, sea level rising and ozone layer depletion [4] which is responsible for different diseases such as cancer. For the mentioned factors, cement industry is considered one of the most polluting industries that does not contribute only to CO_2 production but also in other emissions such as NO_X, SO_X, VOC_S and PMs in addition to the excessive raw materials consuming from quarries which threatened the raw material and exposes it to early depletion. The concerns increased about the environmental and public health future if the current trend of CO_2 production continued or increased which opened the doors of acceptance on new and modified solutions of cement industry. This research seeks new approaches to produce more sustainable and environmentally acceptable cement production methods.

Objectives

1) Identifying emission sources at cement production plants.
2) Develop a closed loop of utilizing CO_2 to regenerate $CaCO_3$.
3) Establish an Aspen plus simulation for the suggested modification.
4) Preforming Mass and Energy balance for process equipment.
5) Determine the size of each piece of equipment used.
6) Preform environmental study, economic study and HAZOP for the modified process.
7) Choose a suitable location for the plant.

Research questions

1) Is it applicable to convert the conventional process into sustainable process?
2) Which could be the method used for capturing the Carbone dioxide produced by the plant and use it to regenerate calcium carbonate?
3) What are the required chemicals for such a process?
4) Is this modification able to be integrated with another industries?

Methodology

- Literature review was made to summarize and discuss different related topics such as cement production process, emissions produced from the process, different capturing technologies and $CaCl_2$ utilization methods.
- Preforming Aspen plus simulation followed with process explanation showing all required mass and energy balances in addition to equipment sizing and cost determination.
- Performing economic and environmental study and HAZOP study.

Timeline

Shown below a Gantt chart that illustrates each task duration and total project duration:

Table 1: project duration and tasks duration

Task ID	Name	Start	Finish
1	Sustainable Cement Production Technology design project	23/9/2024	17/3/2025
2	Literature reviews and theoretical studies	23/9/2024	11/11/2024
3	Cement production process selection and simulation	11/11/2024	25/11/2024
4	Design of modified cement process plant	26/11/2024	16/12/2024
6	Environmental study and evaluation	16/12/2024	7/1/2025
7	Perform HAZOP study	7/1//2025	21/1/2025
8	Site selection	21/1/2025	3/2/2025
5	Modified process simulation	3/2/2025	24/4/2025
9	Economic study	25/2/2025	17/3/2025

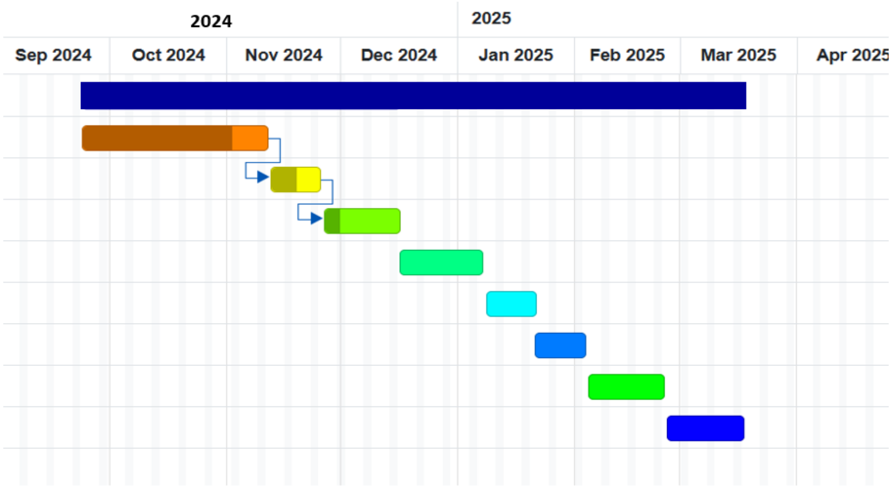


Figure 2: Gantt chart

Main results

- Successful integration of mass and material in the process where CO_2 produced by a conventional cement plant is recycled to regenerate CaCO3 and reduce the quarrying process of calcium carbonate.

Chapter Two

Literature review

The industry in Egypt

Egypt's cement manufacturing, which is one of the most ancient industries in Egypt includes 18 operating companies and consumes up to first half 48.7million tons of cement last year dropped to 44.9 million tons this year with total investments exceeding 255 billion EGP according to Ministry Trade and Industry. Since 1975, Egypt has significantly increased its cement manufacturing, which now accounts for 1.5% of world production. However, the dust emissions from these processes account for 6% of Greater Cairo's PM10 levels, with concentrations as high as 30% around cement facilities. New regulatory guidelines, set to be adopted in 2010, seek to reduce dust emission limitations from 300 mg/m^3 to 100 mg/m^3 for existing facilities and from 100 mg/m^3 to 50 mg/m^3 for new facilities. The Egyptian Environmental Affairs Agency's (EEAA) monitoring shows that new plants obtain a 98% compliance rate, while older facilities reach 92%. Furthermore, there are considerable prospects to improve cleaner production and pollution control, such as the utilization of un-conventional fuels in cement kilns, lowering nitrogen oxides (NOx), reducing dust emissions, using silica fume waste, recycling bypass dust, and effectively managing hazardous waste.

Critical Building Material

Cement manufacture is an important industry as it serves as critical building material for global construction and infrastructure projects. Cement is used as a strength-giving substance in the production of concrete, making it necessary for many buildings. It is expected that worldwide cement output reached 4.1 gigatons in 2019. [1]

The key component that holds concrete components together and provides it with its remarkable brilliance and versatility is cement. Concrete is a building material that satisfies the current needs and requirements of buildings and can face future challenges. The main function of cement is to hold together the sand and particles that make up concrete.

The cement manufacturing process is divided into three stages: mining and input preparation, chemical reactions that produce clinkers, and clinker grinding with additional improvements to produce cement. Currently, concrete contributes 8% of the world's carbon emissions, a percentage that is projected to increase as developing nations strive to develop sophisticated infrastructure. The demand for concrete and cement, if left unchecked, constitutes a significant threat to the world goal of reaching net-zero emissions.

Economics and infrastructure

Cement manufacture is extremely significant in today's globe. It contributes to the construction of infrastructure, housing, and industries, so promoting economic growth, job creation, and sustainable development. The cement business produces millions of jobs worldwide, boosting the economy and improving people's lives. Cement is crucial for infrastructure development since it assures the strength and safety of buildings and structures. As more people move to cities, the demand for housing and companies grows. This expansion results in the creation of comfortable living spaces and thriving commercial areas. Governments around the world invest in infrastructure projects to help the economy thrive, and cement manufacturing is a significant component of these efforts. It contributes to the improvement of public services and facilities, hence improving people's lives.

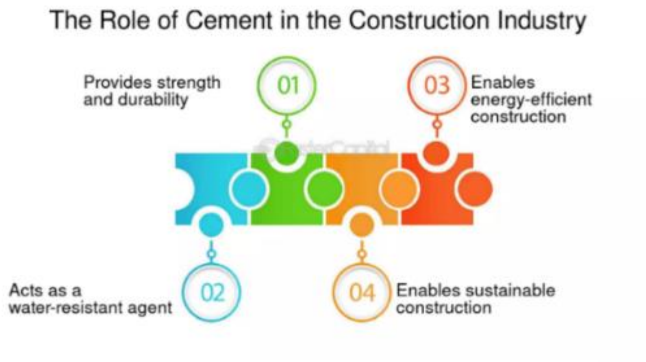


Figure 3 The Role of Cement in the Construction Industry

Market demand and sustainability

The cement business also serves the growing needs of local markets, particularly in emerging countries where the population is rapidly increasing. It responds to market demands by creating several types of cement for diverse construction applications, including more ecologically friendly solutions. Cement production is essential in international trade, Countries with robust cement businesses can export their products to surrounding markets, boosting their economies. Exporting cement promotes and assists other countries expand their infrastructure, which improves economic cooperation and progress. Many nations can manufacture cement domestically and depend less on imports because they have an abundance of natural resources, such as limestone. Through the application of innovative technology, conscientious environmental practices, and continuous research and development, the cement industry is placing an increasing emphasis on sustainability. Making cement can reduce its environmental impact by employing alternative fuels and increasing energy efficiency. Cement businesses help safeguard the environment and fight climate change on a worldwide scale by implementing these ethical practices

Figure 4 The Economic Impact of Cement industry

Production of Cement

The manufacture of cement includes a set of carefully controlled chemical and physical processes that transform raw materials into a fine powder capable of hardening when mixed with water. Understanding the manufacturing process provides valuable insight and knowledge into the composition, efficiency, and sustainability of this material. The manufacturing of cement is divided into two processes; dry and wet processes, as of today the dry process is now very common in use and almost the wet process is no longer in use. Because wet cement plants continued to grow in number and size and wet process was the popular choice as a process of manufacture of cement till the 50s. At this point, the cost of fuel began to increase and the growth of demand for cement with time could not cope with the high use of energy and water that the wet process used, so shifting to another process was necessary at this point. The wet process was simple and required less process control, instrumentation, and labor. Nevertheless, it consumed a large quantity of heat energy in drying the slurry, thus shifting the dry process.

The cement manufacture is considered a dual-stage process, the clinker generation and the grinding of cement. In the initial stage, the feedstock is supplied to the kiln process to generate clinker. Clinkers contain aluminates, and calcium ferrites acquired by reducing calcium, alumina, silica, and iron oxides that reside in the input materials supplied. Clinker manufacture begins by quarrying the primary natural feedstock, usually consisting of either marl (origin of $CaCO_3$) and clay, chalk, sand, iron ore, or shale (resource of alumina, silica or iron oxides). Following the next stage, the clinker gets grounded by use of a grinding mill with the addition of calcium sulphates (anhydrite or gypsum) alongside the potential additions of alternative minerals to modify the cement characteristics to obtain different types of final cement product with the desired performance according to the applications it will be used for.

The dry process of cement production

Quarrying process and acquiring raw materials

During the quarrying technique, feedstock, namely shale, limestone, or clay are withdrawn from quarries employing different methods like drilling processes or blasting. The retrieved materials are then transferred to the cement facility, where they endure crushing, grounding, and blending creating a homogenous mixture of the raw materials.

This process will allow the consistency and homogeneity of the feedstock to maintain the standard and chemical composition of the mix.

Raw mix grinding

The ground and mixed raw materials are additionally ground into a crushed powder using a grinding mill. The most used types of mills to perform this process either vertical roller or ball mills. These mills' jobs are to decrease the size of the particles of the raw mix by using mechanical forces techniques to turn them into fine powder. This process will increase the raw mix's surface area, thus improving the chemical reactions in the upcoming steps.

Preheating and Pre-calcining

The fine powdered raw mix gets preheated as well as recalcined to enhance energy effectiveness and lower fuel usage. After entering a preheater, the raw mixture will meet hot kiln gases. Before the raw mixture enters the kiln, this preheating phase aids in drying it out and warming it up to remove any moisture content. After that, the heated raw mixture is fed to pre-calciner that works on the uncomplete decomposition of carbonates and works on decreasing the amount of heat needed for the calcination process since the mixture is partially heated.

Clinker production

Kiln is a huge rotary furnace that inside temperature reaches 1450℃. This durance is responsible for thermal treatment, and it is where the calcination process happens. At this process calcium carbonate turns into calcium-oxide and carbon dioxide. Most of the cement production process is due to this stage. The outer of the calcination process is called clinker and it is the main component of cement. The final cement characteristics depend mostly on the clinker properties.

Cement grinding

This step happens in a unit called ball mill. The balls inside the ball mill are formed from ceramics or steel. In this step of the process the clinker is further grinded with gypsum. The gypsum is added to enhance the properties of cement. The product of this step is a fine powder of clinker and gypsum.

Cement storage and packing

After grinding, cement is kept in silos till the packing time. The proper storage conditions are important to maintain the cement properties and structure. Based on the client's requirements the cement could be packed in bulks or bags.

Table 2: Comparison between the Wet and Dry processes

Process	Advantages	Disadvantages
Wet Process	Better Mixing and Homogenization: The slurry form ensures uniform blending of raw materials. Easier Handling: Transporting and processing raw materials in liquid can be simpler. Suitable for lower grade Limestone: Can be used for raw materials with high moisture content.	High Energy Consumption: Requires more fuel to evaporate water in the slurry. Higher CO_2 Emissions: More fuel usage results in increased carbon emissions. Longer Kilns Needed: Wet process kilns are larger than dry ones and require more space. Higher Production Cost: Increased fuel and maintenance costs.
Dry Process	Energy Efficient: Uses preheaters and precalciners to reduce fuel consumption. Lower CO_2 Emissions: More environmentally friendly due to reduced fuel use. Lower Cost: Requires less fuel and shorter kilns, reducing operational costs. Faster Production: More efficient material handling and shorter kiln times.	Complex Process: Requires advanced equipment like cyclone preheaters and blending silos. Raw Material Preparation: Dry grinding requires careful control to ensure homogeneity. Dust Issues: Higher dust generation during processing, requiring effective dust control systems.

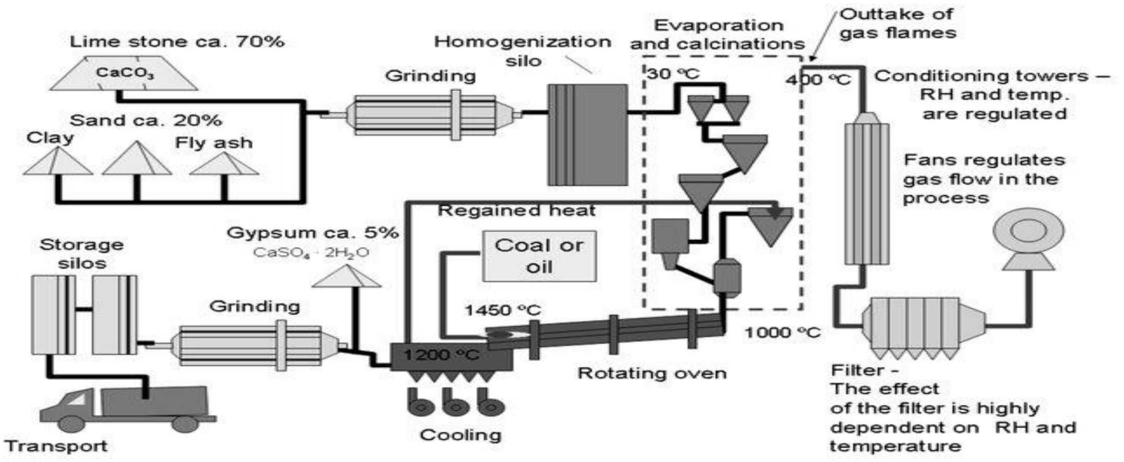


Figure 5: The dry cement production process

Different Wastes in Cement Production

Fly Ash:

The cement industry is considered one of the most crucial sectors in a country's advancement. Nevertheless, the construction activities of the cement field also have environmental consequences, which include air pollution. One of the results of combusting fuel in the cement sector is fly ash. If it is not taken care of properly, the air and the neighboring environment. Fly ash is typically created from the electricity manufacturing procedure. Coal fly ash or CFA is a side product of combusting pulverized coal in thermal power factories. Relying on the category and quality, flying ash (FA) constitutes of distinct proportions of oxides- mainly silica, alumina as well as calcium and is able to showcase pozzolanic activity [14]. FA with pozzolanic characteristics makes it unlikely to replace cement and fine aggregate in concrete. Coal fly ash is produced in coal-fire industries as well as steam plants when coal is broken down and blown together with air to the combustion section of a boiler which immediately ignites, produces heat and creates a liquid mineral leftover as shown in figure one below [15]:

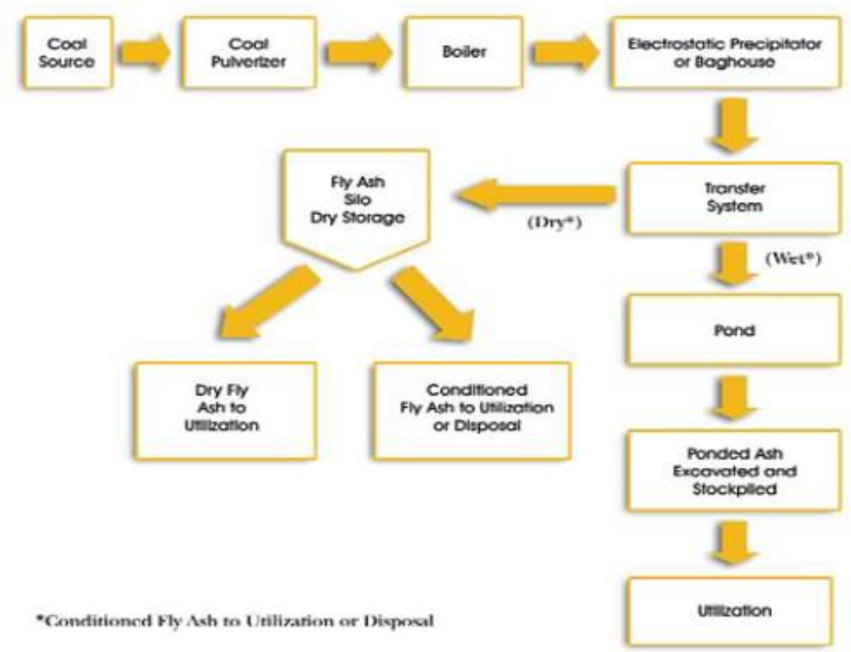


Figure 6 Flow chart of utilization of fly ash

The heat is withdrawn from the radiators using boiler tubes to lessen the temperature of gas lines and have the produced liquid minerals solidified then disposed as ash. The waste of fly ash created from the incineration of coal constitutes of the elements CaO, Al_2O_3, Na_2O, Fe_2O_3, MgO, SiO_2, K_2O together with other metal oxides. Other secondary elements present in fly ash are Cd, Cr, Hg and Pb. Fly ash is a commercial by-product called environmental contaminant. Fly ash is classed as waste in some countries. FA is still an issue in numerous countries because of the reliance on coal energy. Depending on statistical data, the total manufacture of fly ash worldwide is 1,200 MT. Figure 2 below shows the formation of fly ash worldwide:

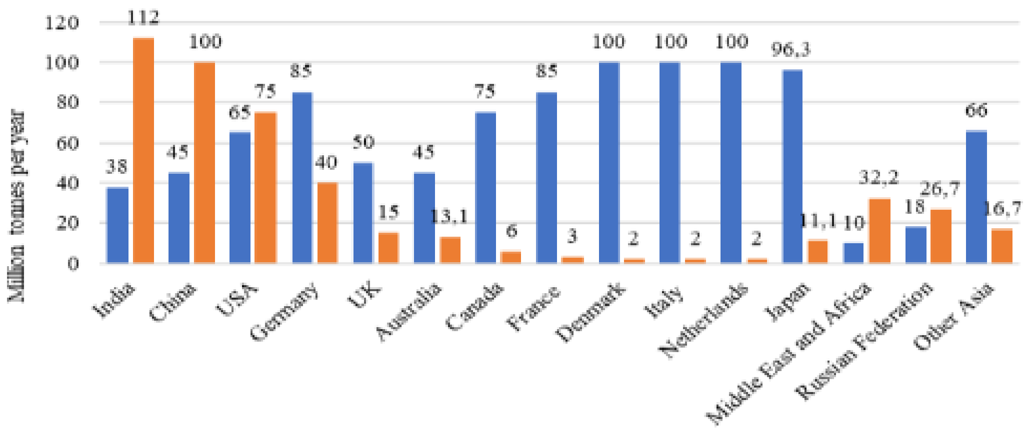


Figure 7 The formation of Fly Ash worldwide

Furthermore, soil performance could be enhanced by concrete waste that is manufactured by grounding concrete waste has been utilized to enhance the power of base soil. The soil effectiveness was assessed by use of the California bearing ratio (CBR).[16] Concrete residual fine addition procured 40% of the entire altered soil weight and enhanced the soil's CHR (California hearing ratio) with an increase of 345%, which reinforced the soil adequately for a road to be built. In addition, it was investigated that the addition of concrete sludge strength to the soil helped balance the soil to construct roads. The cement slurry was constructed by an available ready-mix concrete plant. Dry cement sludge granules being added to soil possessing an increased humidity content lessened the water's percentage, frost heave, and plasticity ratio and enhanced the load-bearing power of the soil. The framework was not explained in depth, but the impacts potentially created by the water's high absorption capability of the concrete dry slurry power which primarily compromised of calcium hydroxide, hydrated cement, and fine sand. The numerous surface granules give the concrete dry slurry an increased distinct specific surface area and robust capability to take in water, so the powder lessens the percentage of water in the soil [17].

Cement Kiln Dust (CKD):

Cement kiln is used for preprocessing in the cement industry where calcium carbonate reacts with minerals that contain silica to form calcium silicate. Kiln dust is highly alkaline caustic fine partial produced by kiln. Most of CKD is unreacted materials like carbonates and oxides for that reason, the dust is recycled again to recover the raw material. However, some CKD requires treatment process while others are recycled directly. According to [18] the composition of the CKD depends of many factors such as the used raw materials and the fuel used to operate the rotary kiln where the main compounds of that dust are lime, iron, silica and aluminum and small concentrations of lead , cadmium and selenium. Cement kiln dust is contributor in many environmental problems such as: global warming, acid rains, decrease crops quality and biodiversity loss[19]. On the other hand, the those dusts are rich with sulfur, magnesium and potassium which make it a great alternative for the chemical fertilizers [18].Another advantage found for adding CKD to the soil is increasing and enhancing the physical and chemical properties of soil which is called soil stabilization. A study made shows that soil strength increases by adding CKD, lime, class C of fly ash, Portland cement as additives noticing that those chemicals could be wastes of a process or even manufactured materials [20].

A study was made show that CKD improve soil properties. Comparing the numerical values, it was found that the raw natural soil has a 7% void space while the clay cured with 25% CKD had void space of 1-2.3% which proves the previous claims. The same experiment was applied by where different percentages of CKD (5%-10%-20%) were added to two soil types and the results indicated that the plasticity index decreased and the PH values increased [21] .However, adding [20] stated that [22] investigated that adding CKD increase the moisture optimum content for soil. Kiln dust is also a cheap and effective way for waste treatment where its strong alkaline nature works on removing moisture from waste.

Figure 8: White Cement sample

Emissions

Cement production is one of the industries that decreases air quality and produces much harmful emissions. According to [23] long term exposure for those emission caused development of pneumoconiosis. The main gasses produced by the cement production are CO_2 as % of CO_2 produced around the world is due to cement production, it is produced by the fuel burning and lime stone calcination[24], [25] .In addition, high temperatures in kiln's burners causes high emissions of nitrogen oxide (NO_x), Sulfur dioxide (SO_2), carbon monoxide (CO) beside other toxic gases and dusts[26]. The next section will be discussing the formation methods of nitrogen oxides.

NO_x are : NO, NO_2 and N_2O.There are three different ways in which NO_X are emitted to the atmosphere Nitrogen oxide emissions reducing in cement production [27]:

1. Thermal NO_X: this type is emitted by burning any gaseous fuel with excess air in high temperatures over 1200. The higher the flame temperature, the bigger the amount of thermal NO_X emitted.
2. Fast NO_X: This type is produced as result of dissociation of HCN beside other dissociation products such as CO_2 and H_2O. The amount of fast NO_X is related to the temperature profile of the flame.
3. Fuel NO_X: This type is formed from compounds containing nitrogen found in solid and liquid wastes. In order to produce fuel NO_X compounds contain nitrogen are converted to HCN and NH_3 which under further oxidation turns into NO_X.

The most dangerous compound of the NOx is NO_2 because it reacts with the moisture in air to produce nitric acid [28]. Recent NO_x control technique involves reduction of NO_x using combustion modification techniques and converting NO_x to nitrogen and water by series of reactions[29], [30].

Other than NO_X, volatile organic compounds (VOCs) are emitted by cement production too. There are many sources for VOCs such as stored gasoline, solvents, stored chemicals and incomplete fuels combustion. However, different organic compounds appeared in analysis of fly ash samples such as polycyclic aromatic hydrocarbons (PAHs) and benzene derivatives. The most recognized PHAs in the sample were Indeno[1,2,3-cd]pyrene, Benzo[α]pyrene, and Benzo(β)fluoranthene and from benzene derivatives, it was chlorobenzene[31]. Furthermore, Hexachlorobutadiene, which was restricted by Stockholm Convention, occupies about 8.5% of the overall emissions[31, 32].

In addition to NO_X as VOCs , Sulphur oxides (SO_X) are another class of chemicals produced by cement production. Its amount is different from plant to the others. The number of SO_X emitted relies on different factors such as fuel type, nitrogen amounts and combustion temperature. SO_x are 90% SO_2 Which is the most toxic gas released to the atmosphere and 10% SO_3 [33, 34]. Using low sulfur content fuels can reduce the amounts of sulfur oxide emissions besides Bio-desulfurization technology. Bio-desulfurization technology depends on biological sulfur natural cycle that happens in three steps [35].

Besides the previous categories of emissions, CO_2 occupies a huge place among them. In 2021, According to the UN climate that the human activities since 1850 lead to increasing in different emissions such as CO_2, CH_4 and nitrous oxide which in turn increased the ocean and atmosphere temperature and caused climate change [36]. The mentioned increase in emissions, which was about 50% since 1850, made the surface temperature increase by 1℃ and it is expected to reach 4.4℃ depending on the greenhouses emissions amounts [37] . However, CO_2 produced from cement plant is in continuous increase as it 1200 million tons in 2010, then it was 1500 million tons in 2015 [38] and it kept increasing as the population increase as a result for the need for cement for construction increases. It was recorded that in 2020,2021,2022 the emissions reached 1.63 $GtCO_2$,1.69 $GtCO_2$ and a small reduction was noticed as the value was1.61 $GtCO_2$ respectively [39]. Producing a tonne of cement is capable to produce from 0.8 to 0.95 tonnes of CO_2 [39]. South Africa is responsible for 1% of total greenhouse gasses globally where 80% of this amount is CO_2 emissions[40]. In the cement industry, CO_2 production could be direct or indirect. The indirect sources are: generation of electricity required for the process, transportation and extraction of raw material which occupies 5% of the total CO_2 evaluation [41]. While the main direct source clinker production chemical reactions where carbonates, which is mostly limestone $CaCO_3$, are decomposed into oxides such as lime and calcium oxide and CO_2. About 60% of cement production gaseous wastes are due to the calcination process [42]. Moreover, it was found that for each tonne of clinker about 250 kg CO_2 is produced [39]. The rest of the CO_2 emissions is produced from burning fossil fuels in order to provide the suitable energy for heating the raw materials to more than 1000℃ [43].

One of the methods used to control the CO_2 emissions from cement production plants is carbon capture. Carbon capturing plants can remove fair amount of carbon dioxide depending of the company project capacities and number of collectors. For example Climeworks established different plants that are able to remove from $50\frac{ton\ CO_2}{year}$ to 4000 $\frac{ton\ CO_2}{year}$ [44].

Carbon dioxide capturing technologies include three stages; 1) capturing CO_2 from the emissions source or straight from the atmosphere; 2) transporting the CO_2 to a distinct site; 3) utilizing it as raw material or future sequestration into a geographical configuration. The typically used carbon capture procedures are known as: Pre-combustion, post-combustion as well as oxy-fuel combustion. Added to these technologies, there is another procedure known as: Direct Air Capture (DAC). The pre-combustion technique involves the gasifying of fossil fuels, which leads to a mixture of synthesis gas being created, consisting primarily of H_2 and CO. A new water stream is added, where the mixture goes through a catalytic water-gas shift reaction, where CO_2 and water react to form CO_2 and H_2. Adding stream and decreasing temperature assist in altering CO into CO_2. Consequently, the excluded CO_2 could be extracted, with a hydrogen-rich fuel gas remaining. The energy specifications for capturing of CO_2 and compressing in pre-combustion capture technologies might compute to half of what is needed for post-combustion technologies. [15] The figure below demonstrates the carbon capture technologies:

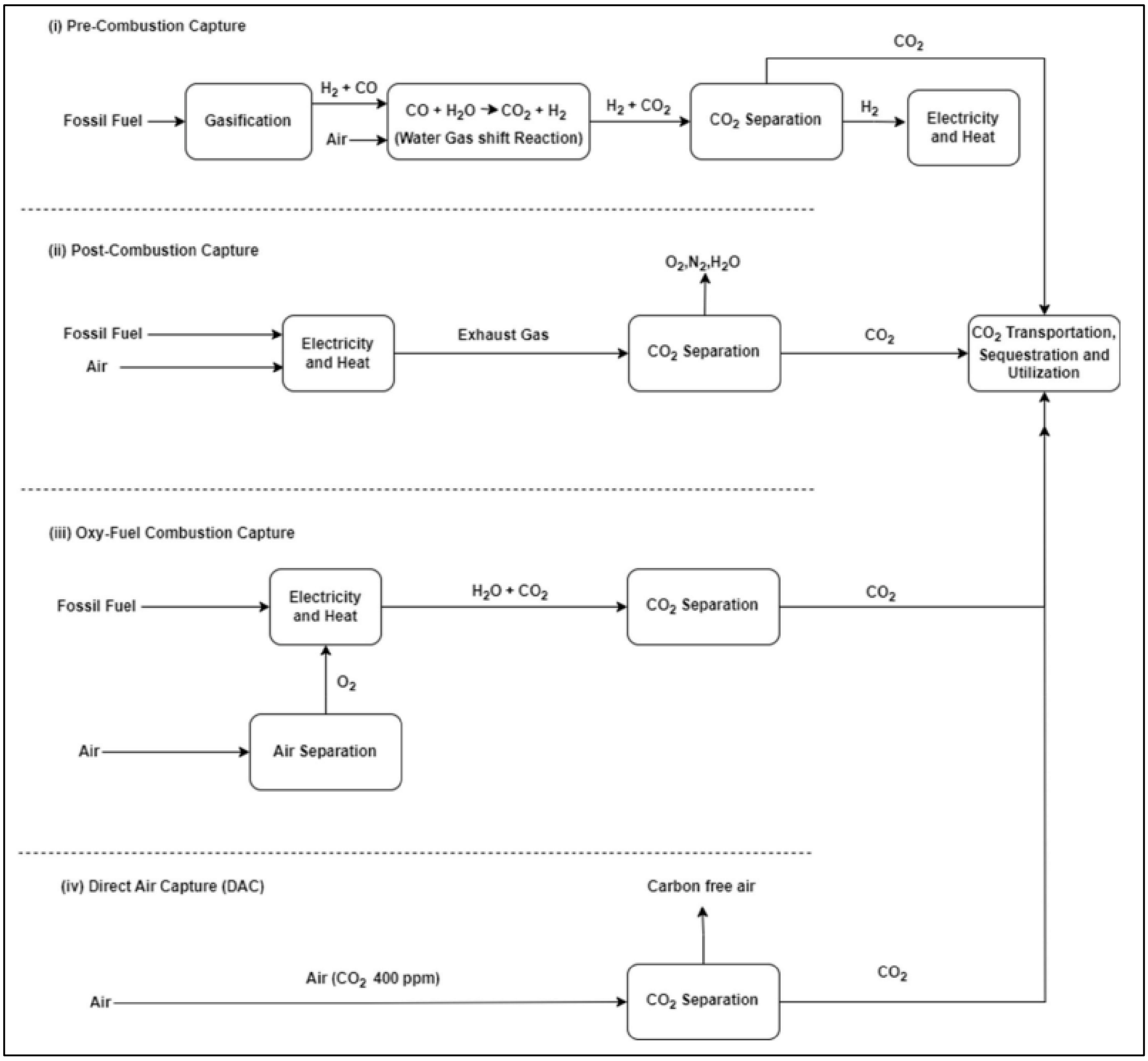


Figure 9 The carbon capture technologies

Numerous technologies to lessen CO_2 emissions, such as binding CO_2 in cementitious products by mineral carbonation techniques are being thought through for execution.

Presently, five parallel schemes can bestow to a low-carbon economy being studied in the cement industry. One of said techniques is using carbon capture and utilizing of storage (CCUS) system. The most suitable CCUS technology for a specific cement plant relies on numerous factors, including, the site, and how accessible locally a geological location is [45]. Mineral carbonation could be executed as a sector of the finals stage of utilization in the CCUS procedure, given that the end products get used commercially. This technique in addition allows recovering of waste to a specific extent. For cement industries sited far from CO_2 storage locations, it is preferable to carry out mineral carbonation by using waste belonging to them if products of said process is possible to recover. [46] In addition, all recently constructed plants are dry procedures with pre-calciners and cyclone pre-heaters. Cyclone preheaters are organized in towers of 1-6 pre-heaters that could amount to heights of 120m. The raw mix goes through the pre-heaters from top to bottom whilst the flue gas stream coming via the kiln goes through the pre-heaters in the countering flow. Thus, the raw meal gets heated, and the remainder water gets vaporized. The raw material then comes in the pre-calciner, where it hits the temperature required to activate the calcination reaction which is around 900^oC. In the pre-calciner, the raw meal gets 90% levels of calcination so that adequate thermal energy input is ensured. Fuel is used up in the pre-calciner and takes up to 60 to 70% of the total fuel usage. An advanced air duct supports the pre-calciner with combusted air from the clinker cooler. Usually, the material enters the pre-calciner from the 2nd lowest pre-heater tower and the calcined substance is gathered in the lowest pre-heating tower and the calcined material is taken in the lowermost pre-heating tower prior to being released to the rotary kiln. The substances exiting the second lowest pre-heater are shipped by the combustion gases and raised to the bottom pre-heater in flow that is co-current. [47]

Furthermore, oxyfuel utilizes an oxygen mixture that is extracted from air and recycled carbon dioxide to be used as the combustion gas, which results in the reduction of CO_2 separation facility's size and complexity. The rate of carbon capture is predicted to be greater than 90%. Though the clinker output and energy efficiency are predicted to become better in an oxy-fuel cement industry, [48] an air separation unit (ASU) taking up 60 kWh.t of clinker is necessary to create pure O_2 for the procedure. Alternate techniques for producing oxygen are being studied that can lessen the energy penalty [49]. Dissimilar to the alternative four systems, entire oxy-fuel combustion would impact the entire cement process. The plan of technically each system is distinct from a typical cement facility to consider distinct gas characteristics and to mitigate gas egress from each process. This is possibly attainable but costly. Complete oxy-fuel uses a few of the most suitable systems for newly built reduced-carbon cement production, however, implementation is hard as the upcoming stage is the manufacture of an entire small cement process [45]. In addition, cement comprises gypsum, clinker as well as admixtures. Due to 80% of CO_2 from the manufacture of cement being released throughout the clinker manufacture, the cement industry presently decreases thermal energy relating to CO_2 levels by using traditional techniques to enhance energy efficiency in the clinker manufacture and by reverting to fuels with reduced carbon footprint, which include, biomass and alternative fuels. Carbon capture systems can satisfy net zero energy CO_2 emissions; this could be done by reducing the ratio of clinker to cement to result in a 6% reduction in CO_2 emissions relating to the process. This is done by substituting some of the clinkers with supplementary cementitious substances, such as:

- Increasing quantities of small additional components to Portland cement
- Increasing quantities of blast furnace slag to blast furnace cement

Nevertheless, it is imperative to make sure the acceptance of stakeholders of both categories of cement by lessening the effect on the quality of cement and preserving the performance of the product. [49] Figure 2 below shows Operationalization of carbon capture in a cement industry:

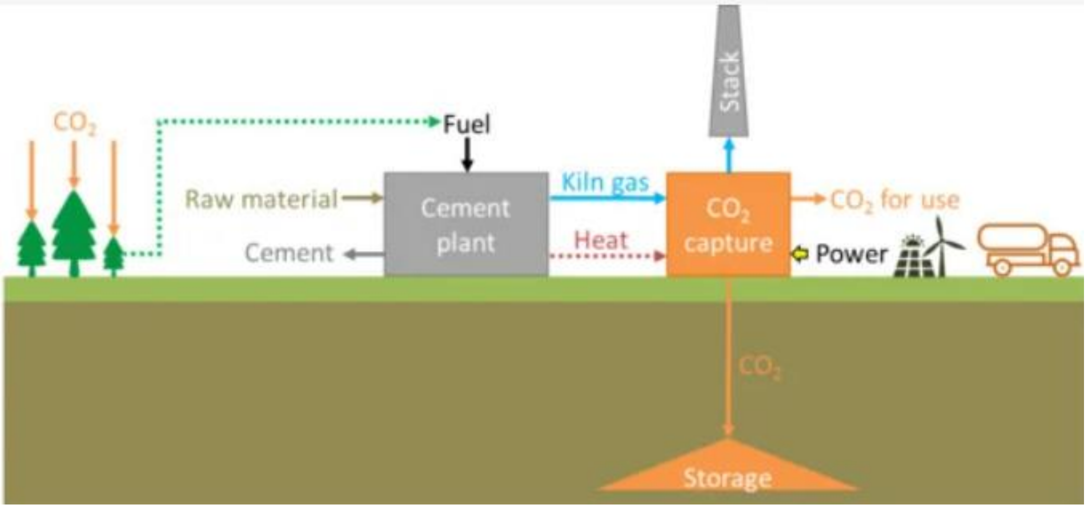


Figure 10 Installation of CO_2 capture infrastructure in the cement industry[50]

Carbon capture methods have faced a major advancement in their applications, specifically in acknowledging the critical difficulties linked with emissions of greenhouse gases. One major application of carbon capture is in power production, where methods, such as PCC (post-combustion capture) are integrated to decrease CO_2 levels from fossil fuel-powered industries. Such as the Petra Nova project in Texas employs PCC technology to obtain roughly 1,6 tons of CO_2 every year. This attained CO_2 is then used for enhanced oil recovery (EOR), efficiently recycling carbon and affecting oil manufacture [51]. Furthermore, oxyfuel combustion procedures, which burn fossil fuels in just oxygen, not air, can generate flue gases that are primarily CO_2, therefore, driving easier storage and capture [52]. The diagram below shows an illustration of carbon injection in oil plants:

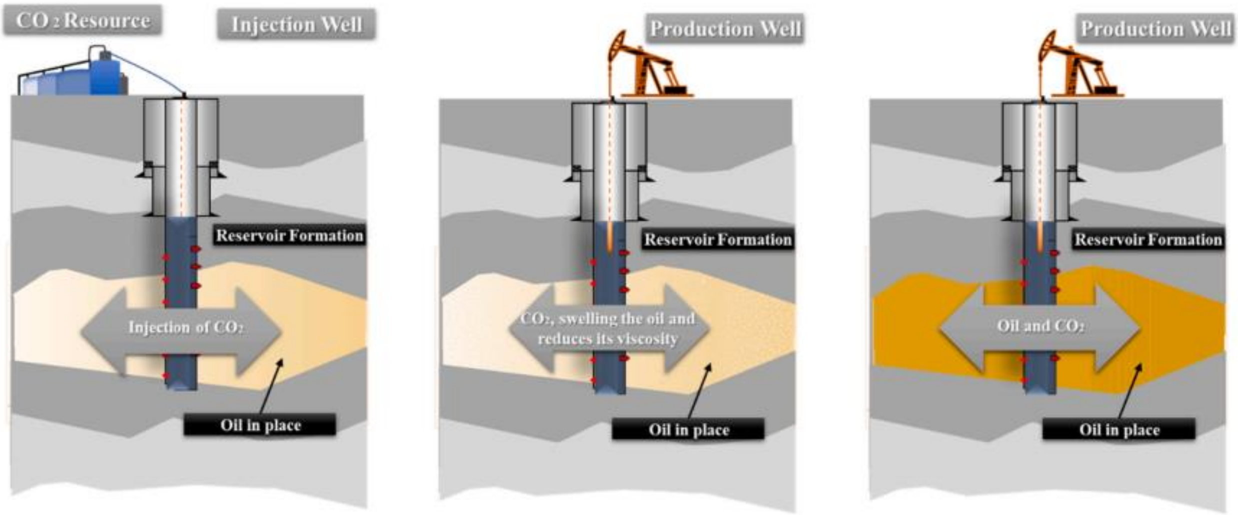


Figure 11: CO_2 injection in oil reservoirs [9]

An additional inventive application of carbon capture is in the commercial sector, distinctly, in cement manufacture, which is liable 8% of worldwide CO_2 levels. The Carbon Clean Solution project in India demonstrates how carbon capture could be implemented within cement industries to obtain above 60,000 tons of CO_2 every year, which can then be preserved and utilized for numerous applications. In addition, Direct Air Capture (DAC) processes are attracting taction since they permit CO_2 to be directly removed from the atmosphere. For instance, companies such as Climeworks are engineering this technology with their Ocra industry in Iceland able of obtaining approximately 4,000 tons of CO_2 annually, which is then mineralized into rock structures [10]. This showcases a large-scale solution to lessen atmospheric CO_2 emissions, tackling the climate dilemma more predominantly.

The agricultural department also offers a bright pathway for carbon capture, specifically via BECCS (bioenergy with carbon capture and storage). This method integrates biomass growth, which absorbs carbon dioxide, with carbon capture processes while biomass conversion. For instance, the Drax Power Station in the UK has started a BECCS pilot project that intends to obtain approximately 1 million tons of CO_2 annually from its biomass production procedure [53]. Furthermore, soil carbon seclusion methods, for example, cover cropping and no-till farming, improving the natural carbon capture abilities of soil, and enhancing the reduction of atmospheric CO_2 emission whilst improving the health of soil [54]. These distinct applications of carbon capture methods not only contribute to the paths to minimizing climate change but also enhance sustainable advancement across numerous sectors.

Chemical Absorption of CO_2 using Ammonium-based Compounds and $CaCl_2$

Chemical Absorption by use of inorganic salts has evolved as a potential method for carbon dioxide capture due to its feasibility for chemical regeneration and decreased energy penalties compared to traditional amine-based solvents. In this procedure, inorganic salts, including calcium chloride ($CaCl_2$) as well as ammonium ions (NH^{4+}), are typically employed into absorbent blends to increase CO_2 uptake and allow the following conversion reactions. For example, $CaCl_2$ can react with carbonate ions obtained from CO_2 absorption to precipitate calcium carbonate ($CACO_3$), proficiently obtaining CO_2 in a steady solid phase. The availability of ammonium compounds, including ammonium hydroxide (NH_4OH), acts as an alkalinity source that allows carbonation and can stabilize many polymorphs of $CACO_3$ in precipitation, enhancing the efficiency and monitoring the absorption procedure[7], in addition, $CACl_2$ solutions have been experimented in biogas upgrading units, where they could bind CO_2 chemically and produce marketable precipitated $CaCO_3$, showcasing their practical applications in industrial CO_2 capturing systems. The synergy between ammonium-based compounds and calcium chloride within absorbent mixtures demonstrates a clean and feasible commercial route for CO_2 utilization and capture[8]. The figure below demonstrates a simple diagram of chemical absorption by CO_2:

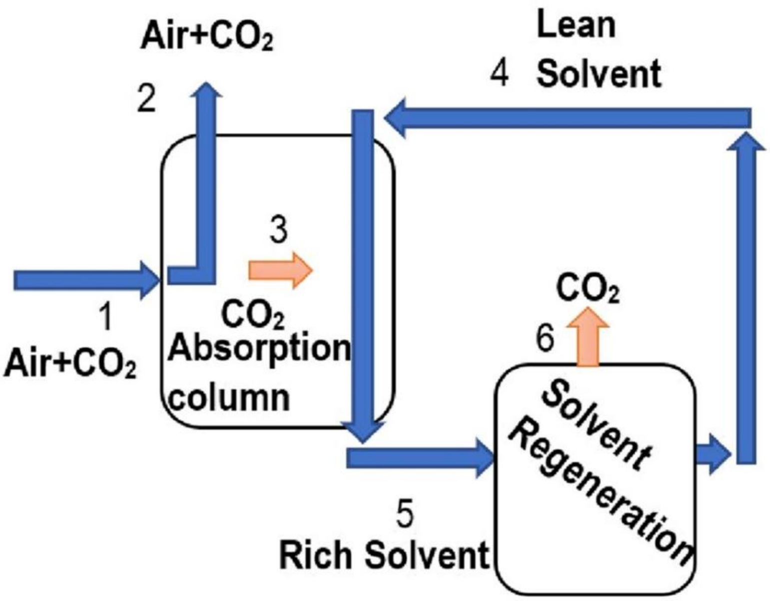


Figure 12 A simple diagram of chemical absorption by carbon dioxide[9]

Inorganic compounds, which include ammonium-based compounds (such as ammonium chloride NH_4Cl, or ammonium hydroxide NH_4OH) or calcium chloride ($CaCl_2$) partake crucial roles in various chemical procedures, specifically in CO_2 capture, mineralization and utilization. $CaCl_2$ behaves as a vital calcium origin in the production of calcium carbonate ($CaCO_3$) via carbonate reactions, where it supplies the needed calcium ions (CA^{2+}) to react with carbonate ions (CO_3^{2+}) originated from absorbed carbon dioxide. Those carbonation reactions are typically added with ammonium salts, which act as alkalinity agents that allow the absorption of CO_2 from gas streams by raising the pH and facilitating carbonate ion production. As demonstrated by Hargis et al (2021), calcium oxide (CaO) reacts with ammonium chloride and water to produce ammonium hydroxide and calcium chloride as shown in the reaction below:

The following equation shows the ammonium hydroxide, water and calcium oxide reaction

$2\ NH_4Cl\ (aq) + CaO\ (s) + H_2O\ (l) \rightarrow 2\ NH_4OH\ (aq) + CaCl_2\ (aq)$

The ammonium hydroxide created in this reaction plays as an alkalinity origin that efficiently absorbs CO_2 gas, synthesizing it into bicarbonate and carbonate species in solutions. During the following precipitation of calcium carbonate, ammonium salts, including ammonia chloride are regenerated, making the procedure clean and cyclic [10]. This exchange highlights the synergistic utilization of ammonium compounds and calcium chloride in obtaining and transforming CO_2 into steady mineral structure, which is a foundation of transpiring CCUS technologies. Furthermore, ammonium-based compounds affect both the polymorphic result of the precipitated calcium carbonate as well as the adsorption of carbon dioxide. Research from Lienodo’s PHD dissertation shows that ammonium ions partake a momentous part in solidifying metastable polymorphs of calcium carbonate, remarkably vaterite. Vaterite is a reduced thermodynamically steady but kinetically preferred polymorph that can be selectively produced by monitoring ammonium concentration and pH environment[11]. The availability of ammonium ions renders the growth rates and nucleation of calcium carbonate crystals, thus preferring the production and stabilizing of spherical vaterite molecules in opposition to the steadier rhombohedral calcite crystals. The equilibrium including ammonium hydroxide are also imperative in regulating the pH of the solution, which straightway influences the carbonate species equilibrium and thus, the kinetics of calcium carbonate precipitation. In addition, higher pH values, brought by ammonium hydroxide availability, higher the concentration of carbonate ions, bringing about the supersaturation required for calcium carbonate crystallization. This monitoring over ion concentration and pH permits tuning the morphology, size and polymorphic distribution of the produced calcium carbonate crystals, which is necessary for enhancing their performance as additives or fillers in commercial applications, which include polymers and cement[11].

The coupled utilization of ammonium-based compounds as well as calcium chloride produces an efficient and clean foundation for CO_2 capture and conversion. These inorganic reagents both allow the mineralization and chemical absorption of carbon dioxide as well as allow precise monitoring over the features of resultant calcium carbonate molecules, along with their size, crystalline phase as well as morphology. Such monitoring is imperative for customizing the substance properties to fulfil the requirements of numerous industrial districts whilst participating in carbon emission management attempts via CCUS methods. The employment of these compounds into CCUS systems illustrates the feasibility to synthesize greenhouse gases into safe, valuable and environmentally harmless substances, thus evolving circular economic ideas and clean industrial applications. The figure below shows the utilization of ammonium-based compounds in carbon absorption:

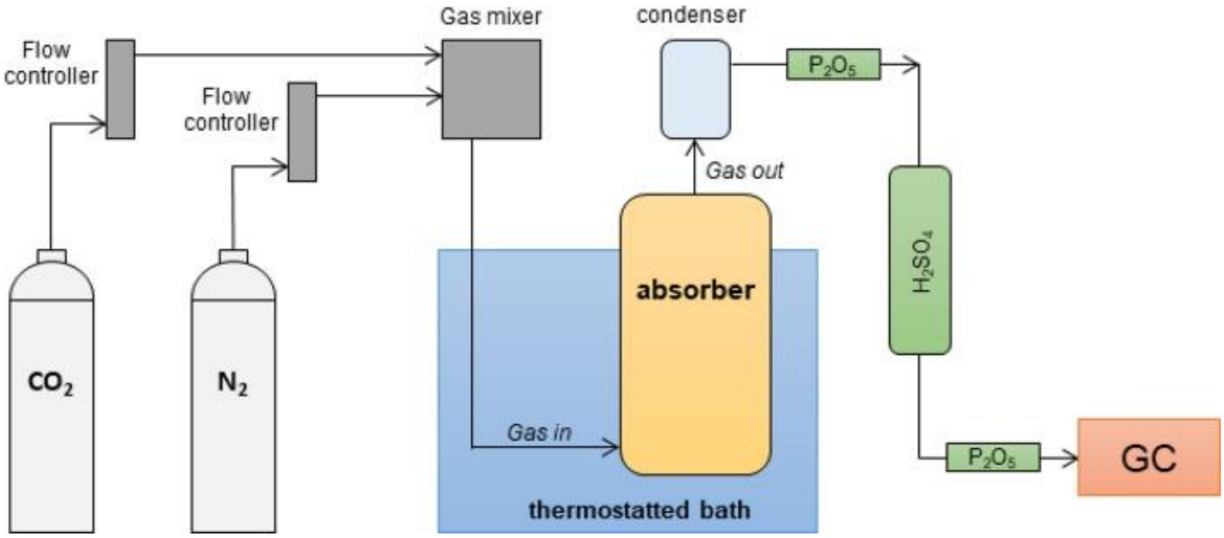


Figure 13 shows the utilization of ammonium-based compounds in carbon capture[12]

Several techniques have been implemented by utilization of ammonium-based compounds and calcium chloride to produce calcium carbonate and carbon dioxide conversion or capture procedures, manipulating their distinct chemical interactions to enhance mineral carbonation as well as material features. One usual method includes using calcium chloride as a calcium origin coupled with ammonium hydroxide or ammonium salts to improve the carbonation procedure. For example, the carbonation of calcium chloride/ ammonium hydroxide solutions permit monitor over calcium carbonate polymorphs, preferring metastable vaterite production under distinct ammonium concentrations, as illustrated in a PhD dissertation centering around carbon dioxide conversion in the cement industry frameworks [11]. The procedure advantages from ammonium hydroxide's part as an alkalinity origin, typically originated from anaerobic digestion of urban waste, advocating CO_2 absorption and precipitation of calcium carbonate with customed crystal size morphology. Ammonium salts such as ammonium chloride have also been implemented mineral carbonation to leaching of calcium from commercial wastes, such as, steel slag, allowing a recyclable system where ammonium chloride partakes both as a regeneration agent and a solvent, therefore, allowing a circular economy model [13]. The ammonium salt derived pH swing procedure improves dissolution of calcium efficiency and outputs of carbonation, making it a viable procedure for carbon dioxide capture and storing using mineralization. Likewise, ammonium carbonate and bicarbonate have been utilized as carbonate sources in the precipitation of calcium carbonate, with research proving their effect on nucleation kinetics, particle size distribution, and polymorph stabilization.

In commercial uses, calcium chloride is coupled with ammonium salt or sodium carbonate (Na_2CO_3) to create PCC (precipitated calcium carbonate) for construction or environmental purposes. For instance, the carbonation of calcium chloride with sodium carbonate is a well-researched while, impulsive or, affected by pH, additives (magnesium ions or ethylene glycol) and temperature. Furthermore, the calcium carbonate through precipitation has been proven as a feasible method, with factors, including molar ratios, reaction time and temperature influencing the morphology and purity of the end-product calcium carbonate[13], [14].

Other methods cover the unification of ammonium-based compounds into carbon capture systems, transcending mineralization[15]. Ammonia compound solvents, such as ammonium salts and aqueous ammonia, have drawn attention for carbon dioxide absorption because of their smaller energy penalty in comparison to traditional amines and their feasibility for regeneration and chemical product co-production[13]. Reviews discuss different ammonia-based carbon capture strategies, centering their operational benefits, for example, ammonia slip as well as prospects for economic possibility via renewable energy deployment as well as chemical co-production.

Moreover, innovative resources and green chemistry pathways deploy calcium chloride with ammonium-based compounds in novel carbon dioxide capture conversion procedures. For example, eutectic additives of $CaCl_2$ and choline chloride have been subjected to ambient air to obtain atmospheric carbon dioxide and synthesize it into $CaCO_3$ nanoparticles in mild conditions, showcasing clean and non-toxic mineralization techniques. All in all, the distinct utilization of ammonium compounds and calcium chloride extends laboratory-scale precipitation, commercial mineral carbonation, CCUS systems, and advanced substance synthesis. These techniques manipulate the chemical synergy among calcium sources and ammonium species to improve carbon dioxide absorption, control calcium carbonate polymorphism as well as enhance particle size and develop clean circular economy procedures in areas such as cement manufacture and waste valorization. The figure below shows a demonstration of mineral carbonization in industrialized applications:

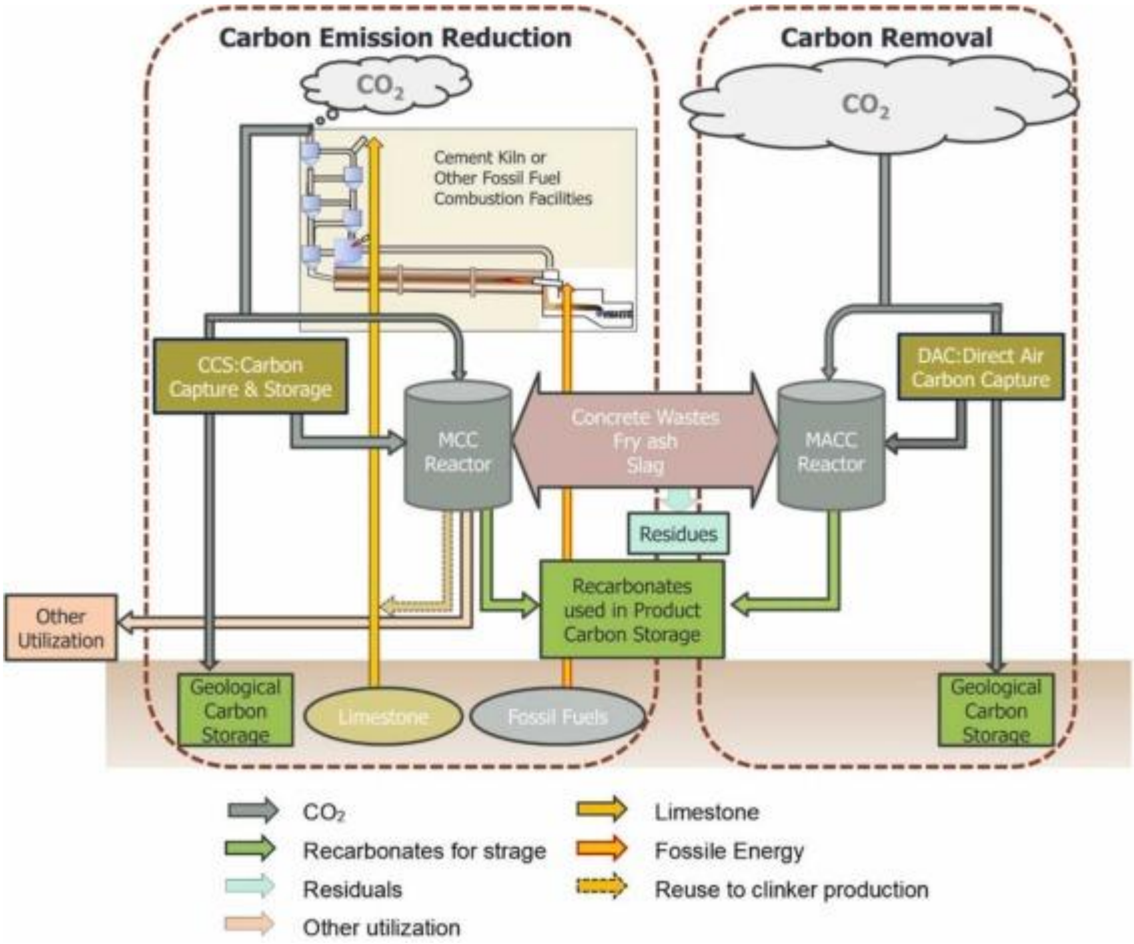


Figure 14 shows suggestions for carbon elimination in cement industry[16]

Methods of Carbon Capture in the Cement Industry

Carbon capture in the cement sector deploys various distinct techniques and methods, each with unique approaches, benefits, obstacles, and degrees of technological advancement. The fundamental methods involve oxy-fuel combustion (partial and full), post-combustion amine scrubbing, direct capture, calcium looping, as well as mineralization-based CCUS. Post-combustion carbon capture, specifically amine scrubbing, is presently the most technologically advanced and extensively researched procedure. It includes the chemical absorption of carbon dioxide from flue gases by using solvents such as MEA (monoethanolamide). This technique aims at the flue gas stream after combustion and is beneficial because of its retrofit capacity in present industries and a firmly established operational understanding from the power industry. Nevertheless, it possesses high thermal energy requirements for solvent regeneration, usually typically ≥2 GJ/t CO_2, which must be met by coupled heat and power (CHP) or waste heat recovery setups, adding to functional expenses and complexity. Capture rates in amine scrubbing could surpass 90%, however, economic possibility relies heavily on the presence of low-grade heat and the supervision of the flue gas impurities that influence solvent deterioration and instrument lifespan [17].

Oxy-fuel combustion alters the combustion procedure by combusting fuel in an oxygen-rich or pure oxygen environment instead of air, forming a flue gas stream with high carbon dioxide concentrations, allowing easier capture. Full oxy-fuel combustion includes full substitution of air with oxygen, needing alterations to the pre-calciner and kiln as well as an airtight design, comprising a two-stage cooler for recycling CO_2 while cooling clinker, although partial oxy-fuel combustion aims only distinct sectors, such as the pre-calciner. These methods perk from feasibly decreasing energy penalties for carbon dioxide separation, but meet obstacles connected to oxygen manufacture expenses and reconstructing complexity. Both versions are typically deemed at TRL (Technology Readiness Level), and 4 -6, with complete oxy-fuel combustion considered less advanced[18]. The figure below shows the incorporation of an oxy-fuel procedure in a cement plant:

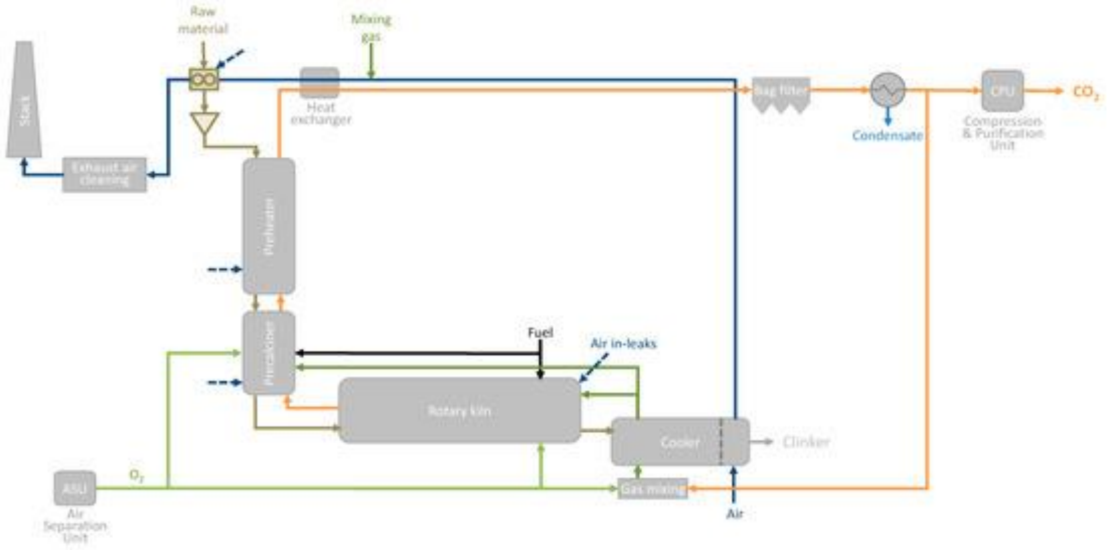


Figure 15 shows oxy fuel carbon capture in a cement plant

Calcium looping or CaL is a novel method that manipulates the reversible carbonation-calcination reaction of CaO to obtain carbon dioxide. In this procedure, CaO reacts with carbon dioxide to create calcium carbonate in a carbonator reactor at lower temperatures. Calcium carbonate is then regenerated by calcination at higher temperatures into calcium oxide, discharging a pure carbon dioxide stream. This technique can obtain carbon dioxide from both calcination and fuel combustion emissions, feasibly mitigating the procedure emissions that comprise approximately 50-60% of the cement sector carbon dioxide yield. Calcium looping provides capture yields up to 90% as well as competitive carbon dioxide avoidance expenses, where some researchers documented from 16 to 60 EUR/t carbon dioxide, with the coupled advantage of using surplus resources, such as commercial residues or limestone. Nevertheless, it needs incorporation with the cement procedure heat streams and has issues concerning the influence of repeated calcium oxide cycling on cement quality as well as sorbent deterioration[17], [19].

Direct capture technologies, including those established by companies such as Calix Ltd, include the isolation of carbon dioxide directly from the raw material or the kiln feed before calcination, thus blocking carbon dioxide discharge during clinker production. This method is at the preceding phases of development (TRL 4 to 5) and requires deploying capture within the cement manufacturing procedure itself, possibly decreasing the requirement for continuous flue gas treatment. Nonetheless, it involves major procedure alterations, such as the installation of new instruments, for instance, DCUs (direct capture units) and novel raw material conveyance systems. This system strikes moderate capture quantities, around 50-60% at decreasing incremental expenses, but needs more pilot and demonstration-scale verification to validate cement quality maintenance as well as economic feasibility[18].

Mineralization-dependent CCU (carbon capture and utilization) represents an innovative and promising pathway, where carbon dioxide is chemically bound into stable carbonate minerals, including calcium carbonate, which can then be used as fillers in concrete or cement end-products. This technique merges mineral valorization with carbon capture, improving the mechanical features of cement materials and allowing the utilization of circular carbon dioxide in the cement sector. Numerous synthetic pathways exist, such as the carbonation of calcium-rich waste sources, including calcium chloride solutions or steel slags, often combined with MEA-based absorption for carbon dioxide capture or ionic liquids before mineralization. LCA or life cycle assessment, as well as techno-economic examinations, showcase that mineralization can substantially decrease the net carbon footprint of cement manufacture. Especially when added with partial replacement of clinker by said carbonated fillers. Nevertheless, obstacles such as procedure scale-up, calcium extraction energy intensity, dissociation of mineralization process, and guaranteeing consistent quality of cement[11], [19].

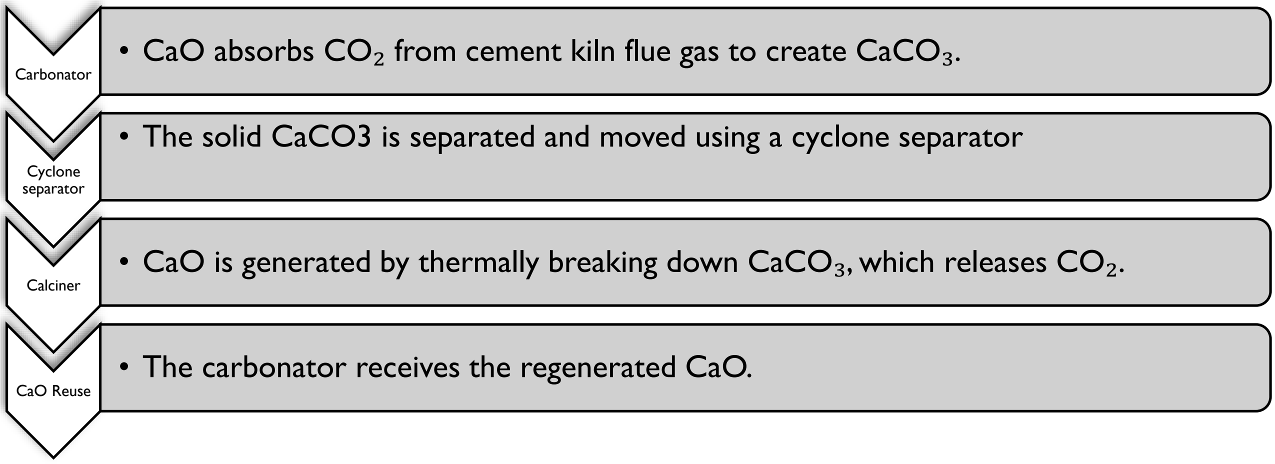
All in all, while amine scrubbing continues to be the most advanced and broadly deployed carbon capture technique in the cement sector, crucial research and test projects are in progress to develop oxy-fuel combustion, calcium looping, direct capture, and mineralization-based carbon capture utilization. Each technology showcases offsets among capture efficiency, energy specifications, integration sophistication as well as economic possibility. The selection of technology is affected by features, including industry retrofitting abilities, regional energy markets together with carbon guidelines policies. Consistent advancement and presentation at commercial scales are imperative to beating technical and economic challenges and attaining significant carbon dioxide mitigation difficult-to-reduce industry.[17], [19]

Calcium carbonate (CaCO3), the raw material for clinkers, is an important part of the cement-making process. It is thermally broken down in a kiln to produce both carbon dioxide and calcium oxide (CaO). The binding qualities of cement are created by the reaction of this CaO with other substances. Furthermore, recycling processes improve kiln operation by assuring consistent feedstock quality and increasing energy efficiency during calcination.

Moreover, to internal reuse, calcium carbonate could be processed and sold as a valuable commodity in a variety of industries, including construction fillers, paper manufacture, plastics, and pharmaceuticals. Selling those waste-derived $CaCO_3$ provides an extra budget for cement factories, while promoting economic sustainability.

Cement and paint bases are made from limestone. Calcium carbonate is used in concrete in India, both in powder and sand form. The study highlights how calcium carbonate powder can replace up to 30% of cement without reducing its strength. Calcium carbonate sand could be used to replace natural river sand completely or partially, boosting concrete strength. Natural sand should be replaced at a 50% rate. The use of cement can be minimized by partially substituting it with other materials and lowering environmental damage [20].

Calcium carbonate has a dual purpose as a recyclable raw material for clinker manufacture and a marketable commodity. Discussions on sustainable cement manufacturing now revolve around CaCO3, as methods to recycle, replace, or value it to reduce its negative effects on the environment are emerging. Innovations like carbonate looping technologies, waste-derived $CaCO_3$, and low-clinker blended like LC^3 Signify how this could be used to preserve cement quality, minimize carbon emissions, improve resource efficiency, and promote the circular economy concept.



- CaO absorbs CO_2 from cement kiln flue gas to create $CaCO_3$.
- The solid CaCO3 is separated and moved using a cyclone separator
- CaO is generated by thermally breaking down $CaCO_3$, which releases CO_2.
- The carbonator receives the regenerated CaO.

Figure 16:$CaCO_3$, CaO and CO_2 cycle.

Carbonate looping technologies

Carbonate looping (CaL); a carbon capture process used to reduce CO_2 emissions from energy-intensive industries like cement manufacture. During the carbonation stage, calcium oxide (CaO) and carbon dioxide (CO_2) undergo a reversible chemical reaction to produce calcium carbonate

$$(CaCO_3).CaO\ (s) + CO_2\ (g) \leftrightarrow CaCO_3\ (s)$$

At higher temperatures, the resultant $CaCO_3$ is broken down into CaO and a concentrated CO_2 stream, allowing CO_2 recovery and storage. By closing the loop, this regeneration process permits CaO to be reused several times. Cement facilities are especially applicable for the process, since they use raw materials based on calcium and run high-temperature kilns. Research indicates that while preserving process continuity, CaL may absorb up to 90% of CO_2 emissions. But there are still issues with sorbent deterioration, energy consumption, and reliable material handling systems. CaL is now more feasible and efficient with recent developments in process control, heat integration, and absorbent stabilized conditions [21].

Calcium Looping in Cement Production: A Dual Benefit for Emissions Reduction and Material Recycling

Calcium Looping (CaL) is a competitive method for CO_2 capture from flue gases[22]. The cement industry is responsible for 5% of CO_2 emissions worldwide. In the dual fluidized bed method known as CaL, CO_2 is regenerated in the calciner after being absorbed by CaO in the carbonator. It provides advantages such as expertise with CaO-bearing materials and the possibility of recycling purge CaO in cement production. The cost of avoiding CO_2 is projected to be around 68.75 €/tCO2, which shows the economic effectiveness of CaL. In large-scale applications, CaL faces challenges such as integrating the process with a CO_2 purification unit. Taking both technical and practical factors into account, the study explores the integration of calcium looping (CaL) in a cement factory. For efficient H_2O and O_2 removal, it is considered a dehydration unit and a cryogenic distillation system. Solid-gas heat exchangers are also introduced for hot sorbent cooling. With emphasis on spent sorbent quality, fuel composition, and economic viability in comparison to amine scrubbing technology, the study also investigates the possible application of CaL spent sorbent in cement production.

CO_2 Capture and Resource Recovery

In cement production, calcium looping is a promising strategy for minimizing carbon dioxide emissions by absorbing and storing them[23]. This revolutionary approach can be employed in cement production to decrease emissions and boost concrete qualities. Using waste-derived calcium carbonate as a substitute raw material can minimize raw material prices and promote the concepts of the circular economy. Calcium looping is a potent post-combustion CO_2 capture method that turns CO_2 from flue gases back into $CaCO_3$ by applying CaO.

This approach encourages sustainable industrial decarbonization and is inexpensive and energy efficient. Various approaches to the usage of $CaCO_3$ in cement manufacturing can have their effects on the environment analyses by a thorough life cycle analysis (LCA). $CaCO_3$-based blended cement compositions, such LC^3 Cement, can cut CO_2 emissions by as much as 40%. Pharmaceuticals, polymers, paints, and paper can all profit from the value-added products that can be made from high-purity $CaCO_3$ such as precipitated calcium carbonate (PCC) or nano-calcium carbonate. Process simulators, AI-based kiln control systems, and Computational Fluid Dynamics (CFD)[24] are examples of complex process optimization technologies that can optimize $CaCO_3$ usage, reduce heat losses.

Environmental Risks and Industrial Reuse of Waste Calcium Chloride Waste calcium chloride, or $CaCl_2$, is a dangerous byproduct of the Solvay process, an industrial method for making sodium carbonate. Many companies, including cement manufacturers, can use this material to cut waste, save money on disposal, and save resources. $CaCl_2$ is a substantial waste stream since it builds in residual brine when calcium carbonate combines with hydrochloric acid or ammonia regeneration. Waste calcium chloride disposal has traditionally created environmental problems due to its high salinity, which can cause soil degradation, aquatic toxicity, and groundwater contamination. Improper disposal can raise saline levels in neighboring bodies, harming freshwater habitats and agricultural land.

Expanding Applications of Calcium Chloride in Industry and Environmental Management

Researchers and companies have devised a variety of utilization methods to solve these challenges and add value to this waste stream. $CaCl_2$ is commonly used as an additive in the cement and concrete industry to speed up cement hydration[25], especially at colder temperatures. However, excessive use may increase the risk of steel reinforcement corrosion. $CaCl_2$ can enhance the setting and durability of geopolymers and other cementitious materials. Additionally, it has applications for desiccants, chemical and industrial feedstock, road upkeep, snow removal, dust management, de-icing, and wastewater treatment. New research examines employing $CaCl_2$ in water treatment for phosphate precipitation or heavy metal immobilization.

Carbonate Looping: A Circular Approach to CO_2 Emission Reduction Using $CaCl_2$ Derivatives

[26]The Carbonate Looping (CaL) technique is being investigated to adapt a 1052 MW coal-fired power station and maintain high power efficiency while lowering emissions. The technique involves a cyclic reaction between CaO and CO_2 in two coupled fluidized bed reactors. The carbonator converts CO_2 to $CaCO_3$, whereas the calciner decomposes $CaCO_3$ into CaO and CO_2 using coal and oxygen for heat. A closed loop is created when the regenerated CaO enters the carbonator and the CO_2-rich stream from the calciner is

prepared for compression and storage. According to the study, the carbonate looping process can cut emissions by up to 99% while incurring a lower energy penalty than standard methods.

Cement Industry Use and Broader Industrial Integration of Waste $CaCl_2$

The Solvay process, a popular commercial method for generating sodium carbonate, generates a substantial byproduct termed calcium chloride ($CaCl_2$). Because of its high solubility and ability to contaminate water bodies, this waste poses environmental risks. Improper disposal of $CaCl_2$ can cause soil contamination, water pollution, and ecosystem disruption. Calcium chloride is commonly used as a setting accelerator in the cement and concrete industries, shortening setting times and improving early strength development[27]. However, excessive use can cause steel reinforcement to corrode, thus it is normally employed in non-reinforced concrete or in conjunction with corrosion inhibitors.

Circular Economy Benefits and Carbon Capture Opportunities from $CaCl_2$
Beyond cement, calcium chloride is used in a variety of industrial applications, including de-icing and anti-freeze[28], dust suppression, desiccants, and refrigeration brines. These applications both reduce environmental impact and give economic benefits by generating new revenue streams.

Waste $CaCl_2$ can be turned back into calcium carbonate ($CaCO_3$) by reacting with CO_2, providing a carbon capture pathway. This process decreases greenhouse gas emissions while producing precipitated calcium carbonate (PCC), a valuable mineral utilized in a variety of industries. PPC is used as reinforcement material and in paper and plastics industry[29]. Calcium chloride is excellent in wastewater treatment, especially for phosphate precipitation and heavy metal immobilization[30]. This method minimizes waste disposal costs, minimizing environmental effects, and preserving natural resources. Integrating $CaCl_2$ utilization can improve material performance and promote economic sustainability.

Waste Stream Composition and Cleaner Production Strategies in the Solvay Process

In this study, waste streams from the Solvay Process—a chemical manufacturing process that calcines limestone to produce sodium carbonate, or soda ash—are examined. The primary byproduct is $CaCl_2$, which produces significant amounts of solid and liquid waste. The waste streams comprise distillation wastewater and solid leftovers, brine purification sludge, and mother liquor. The study's goal is to determine the impact of raw material purity on waste creation, as well as to research Lake Traunsee regeneration after closure. The results demonstrate that the process's solid wastes contain large levels of inert, insoluble chemicals that accumulate in bodies of water. The study suggests that solid, insoluble wastes are more damaging than dissolved salts because of sedimentation and long-term ecological damage. To achieve cleaner production, use higher-purity limestone, increase NaCl conversion to Na_2CO_3, and reduce solid waste at the source [31].

The Potential of Calcium Chloride Waste in Egypt's Cement Industry

Egypt has multiple soda ash factories that employ the Solvay process to produce substantial amounts of calcium chloride ($CaCl_2$) as a byproduct. This trash has the potential to generate hundreds of thousands of tons annually. However, majority of Egypt's industrial brine waste is either released untreated or partially reused in low value uses, resulting in soil and aquifer salinity. Egypt is one of the world's top 12 cement producers, with an annual output of over 80 million tons. $CaCl_2$ could have a significant influence when used as a cement accelerator, particularly in non-reinforced infrastructure and precast concrete projects.

This can shorten curing periods by about 30-40%, enhancing efficiency in large-scale projects. $CaCl_2$ waste valorization supports Egypt's Vision 2030 and Green Economy Strategy. Furthermore, it could produce value-added products and lowering the reliance on imported raw materials by recovering $CaCl_2$ for dust management, de-icing, or conversion to PCC for paints and plastics. Research institutions and industry can work together to create life cycle assessments and industrial constructive collaboration models.

Chapter Three

Methodology and process Design

Process Description

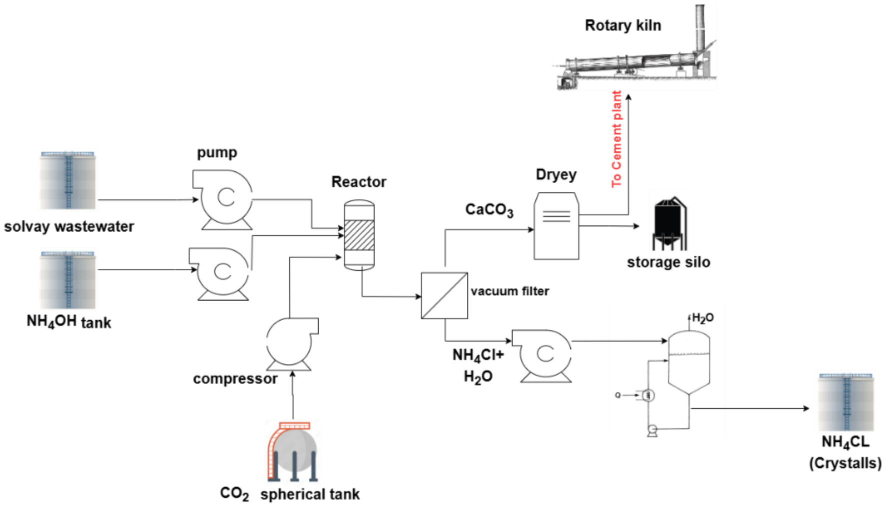


Figure 17: suggested modified process

Shown in Fig.16 The CO_2 will be captured from all CO_2 sources in the process from both the calcination process and from the flue gas produced from burning fuel used to operate the kiln. $CaCl_2$ and NH_4OH will be pumped into batch reactor with the captured CO_2. The product from the reactor will be fed into a rotary drum which will separate the $CaCO_3$ from the sludge containing NH_4Cl. The sludge will be processed to remove unwanted water and get a pure crystal of NH_4Cl which will be either sold or directed to the fertilizer industry. The dried $CaCO_3$ either sold or recycled to the kiln as regenerated raw material hence we obtained a closed CO_2 cycle.

Simulation steps

1. Since this process contains solid materials processing so ASPEN plus software was chosen to simulate the process.
2. The fluid package ELECNRTL was chosen, and all required components were defined to the system. (CO_2, NH_4HCO_3, NH_4OH, $CaCl_2$, NH_4CL, $CaCO_3$)
3. All required equations are entered into the simulation environment.
4. All required equipment is set to the simulation environment.

Notes:

1. The determined amount of entering CO_2 was chosen based on literature[32]. The CO_2 sources are both calcination process in kiln and flue gas from the burned fuel used to operate kiln. It was found that calcination is responsible for 60–65% (about 0.5-0.6 ton) carbon dioxide emissions and fuel combustion accounts for 35–40% (about 0.3-0.4 ton) of total cement emissions. Thorough that, it could be assumed that total amount of CO_2 is 900,000 tons CO_2/year which is ≈ $102669.4045\frac{\mathrm{kg}}{\mathrm{hr}}$.
2. Other components flow are calculated either by simulation or stichometry.
3. Some process steps that could be done in one step were expanded in the simulation for simulation purposes. For example, the mixed CO_2, Solvay and NH_4OH could be directly fed to one reactor only but the results were not good if compared by the actual followed approach in the simulation.

Set of equations used

Overall equation

$$CaCl_2 + 2NH_4OH + CO_2 \rightarrow CaCO_3 + 2NH_4Cl + H_2O$$

Equations sequences

$$CO_2 + NH_3 + H_2O \rightarrow NH_4^+ + HCO_3^-$$

$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3 + H_2O$$

$$Ca^{2+} + 2Cl^- \rightarrow CaCl_2$$

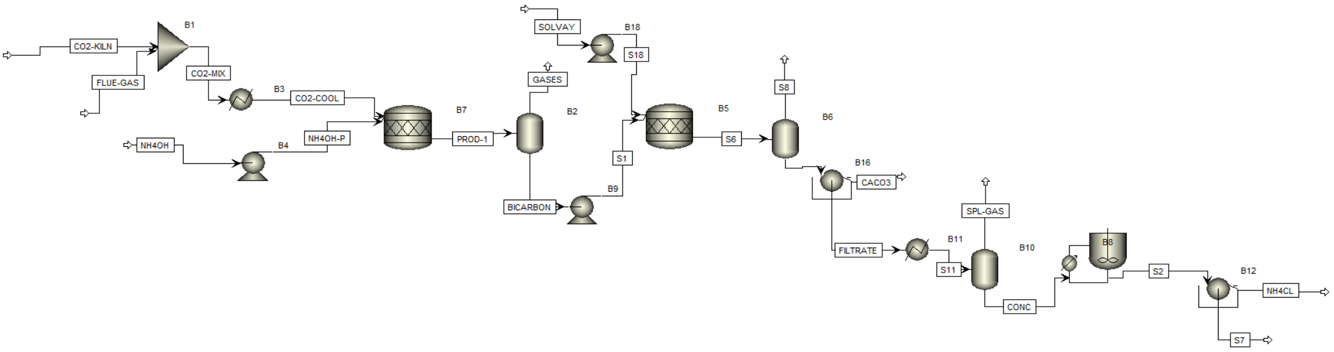


Figure 18: Simulated modified process using Aspen Plus

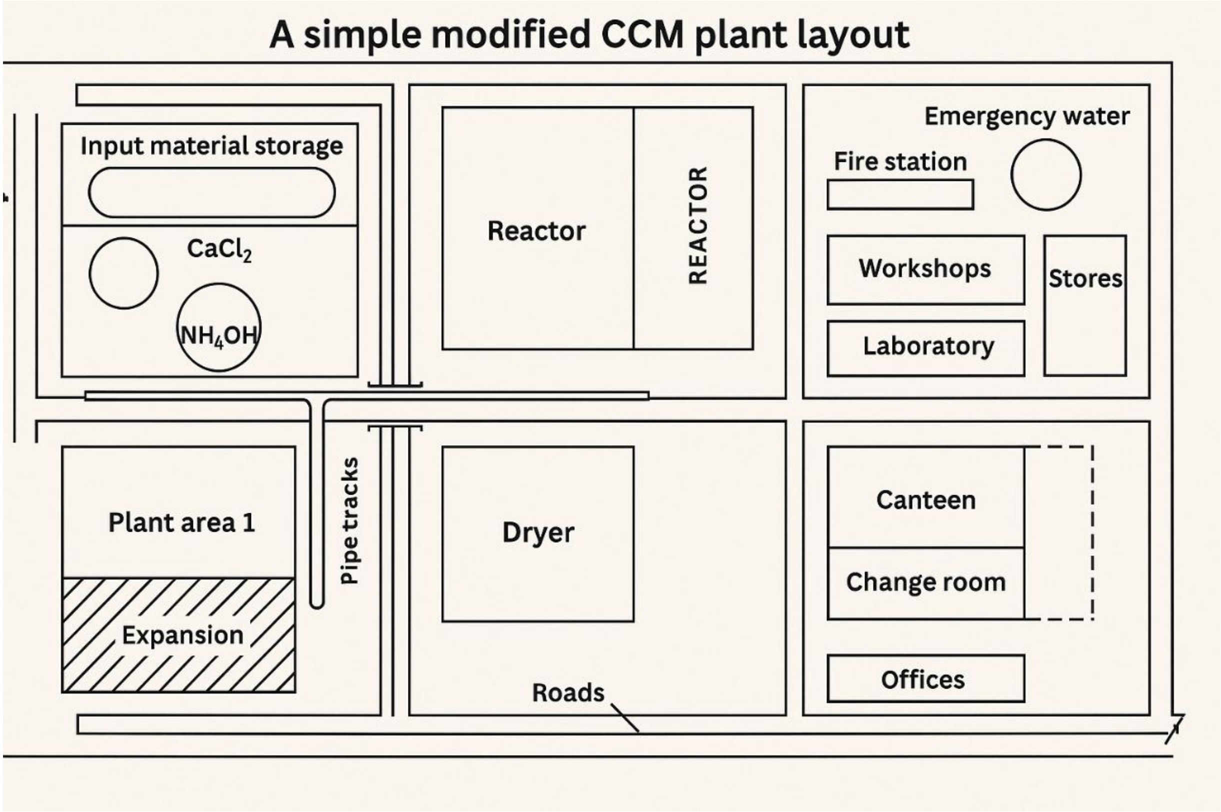


Figure 19:plant layout

Chapter Four

Simulation Results

Mass and Energy balance

Table 0-1: Mass and Energy balance

	Units	BICARBON	CACO$_3$	CO$_2$-COOL	CO$_2$-KILN	CO$_2$-MIX	CONC	FILTRATE	FLUE-GAS	GASES	NH$_4$CL
From		B2	B16	B3		B1	B10	B16		B2	B12
To		B9		B7	B1	B3	B8	B11	B1		
Stream Class		MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD
Temperature	C	40	30.00007695	40	30	170.3104858	120	30.00007682	350	40	10
Pressure	bar	1	1	2	1.01325	1.01325	1	1	1.01325	1	1
Molar Vapor Fraction		0	0	1	1	1	0	0	1	1	0
Molar Liquid Fraction		1	0	0	0	0	0.999999999	0.999981323	0	0	0
Molar Solid Fraction		0	1	0	0	0	5.52E-10	1.87E-05	0	0	1
Mass Vapor Fraction		0	0	1	1	1	0	0	1	1	0
Mass Liquid Fraction		1	0	0	0	0	0.999999998	0.999899378	0	0	0
Mass Solid Fraction		0	1	0	0	0	1.84E-09	0.000100622	0	0	1
Molar Enthalpy	kcal/mol	-72.35071079	-288.2751285	-58.98686693	-94.01370891	-57.85130101	-46.9223422	-67.29712514	-19.52891012	-27.71048038	-75.44056781
Mass Enthalpy	kcal/kg	-3093.737283	-2880.239716	-1563.047721	-2136.199413	-1532.957231	-1564.307965	-3622.542225	-628.0939573	-905.9281467	-1410.333487
Molar Entropy	cal/mol-K	-46.80437521	-62.57481701	0.855523306	0.834685972	5.227810576	-38.27719417	-38.13798178	7.021035835	0.860140501	-90.30882882
Mass Entropy	cal/gm-K	-2.001368598	-0.625202993	0.022669856	0.018965912	0.138527741	-1.276094008	-2.052932411	0.225812406	0.028120245	-1.688290123
Molar Density	mol/cc	0.043537325	0.027075324	7.72E-05	4.04E-05	2.75E-05	0.062796527	0.055541827	1.96E-05	3.85E-05	0.02852253
Mass Density	kg/cum	1018.171909	2709.893323	2.913910338	1.777648118	1.037895499	1883.618947	1031.818276	0.607985789	1.17694962	1525.70711
Enthalpy Flow	Gcal/hr	-749.2501355	-699.5211356	-160.4771787	-131.593393	-157.3878061	-272.9449115	-8760.427791	-25.79441303	-43.10322328	-137.9979785
Average MW		23.38618446	100.0872	37.73836598	44.0098	37.73836598	29.99559119	18.57731973	31.0923388	30.58794506	53.49129726
Mole Flows	kmol/hr	10355.80891	2426.574707	2720.557763	1399.725577	2720.557763	5816.949852	130175.3644	1320.832185	1555.48452	1829.227728
Mass Flows	kg/hr	242182.8575	242869.068	102669.4045	61601.64271	102669.4045	174482.8497	2418309.366	41067.76181	47579.07505	97847.76416
CO$_2$	kg/hr	17.77303162	0	73808.85038	61601.64271	73808.85038	0.227653939	1637.283986	12207.20767	16170.61593	0
AMMON-01	kg/hr	2015.385482	0	0	0	0	0.246929732	5.720722779	0	979.381646	0

WATER	kg/hr	135514.9038	0	951.8064661	0	951.8064661	73.99357404	2237683.729	951.8064661	2521.387829	0
$CACL_2$	kg/hr	0	0	0	0	0	0	0	0	0	0
NH_4CL	kg/hr	0	0	0	0	0	0	0	0	0	97847.38203
N_2	kg/hr	0.970619219	0	26640.79633	0	26640.79633	3.54E-10	0.002359625	26640.79633	26639.82571	0
O_2	kg/hr	0.087411393	0	1267.951348	0	1267.951348	9.66E-11	0.000410565	1267.951348	1267.863937	0
CA^{++}	kg/hr	0	0	0	0	0	24688.80073	24591.3642	0	0	0
H^+	kg/hr	1.40E-06	0	0	0	0	0.003436073	0.005373604	0	0	0
NH_4^+	kg/hr	25353.07038	0	0	0	0	35757.61152	36835.80758	0	0	0
$CACO_3(S)$	kg/hr	0	242869.068	0	0	0	0.000321415	243.3362446	0	0	0.382131091
NH_2COO^-	kg/hr	31133.86523	0	0	0	0	3.76E-09	1.585043109	0	0	0
HCO_3^-	kg/hr	42369.37356	0	0	0	0	2.07E-08	3348.082855	0	0	0
OH^-	kg/hr	0.054414315	0	0	0	0	3.63E-10	0.000660333	0	0	0
CL^-	kg/hr	0	0	0	0	0	113961.9656	113961.9656	0	0	0
CO_3^{--}	kg/hr	5777.373511	0	0	0	0	2.23E-15	0.482180816	0	0	0
NH_4HCO_3	kg/hr	0	0	0	0	0	0	0	0	0	0
Volume Flow	cum/hr	237.8604786	89.62311023	35234.23599	34653.45143	98920.75317	92.63171302	2343.735735	67547.23971	40425.75334	64.13273131

Table 0-2: Mass and Energy balance continued

	Units	NH4OH	NH4OH-P	PROD-1	S1	S2	S6
Description							
From			B4	B7	B9	B8	B5
To		B4	B7	B2	B5	B12	B6
Stream Class		MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD
Cost Flow	$/hr						
Total Stream							
Temperature	C	40	40.02111647	40	40	10	30
Pressure	bar	1.01325	2	2.0265	1	1	1.01325
Molar Vapor Fraction		0	0	0.109271684	0	0	0
Molar Liquid Fraction		1	1	0.890728316	1	0.534492342	0.982154396
Molar Solid Fraction		0	0	0	0	0.465507658	0.017845604
Mass Vapor Fraction		0	0	0.134143743	0	0	0
Mass Liquid Fraction		1	1	0.865856257	1	0.433547502	0.911305057
Mass Solid Fraction		0	0	0	0	0.566452498	0.088694943
Molar Enthalpy	kcal/mol	-58.06849584	-58.06786795	-67.64957759	-72.35071152	-69.77365794	-71.41559937
Mass Enthalpy	kcal/kg	-3258.917996	-3258.882757	-2746.060335	-3093.737313	-1587.248876	-3546.354509
Molar Entropy	cal/mol-K	-39.22220029	-39.2215034	-41.85748313	-46.80437304	-56.52935734	-38.51057675
Mass Entropy	cal/gm-K	-2.201226887	-2.201187777	-1.699096702	-2.001368504	-1.285960369	-1.912357506
Molar Density	mol/cc	0.048996961	0.048997351	0.000703889	0.043537345	0.045816602	0.054165725
Mass Density	kg/cum	873.0443198	873.051265	17.34041478	1018.172377	2014.045791	1090.775808
Enthalpy Flow	Gcal/hr	-609.7192064	-609.7126135	-795.7037496	-749.2501427	-276.947369	-9498.380678
Average MW		17.818336	17.818336	24.63513883	23.38618448	43.95886429	20.13774968
Mole Flows	kmol/hr	10500	10500	11762.13922	10355.8089	3969.225309	133001.4837
Mass Flows	kg/hr	187092.528	187092.528	289761.9325	242182.8575	174482.6367	2678350.586
CO_2	kg/hr	0	0	9624.141775	17.77272454	0.027501943	16061.75192
AMMON-01	kg/hr	35757.23452	35757.23584	1636.610221	2015.384512	0.034280063	1.700302676
WATER	kg/hr	151321.0092	151321.0106	133783.4391	135514.8836	73.92378906	2236971.274
$CACL_2$	kg/hr	0	0	0	0	0	0
NH_4CL	kg/hr	0	0	0	0	98835.73942	0
N_2	kg/hr	0	0	26640.79633	0.970619219	3.54E-10	0.970619219
O_2	kg/hr	0	0	1267.951348	0.087411393	0	0.087411393
CA^{++}	kg/hr	0	0	0	0	24688.6463	26816.19772
H^+	kg/hr	4.58E-11	4.58E-11	2.04E-06	1.40E-06	2.51E-09	0.017599092
NH_4^+	kg/hr	7.35207923	7.350679426	28359.33899	25353.09149	2428.874724	36840.15183

$CACO_{3(S)}$	kg/hr	0	0	0	0	0.385991001	237556.1522
NH_2COO^-	kg/hr	0	0	25916.08062	31133.79839	0.040476719	1.42564715
HCO_3^-	kg/hr	0	0	55705.39167	42369.37094	0.001238583	10138.44833
OH^-	kg/hr	6.932237578	6.93091771	0.048612308	0.054415052	1.40E-09	0.000199296
CL^-	kg/hr	0	0	0	0	48454.96294	113961.9656
CO_3^{--}	kg/hr	0	0	6828.133867	5777.443316	1.23E-06	0.442788251
NH_4HCO_3	kg/hr	0	0	0	0	0	0
Volume Flow	cum/hr	214.2990038	214.297299	16710.2077	237.8603692	86.63290448	2455.454701

Table 0-3: Mass and Energy balance continued

	Units	S7	S8	S9	S11	S18	SOLVAY	SPL-GAS	S7
From		B12	B6	B6	B11	B18		B10	B12
To				B16	B10	B5	B18		
Stream Class		MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD	MIXCIPSD
Temperature	C	10	30	30	120	30.18582938	30	120	10
Pressure	bar	1	1.01325	1.01325	1	1	1.01325	1	1
Molar Vapor Fraction		0	1	0	0.955335017	0	0.000997835	1	0
Molar Liquid Fraction		0.991365856	0	0.98168199	0.044664983	0.988569375	0.987465199	0	0.991365856
Molar Solid Fraction		0.008634144	0	0.01831801	2.47E-11	0.011430625	0.011536966	0	0.008634144
Mass Vapor Fraction		0	1	0	0.927849244	0	0.002170591	1	0
Mass Liquid Fraction		0.987102983	0	0.908644916	0.072150756	0.942059561	0.939349939	0	0.987102983
Mass Solid Fraction		0.012897017	0	0.091355084	1.34E-10	0.057940439	0.05847947	0	0.012897017
Molar Enthalpy	kcal/mol	-64.92969515	-92.53403339	-71.34095121	-56.59480921	-70.86943967	-70.86943475	-57.04702813	-64.92969515
Mass Enthalpy	kcal/kg	-1813.135273	-2154.291533	-3554.796759	-3047.845096	-3589.155474	-3589.155229	-3163.20686	-1813.135273
Molar Entropy	cal/mol-K	-27.6553313	0.713766228	-38.5851796	-9.664977811	-37.84091661	-37.83919096	-8.327264726	-27.6553313
Mass Entropy	cal/gm-K	-0.772263855	0.016617243	-1.922633061	-0.520495707	-1.916438645	-1.916351253	-0.461739406	-0.772263855
Molar Density	mol/cc	0.095110272	4.04E-05	0.054493412	3.22E-05	0.055823592	0.02350099	3.08E-05	0.095110272
Mass Density	kg/cum	3405.968119	1.735414993	1093.624228	0.598274577	1102.261165	464.0373008	0.555121336	3405.968119
Enthalpy Flow	Gcal/hr	-138.9493905	-36.99382115	-9459.948472	-7370.632342	-8743.784737	-8743.784141	-7097.68743	-138.9493905
Average MW		35.81072858	42.95334776	20.06892547	18.56879449	19.74543599	19.74543597	18.03455501	35.81072858
Mole Flows	kmol/hr	2139.99758	399.7861089	132601.9392	130235.1301	123378.7762	123378.7764	124418.1803	2139.99758
Mass Flows	kg/hr	76634.87251	17172.15177	2661178.434	2418309.366	2436167.728	2436167.728	2243826.516	76634.87251
CO_2	kg/hr	0.027501943	16878.79637	1637.185892	4160.646106	5917.96997	6495.610696	4160.418452	0.027501943
AMMON-01	kg/hr	0.034280063	0.035988718	5.720790873	1024.150957	0	0	1023.904027	0.034280063

WATER	kg/hr	73.92378906	292.264151	2237683.689	2238716.185	2106653.787	2106890.243	2238642.191	73.92378906
$CACL_2$	kg/hr	0	0	0	0	0	0	0	0
NH_4CL	kg/hr	988.3573942	0	0	0	0	0	0	988.3573942
N_2	kg/hr	3.58E-10	0.968259594	0.002359625	0.002359625	0	0	0.002359625	3.58E-10
O_2	kg/hr	0	0.087000829	0.000410565	0.000410565	0	0	0.000410565	0
CA^{++}	kg/hr	24688.6463	0	24591.45392	24688.80073	65418.08056	64892.26173	0	24688.6463
H^+	kg/hr	2.51E-09	0	0.005374184	0.003436073	0.008911386	0.003997517	0	2.51E-09
NH_4^+	kg/hr	2428.874724	0	36835.80744	35757.61152	0	0	0	2428.874724
$CACO_{3(S)}$	kg/hr	0.00385991	0	243112.1802	0.000321415	141152.6288	142465.7976	0	0.00385991
NH_2COO^-	kg/hr	0.040476719	0	1.585283759	3.76E-09	0	0	0	0.040476719
HCO_3^-	kg/hr	0.001238583	0	3348.355072	2.07E-08	3063.047763	1461.598318	0	0.001238583
OH^-	kg/hr	1.40E-09	0	0.000660447	3.63E-10	0.000203196	0.000437491	0	1.40E-09
CL^-	kg/hr	48454.96294	0	113961.9656	113961.9656	113961.9656	113961.9656	0	48454.96294
CO_3^{--}	kg/hr	1.23E-06	0	0.482320529	2.23E-15	0.23931707	0.247492544	0	1.23E-06
NH_4HCO_3	kg/hr	0	0	0	0	0	0	0	0
Volume Flow	cum/hr	22.50017317	9895.127008	2433.35724	4042139.609	2210.154731	5249.939443	4042046.978	22.50017317

Equipment design

- Tanks design

Tank 1: Solvay wastewater

Design parameters and assumptions:

Table 4: Solvay wastewater Design tank

Material	**$CaCl_2$**
Temperature (℃)	30
Pressure (bar)	1.01325
Volume Flow ($\frac{m^3}{hr}$)	2625

Equipment specifications:

Assuming the residence time is 2 hr

$$V = Q.t$$

$$v = 2625\frac{m^3}{hr} * 2\text{hr} \approx 5250\ m^3$$

Assuming 2 tanks

$$\frac{5250\ m^3}{2} = 2625m^3$$

Assuming that H = $1.5D_{tank}$

$$V = \frac{\pi}{4} * D^2{}_{tank} * H$$

$$2625m^3 = \frac{\pi}{4} * D^2{}_{tank} * 1.5D_{tank}$$

$$D_{tank} = 13m$$

Then

$$H = 19.5m$$

Tank 2: Ammonium Hydroxide tank

Design parameters and assumptions:

Table 5:Ammonuim tank design

Material	NH_4OH
Temperature (℃)	40
Pressure (bar)	2
Volume Flow ($\frac{m^3}{hr}$)	107

Equipment specifications:

Since ammonia is volatile, floating roof tank will be used. It is also recommended to install a pressure relief valve

Assuming the residence time is 2 hr

$$V = Q.t$$

$$v = 107\frac{m^3}{hr} * 2\text{hr} \ \approx 214m^3$$

Assuming 2 tanks

$$\frac{214\ m^3}{2} = 107m^3$$

Assuming that H = $1.5D_{tank}$

$$V = \frac{\pi}{4} * D^2{}_{tank} * H$$

$$107m^3 = \frac{\pi}{4} * D^2{}_{tank} * 1.5D_{tank}$$

$$D_{tank} = 4.5m$$

Then

$$H = 6.75m$$

Since storage tanks diameter range from 3m to 114m[33], both diameters are accepted.

- Reactor design

Dimensional calculation for a batch reactor with a heterogeneous reaction, the design implies standard chemical engineering heuristics[34], [35], [36]

$$CaCl_2 + CO_2 + 2NH_4OH \rightarrow CaCO_3 \text{ (ppt)} + 2NH_4Cl.$$

Total Liquid Volume

Rector volume $v = Q \times R$

Q= B4 + B18

Q = 214.299 + 2210.15 = 2424.45 m³/hr.
Residence time (R) = 20 minutes = 0.333 hours[37]
Reactor Volume (V)= Q × R = 2424.45 × 0.333 = 807.34 m^3

$$(V)\text{actual} = \frac{reactor\ volume}{0.6}$$

$V_{actual} = 1345.57\ m^3$

Divide Into 3 parallel Reactors, $V_{actual} = 448.52\ m^3$

Dimensions of Each Reactor

$$V = \frac{\pi}{4} \times D^2 \times H$$

H/D ratio = 1.5 (based on design heuristics for batch reactors using solids. This ratio offers improved mixing, temperature control, and maintenance).

Diameter (D)= 6.11 m , and Height (H)= 9.17 m

Batch cycle

It takes 10 to 20 minutes to charge and load the reactor with reactants (CO_2, NH_4OH, and $CaCl_2$). The primary reaction phase (residence time) takes 20 minutes. Discharging and unloading the product (precipitated $CaCO_3$ and NH_4Cl solution) takes around 10-15 minutes. Cleaning/Reset takes around 10 to 30 minutes, cleaning time is increased by solids formation ($CaCO_3$) because of the risks of fouling and buildup. CO_2 pressure and ammonia handling influence safe charging and discharging procedures[38], [39].

Table 6: Reactor details

Charging	**5–20% of total cycle time**
Reaction	Based on experimental or kinetic data
Discharging	5–15% of total cycle time
Cleaning	10–30% of cycle time (especially with solids)

- Total batch time = Charging + Reaction + Discharging + Cleaning
- Assume 40% margin (due to solid formation and gas handling)

Total batch time = 67 min

Design Considerations

Heat is released during the calcium carbonate reaction, which may result in an uncontrollably high temperature that might compromise conversion and pose safety hazards. Internal cooling coils or a cooling jacket are suggested heat removal designs to avoid this. Temperature sensors, automatic coolant valves, and emergency shutdown if the temperature rises over the set point should all be included in the design of these systems.

Since improperly handled materials could potentially settle, obstruct outlets, or harm equipment, solid management and discharge are also essential to the reaction. An agitator with off-bottom clearance, a large-diameter valve or pneumatic discharge system, and a conical-bottom reactor or sloped base are suggested discharge designs. After every batch, cleaning and maintenance procedures include manual flushing or Clean-In-Place (CIP) and a hot water or mild acid wash to remove scale.

To effectively disseminate CO_2 into the liquid phase, a CO_2 gas distributor is required. A sparger or gas distributor ring at the reactor's bottom is part of a suggested gas distributor system, which should maintain a consistent CO_2 flow rate, keep gas velocity within range, and place the distributor to prevent dead zones and encourage bubble rise through suspension. To prevent over pressurizing the reactor, safety precautions include a gas shutdown valve, flowmeter, pressure relief valve, and back-pressure control.

- Flash Drum Desing

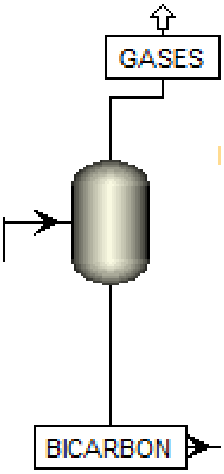


Figure 20 A flash drum used in the aspen v14 simulation

The Inputs and outputs of the drum include:

- Stream B7 product to B2
- Outputs are biocarbon and gases
- Range of flow rate is: mean flow:13,669 kg/h and maximum flow of 242,184kg/hr

Equipment Sizing

Residence Time: 10 minutes to achieve vapor-liquid isolation

Volume: $Flowrate\ x\ Time\ of\ Residence = \frac{242{,}183}{60} x\ 10 = 40{,}364\ kg$

$\frac{40.364}{800} = 50.5\ m3$, round up to 55m^3

Density: 800 kg/m^3 (assumption based on mixture of water-ammonia-carbonate)

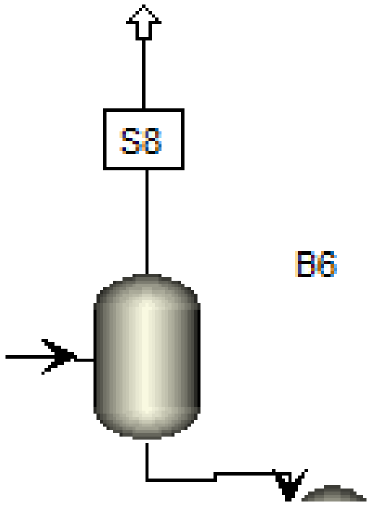


Figure 21 Calcium carbonate pressure vessel

Primary inputs and outputs include:

- **Primary Input:** Stream S6 coming from B5
- **Outputs:** calcium carbonate and liquid/gas
- Flow rate variation: Mean(B6):151,262 kg/hr, Maximum: 2.66x10^6 kg/hr

Equipment Sizing

Time of residence: 20-30 minutes due to crystallization

Assume maximum flow: $\frac{2{,}661{,}178{,}kg/hr}{60}\ x\ 30 = 1{,}330{,}530\ kg$

Slurry Density: 1100 kg/m^3

Volume: $\frac{1{,}330{,}530\ kg}{1100\ kg/m^3}$= 1210 m^3, round up to 1300m^3

- Multi- phase Evaporator design

Three stages multi effect evaporator desgin

Assumed all three areas of evaporators are equal

- No NH_4Cl loss in vapor (non-volatile)
- Vapor is only water
- Neglect boiling point elevation and heat losses

- Saturated steam used for 1st effect
- Latent heat of vaporization of water: **λ = 2257 kJ/kg**
- Specific heat of feed = **Cp = 4.18 kJ/kg·K**

Design Givens

- Feed flowrate: 85,000 kg/h
- Feed composition: 60% water / 40% NH_4Cl
- Feed temperature: 80°C
- Product concentration: 85% NH_4Cl
- Number of effects: 3

Mass Balance

Feed:
- Water = 85,000 × 60% = 51,000 kg/h
- NH_4Cl = 85,000 × 40% = 34,000 kg/h

Product:
- NH_4Cl = 85% → Product flowrate = 34,000 / 0.85 = 40,000 kg/h
- Water in product = 40,000 × 15% = 6,000 kg/h

Water evaporated = 51,000 - 6,000 = 45,000 kg/h

Heat Duty Calculations

Preheating duty (to 100°C):
Q preheat = 85,000 × 4.18 × (100 - 80) = 7.106×10^6 kJ/h

Evaporation duty:
Q evaporator = 45,000 × 2257 = 1.0157×10^8 kJ/h = 28,270 kW

Vapor Distribution per Effect

Each effect evaporates: 45,000 / 3 = 15,000 kg/h

Heat Exchanger Sizing (Area)

Table 7:Evaporators data

Effect	Water Evaporated (kg/h)	Heat Duty (kW)	U (W/m²·K)	ΔT (°C)	Area (m²)
1st	15,000	9,404	2,500	15	250.8
2nd	15,000	9,404	2,000	15	313.5
3rd	15,000	9,404	1,800	15	348.3

Steam Requirement

Steam for 1st effect:
$\dot{m}_{steam} = (9{,}404 \times 3600) / 2257 \approx 15{,}000$ kg/h

Steam Economy = 45,000 / 15,000 = 3.0

Summary

- Feed: 85,000 kg/h (40% NH_4Cl)
- Product: 40,000 kg/h (85% NH_4Cl)
- Water evaporated: 45,000 kg/h
- Steam required: 15,000 kg/h
- Heat exchange areas:
  - 1st Effect: 251 m²
  - 2nd Effect: 314 m²
  - 3rd Effect: 348 m²

Chapter Five

Economic and Environmental Evaluations

Economic study

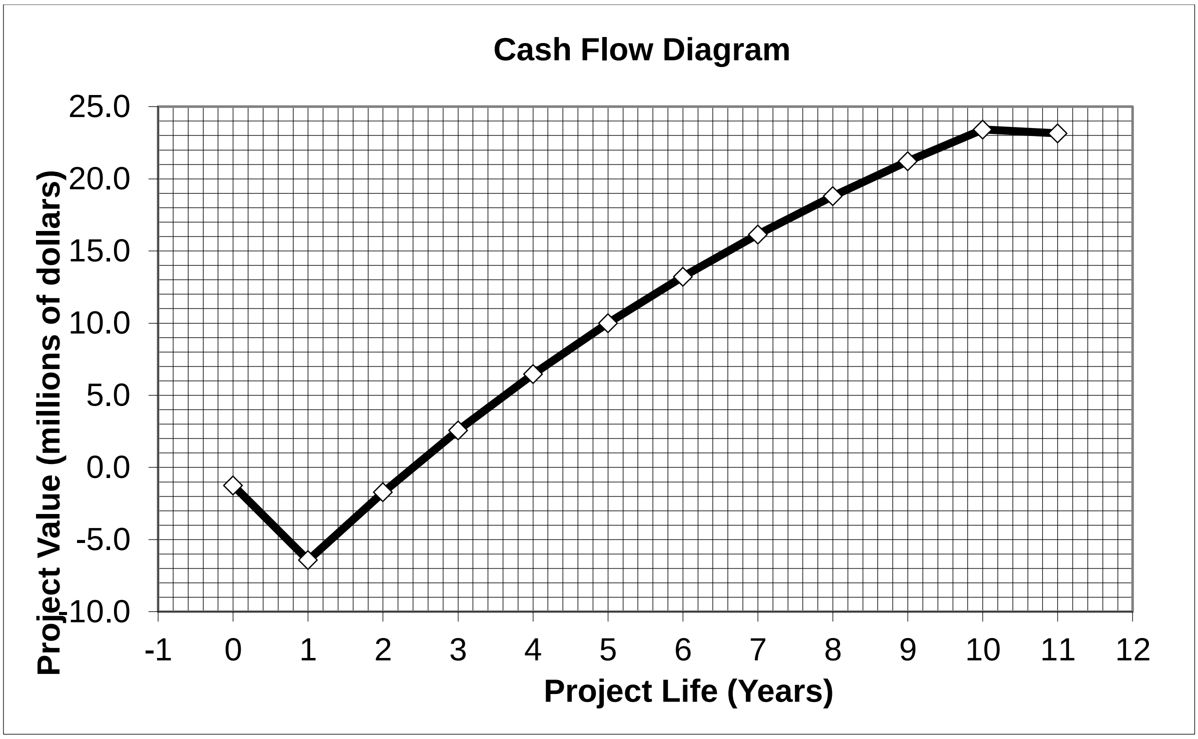


Figure 22 shows the cash flow diagram

The cash flow diagram shows an initial investment of $500 million, with a net positive income annually of $500 million due to energy savings of the modified cement plant, with a payback period in the second year. This project is shown to be very promising with a high value of ROI. The net present value is also shown to be $395,334,3000

Utilities Cost

Table 8 shows the utilities expenses

Name	Fluid	Rate	Rate Units	Cost per Hour	Cost Units
Electricity		958.71	KW	74.300025	USD/H
Cooling Water	Water	0.073508	MMGAL/H	8.82096	USD/H
Steam @100PSI	Steam	6205.254	KLB/H	50510.76756	USD/H

Table 9 shows the equipment expenses

Name	Equipment Cost [USD]	Installed Cost [USD]	Equipment Weight [LBS]	Installed Weight [LBS]
B10-flash vessel	3448700	4762200	1095500	1316476
B5	1170100	1602900	284600	348127
B2-flash vessel	59600	301100	11000	34005
B11	4585800	7008600	823200	1203818
B12	-	-	-	-
B1	-	-	-	-
B6-flash vessel	301500	727500	67100	121525
B16	-	-	-	-
B7	387400	651200	48300	77219
B18	228600	572000	8700	60402
B9	30100	119000	1700	14029

The summary of the overall expenses it shown as:

Table 10 shows the summary of the economic study conducted on aspen v14

Total Capital Cost [USD]	23788400
Total Operating Cost [USD/Year]	481717000
Total Raw Materials Cost [USD/Year]	-
Total Product Sales [USD/Year]	-
Total Utilities Cost [USD/Year]	443506000
Desired Rate of Return [Percent/'Year]	20
P.O. Period [Year]	-
Equipment Cost [USD]	18172800
Total Installed Cost [USD]	25143100

Environmental study

The research's modified cement process takes a circular approach to CO_2 management, which differs significantly from traditional cement manufacturing processes. Traditionally, cement factories generate significant amounts of CO_2 during calcination and fuel combustion, with limited collection or reuse. Our technique absorbs CO_2 from two main sources of emissions: limestone calcination and kiln flue gases. CO_2 is collected and combined with $CaCl_2$ and NH_4OH in a batch reactor, resulting in $CaCO_3$ and NH_4Cl. Unlike normal techniques that dump CO_2 into the atmosphere, our technology converts it into useful by-products. The $CaCO_3$ produced can be sold or reused in the kiln, creating a closed CO_2 cycle. Drying collects the NH_4Cl byproduct from sludge, which may then be used in fertilizer production. This integrated technique reduces net CO_2 emissions, raw material utilization, and produces marketable chemical co-products, providing environmental and economic benefits over traditional cement production.

Table 11: Environmental Evaluation

Environmental Aspect	Conventional Cement Plant	Modified Process (This Design)
CO_2 Emissions	High	Up to 40–50% reduction by reuse of captured CO_2
Raw Material Usage	Pure limestone ($CaCO_3$) mined	Partial substitution by recycled $CaCO_3$ (precipitated)
By-Product Waste	Minimal reuse: most CO_2 vented	NH_4Cl captured and valorized; $CaCl_2$ reused from Solvay
Air Pollution	Requires expensive post-treatment	Reduced emissions via CO_2 capture and clean gas streams
Water Pollution Risk	High if NH_4OH or $CaCl_2$ released	Controlled NH_4OH conversion, minimal aqueous discharge
Energy Consumption	High for capture	Moderate (captures CO_2 directly at source, no compression)

Challenges and Limitations

The additional utilization process will be significantly expensive and will add extra costs to the capital cost of a cement manufacturer as it contains new extra equipment such as batch reactor, crystallizer, pumps, vacuum filter and compressor, moreover, extra costs for the energy consumption costs for this equipment which may be a drawback for a cement plant to implement this technology. So, the use of renewable energy in this case can save fuel and electricity costs for the equipment. Also, the implementation of this technology would be expensive, but in the long term it would save energy consumption costs on the equipment. Another challenge is this addition area for cement plant may not have a previously designed area which would make it hard to implement it. A newly designed plant with an already considered this part of additional area could be better, as environmental study could be done, costs and risk assessments studies could be also done like the hazard and operability study (HAZOP) which is a good fit with a new plant rather than an already existing plant. Also, this new idea would need to be implemented and prove to successfully in order to be worth it for other plants to implement the idea for the additional part in the plant

Chapter Six

HAZOP study

It stands for Hazard and Operability study, it is a qualitative technique that involves a multidisciplinary team reviewing a process or system for a factory or industry, using guide words to identify potential deviations from the required design available[40]. These deviations are then analyzed for their potential consequences, which can range from safety hazards to operational problems.

The Hazop study will be conducted for the extended process in the cement plant for the manufacturing of the NH_4OH crystals and the recovery of the $CaCO_3$. First the process will be divided into 2 nodes shown. Each one of the nodes will be treated as a whole system. The first node as shown starts from the beginning of the process till the product coming from the batch reactor, it will include the two pumps, two tanks, compressor, batch and the spherical tank, it will end at the outlet stream of the batch. The second node will be the rest of the second part of the flowsheet which will be the vacuum filter, pump, dryer, storage silo and the crystallizer.

Some considerations were taken; the first consideration is three main parameters are to be considered which are the flow, pressure and temperature. The second consideration is the use of less/no, more and no keywords or guidewords for these parameters.

Table 12: Node 1 for HAZOP

Parameter	***Guideword***	***Deviation***	***Causes***	***Consequences***	***Recommendations***
Flow	Less/No	Less/No Flow from the $CaCl_2$ tank	Valve failure or closed or blockage of pipe	Pump damage	Backup pump/ automatic valve/regular checkup on valve and regular checkup on pipes
		Less/No Flow from the NH_4OH tank	Valve failure or closed or blockage of pipe	Pump damage	Backup pump/ automatic valve/regular checkup on valve and regular checkup on pipes
		Less/No flow from pump 1	Pump failure or not	Incomplete reaction in Batch reactor/ Off-spec product	Backup pump/ regular checkup and maintenance for pump

			operating properly		
		Less/No flow from pump 2	Pump failure or not operation properly	Incomplete reaction in Batch reactor/ Off spec product	Backup pump/ regular checkup and maintenance for pump
		Less/No flow from spherical tank	Valve failure or closed	Compressor damage	Backup compressor/ automatic valve/ regular checkup on valve
		Less/No flow from compressor	Compressor failure or not operating properly	Incomplete reaction in Batch reactor/ Off spec product	Backup compressor/ regular checkup and maintenance for the compressor
		Less/No flow from Batch reactor	Blockage in pipe	Overflooding in Batch reactor results in damaging of Batch reactor and product	Regular maintenance and cleaning for pipe
	More	More flow from $CaCl_2$ tank	Valve broken or failure	Pump damage	Backup pump/ automatic valve/regular checkup on valve
		More flow from NH_4OH tank	Valve broken or failure	Pump damage	Backup pump/ automatic valve/regular checkup on valve
		More flow from pump 1	Pump failure or not operating properly	Pump damage/ Affect parameters of reaction in Batch reactor/ Off spec product/ damage Batch reactor	Backup pump/ regular checkup and maintenance for pump
		More flow from pump 2	Pump failure or not	Pump damage/ Affect parameters of reaction in Batch	Backup pump/ regular checkup and maintenance for pump

			operating properly	reactor/ Off spec product/ damage Batch reactor	
		More flow from spherical tank	Valve failure or broken	Compressor damage	Backup compressor/ automatic valve/ regular checkup on valve
		More flow from compressor	Compressor failure or not operating properly	Affect parameters of reaction in Batch reactor/ Off spec product/ damage Batch reactor	Backup compressor/ regular checkup and maintenance for the compressor
Pressure	More	More pressure in Batch reactor	2 pumps and compressor overflowing in Batch reactor more than the proposed design	Damage or rupture in the Batch reactor	Pressure relief system/checkup and regular maintenance for pumps and compressor
		More pressure in spherical tank	Overflowed with CO_2/ Blockage of pipe leading to buildup	Damage or rupture could lead to explosion of the tank	Pressure relief valve/ controller and sensor on tank to detect pressure and level of CO_2/ Regular maintenance and checkup on pipe

Table 13: Node 2 for Hazop

Parameter	***Guideword***	***Deviation***	***Causes***	***Consequences***	***Recommendations***
Flow	Less/No	Less/No flow from pump	Pump failure or not operating properly/ blockage in pipe	No/less flow entering crystallizer/ decrease the yield of product	Backup pump/ Regular checkup and maintenance for the pump/ regular maintenance and cleaning for the pipe
		Less/No flow from vacuum filter	Blockage in pipe/ Vacuum filter not operating properly	Vacuum filter may overflood resulting in damaging of machinery and product/ Pump damage	Regular maintenance for pipe and Vacuum filter
	More	More flow from pump	Pump failure	Overflow in crystallizer system/ poor crystals formation	Regular maintenance and checkup for pump
Pressure	Less	Less pressure in vacuum filter	Vacuum pump failure	Poor filtration/ off spec product	Pressure sensors, regular maintenance for vacuum system
	More	More pressure in vacuum filter	Vacuum pump failure	Poor filtration/ off spec product	Pressure sensors, regular maintenance for vacuum system
Temperature	Less	Less temperature from outlet in heat exchanger	Heat exchanger failure	Affect the yield of the crystallizer	Regular maintenance and checkup for the heat exchanger
		Less temperature from outlet of dryer	Dryer failure or control issue	$CaCO_3$ product will not be dried well affecting the product quality	Regular maintenance and checkup for the drier

Chapter Seven

Location Selection Criteria

A proposed cement plant with a CO_2 capture unit will be located based on a few criteria, including labor availability, infrastructure, environmental legislation, logistics, and proximity to raw materials.

Proposed Location: Abu Qir, Alexandria Governorate

In Alexandria, Egypt, the planned site next to the Abu Qir Industrial Zone would offer convenient access to supplies of waste $CaCl_2$ and NH_4OH. Cement factories close to Alexandria can supply the large volumes of waste $CaCl_2$ produced by the Solvay Process, which is run by Abu Qir Fertilizers and Chemical Industries, his would guarantee a steady, affordable supply of $CaCl_2$, lowering the emissions and transportation costs, and boots the objectives of the circular economy by reusing industrial waste. Potential suppliers also include popular fertilizer firms like Abu Qir Fertilizers and Helwan Fertilizers Company. Abu Qir, a government-designated industrial zone, provides easy access to $CaCl_2$ and NH_4OH waste streams, allows import/export of materials and goods, and provides skilled labor near Alexandria University and vocational training centres.

Location Comparison and Ranking

Emissions control is essential for lowering the carbon footprint linked to the transportation of raw materials and advancing sustainability. Better monitoring and regulatory compliance are made possible by the city's placement within the industrial sector. The industrial environment includes the projected cement/CO_2 capture facility, the Solvay factory, and plants that produce NH_4OH.

On a scale of 1 (low) to 5 (ideal) Overall, Alexandria and Kafr El Sheikh are most outstanding locations. They both have access to industries that make ammonia-based compounds like NH_4OH and are near supplies of waste calcium chloride. Ammonia-related factories are among the many chemical factories in Alexandria, a sizable industrial urban area. Although there are fewer of these industries in Kafr El-Sheikh, it is still a viable choice. Transportation-wise, Kafr El-Sheikh is reasonably linked and still getting better, whereas Alexandria boasts great road, rail, and port connectivity. There are plenty of skilled professionals in Alexandria as well, and Kafr El-Sheikh gains from nearby training facilities and colleges.

Alexandria has easy access to northern Egypt's major cities and industry. Additionally, Kafr El-Sheikh and Ain Sokhna are conveniently situated close to Cairo and the Nile Delta. Alexandria's environmental laws are reasonable and manageable.

Table 14 Comparison and Ranking table

Criteria	***Kafr El-Sheikh***	***Alexandria***	***Ain Sokhna***	***Asyut***
$CaCl_2$ source ***(Solvay)*** ***Closeness to waste source***	*5*	*5*	*3*	*1*
NH_4OH source ***Closeness to waste source***	*4*	*5*	*3*	*1*
Infrastructure & transport ***Roads and industrial zones***	*4*	*5*	*5*	*3*
Labor & skilled workforce	*4*	*5*	*4*	*3*
Access to cement markets	*4*	*5*	*4*	*2*
Environmental compliance potential	*4*	*4*	*3*	*3*
Wind direction	*5*	*3*	*4*	*5*

Table 15 total scores and ranking

Location	**Score (out of 35)**	**Rank**
Alexandria	32	1
Kafr El-Sheikh	30	2
Ain Sokhna (Suez)	26	3
Asyut (Upper Egypt)	18	4

Chapter Eight

Conclusion

This research has explored the challenges and opportunities associated with sustainable cement production, highlighting the significant environmental impact of traditional cement manufacturing. Key findings indicate that cement production is a major contributor to CO_2 emissions, accounting for nearly 8% of global emissions. The analysis of alternative materials such as fly ash and cement kiln dust (CKD), along with advancements in carbon capture technologies, shows promising pathways for reducing the industry's carbon footprint. Additionally, improvements in energy efficiency and the integration of sustainable raw materials have been identified as essential strategies for minimizing environmental impact while maintaining cement quality and performance.

The implications for industrial sustainability are profound, as implementing eco-friendly cement production techniques can significantly reduce the emissions of CO_2 and resource consumption. The adoption of carbon capture and utilization (CCU) technologies offers a viable method to mitigate CO_2 emissions. Furthermore, utilizing industrial byproducts as supplementary cementitious materials enhances waste valorization and promotes a circular economy within the construction industry. The research succeeded in producing NH_4CL from a cement plant in addition to regenerating the raw material through closed loop of CO_2 and CO_2 capturing. The best location selected for the suggested plant was Alexandria based on different environmental and economic reasons.

Future research should focus on optimizing the efficiency of carbon capture systems in cement plants, exploring novel binding agents to reduce clinker dependency, and assessing the long-term durability of sustainable cement formulations. Additionally, further studies on the economic feasibility and scalability of alternative cement production methods will be crucial for widespread industry adoption.

In conclusion, achieving sustainability in cement production requires a combination of technological advancements, support, and industry commitment. By integrating innovative solutions and sustainable practices, the cement industry can help in achieving the goal of a greener future while meeting the growing demand for infrastructure development. Continued research and development in this field will be essential to ensure a balance between economic growth and environmental responsibility.

Chapter Nine

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