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Author
Hasanbeigi, Ali

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Ali Hasanbeigi, Lynn Price, Elina Lin

China Energy Group
Energy Analysis and Environmental Impacts Department
Environmental Energy Technologies Division
Lawrence Berkeley National Laboratory

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Abstract

Globally, the cement industry accounts for approximately 5 percent of current anthropogenic carbon dioxide (CO_2) emissions. World cement demand and production are increasing significantly, leading to an increase in this industry's absolute energy use and CO_2 emissions. Development of new energy-efficiency and CO_2 emission-reduction technologies and their deployment in the market will be key for the cement industry's mid- and long-term climate change mitigation strategies. This report is an initial effort to compile available information on process description, energy savings, environmental and other benefits, costs, commercialization status, and references for emerging technologies to reduce the cement industry's energy use and CO_2 emissions. Although studies from around the world identify a variety of sector-specific and cross-cutting energy-efficiency technologies for the cement industry that have already been commercialized, information is scarce and/or scattered regarding emerging or advanced energy-efficiency and low-carbon technologies that are not yet commercialized. This report consolidates available information on nineteen emerging technologies for the cement industry, with the goal of providing engineers, researchers, investors, cement companies, policy makers, and other interested parties with easy access to a well-structured database of information on these technologies.

Contents

Acronyms

ASTM	American Society for Testing and Materials
$CaCO_3$	limestone
CaO	lime
$Ca(OH)_2$	calcium hydroxide
CCR	calcium carbide residue
CCS	carbon capture and storage
CO_2	carbon dioxide
EMC	energetically modified cement
FBK	fluidized bed kiln
g	gram
GBFS	granulated blast furnace slag
GJ	gigajoules
H_2O	water
kg	kilogram
kWh	kilowatt-hour
MEA	monoethanolamine
MgO	magnesium oxide
µm	micrometer
mm	millimeter
Mt	million tonnes
NOx	nitrogen oxide
NSP	new suspension preheater
OPC	Ordinary Portland cement
PSC	Portland slag cement
SO_2	sulfur dioxide
psi	pounds per square inch
tpd	tons per day
U.S. EPA	United States Environmental Protection Agency

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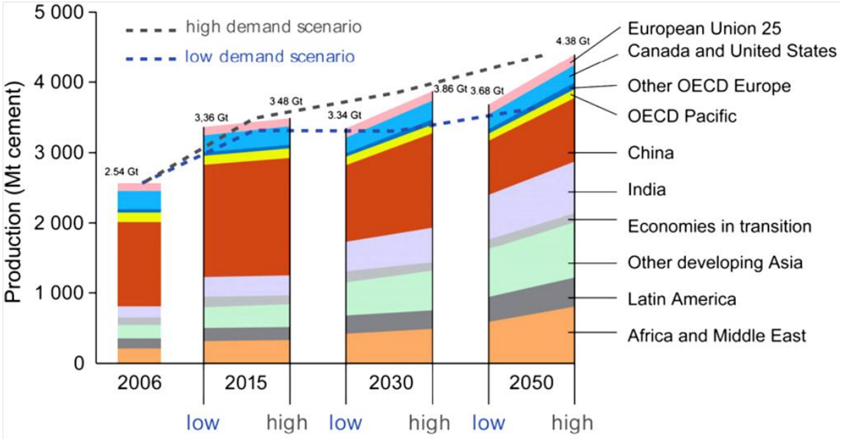
1. Introduction

The cement industry accounts for approximately 5 percent of current anthropogenic carbon dioxide (CO_2) emissions worldwide (WBCSD/IEA 2009a). World cement demand and production are increasing; annual world cement production is expected to grow from approximately 2,540 million tonnes (Mt) in 2006 to between 3,680 Mt (low estimate) and 4,380 Mt (high estimate) in 2050. The largest share of this growth will take place in China, India, and other developing countries on the Asian continent (Figure 1) (WBCSD/IEA 2009b). This significant increase in cement production is associated with a significant increase in the cement industry's absolute energy use and CO_2 emissions.



Note: OECD is an acronym for the Organization for Economic Co-operation and Development

Figure 1. Annual world cement production (WBCSD/IEA 2009b)

Studies have documented the potential to save energy by implementing commercially-available energy-efficiency technologies and measures in the cement industry worldwide (Worrell et al. 2000; Hasanbeigi et al. 2010; IEA 2007; UNIDO 2010). However, today, given the projected continuing increase in absolute cement production, future reductions (e.g., by 2030 or 2050) in absolute energy use and CO_2 emissions will require further innovation in this industry. Innovations will likely include development of different processes and materials for cement production or technologies that can economically capture and store the industry's CO_2 emissions. The development of these emerging technologies and their deployment in the market will be a key factor in the cement industry's mid- and long-term climate change mitigation strategies.

Many studies from around the world have identified sector-specific (e.g., Worrell et al. 2008; APP 2009; CSI/ECRA 2009) and cross-cutting (e.g., U.S. DOE AMO 2011) energy-efficiency technologies for the cement industry that have already been commercialized. However, information is scarce and scattered regarding emerging or advanced energy-efficiency and low-carbon technologies for the cement industry that have not yet been commercialized. This report consolidates available information on emerging technologies for the cement industry with the goal of giving engineers, researchers, investors, cement companies, policy makers, and other interested parties easy access to a well-structured database of information on this topic.

This report also includes the concrete production sector because cement is the essential binding agent in concrete. Concrete is used worldwide as a building material and is the second-most-consumed substance on earth after water. Global concrete production is approximately 5.3 billion cubic meters per year (Roskos et al. 2011). Many emerging technologies focus on alternative materials and processes to reduce the carbon footprint of concrete.

The information presented in this report is collected from publically available sources. Although the report covers the main emerging energy-efficiency and low-carbon technologies for cement and concrete production, the list of emerging technologies addressed is not exhaustive.

The information about the 19 technologies covered in this report is presented using a standard structure for each technology. First, we briefly describe the technology, including background, theory, pros and cons, barriers and challenges, and case studies if available. Next, we present the energy, environmental, and other benefits of the technology as well as cost information if available. For most technologies, we include a block diagram or picture. Finally, we identify the commercialization status of each technology along with resources for further information. The commercialization status for each technology is as of the writing of this report and uses the following categories:

- Research stage: the technology has been studied, but no prototype has been developed
- Development stage: the technology is being studied in the laboratory, and a prototype has been developed
- Pilot stage: the technology is being tested at an industrial-scale pilot plant
- Demonstration stage: the technology is being demonstrated and tested at the industrial scale in more than one plant but has not yet been commercially proven
- Semi-commercial stage: the technology is proven and is being commercialized but has a very small market share

Table 1 lists the 19 technologies covered in the report.

The nature of emerging technologies is that many are proprietary and/or the primary source of information about them is the manufacturers who are developing them. In some cases, we mention the names of companies that are developing or providing a technology so that readers can obtain more information about the company and product. It should be noted that the purpose of this report is solely informational.

Table 1. Emerging energy-efficiency and CO_2 emissions-reduction technologies for cement and concrete production

No.	Section	Category/Technology Name	Commercialization status
	3.1.	**Emerging grinding technologies**	
1	3.1.1.	High activation grinding	Semi-commercial
	3.2.	**Emerging kiln technologies**	
2	3.2.1.	Fluidized bed kiln	Demonstration stage
	3.3.	**Emerging alternative raw material technologies**	
3	3.3.1.	Use of steel slag as kiln raw material - CemStar® Technology	Semi-commercial
4	3.3.2.	Non-carbonated raw material for cement production – use of carbide slag	Semi-commercial
5	3.3.3.	Cement with low lime saturation factor	Semi-commercial
6	3.3.4.	Calcareous oil shale as an alternative raw material	Pilot stage
	3.4.	**Emerging alternative cement products**	
7	3.4.1.	Cement primarily of fly ash and recycled materials	Semi-commercial
8	3.4.2.	Cement and construction materials based on magnesium oxide	Pilot stage
9	3.4.3.	Geopolymer cement	Demonstration stage
10	3.4.4.	Celitement: A hydraulic binder based on calcium hydrosilicates	Development stage
	3.5.	**Emerging carbon capture technologies for the cement industry**	
11	3.5.1.	Oxygen enrichment technology	Oxy-fuel technology: Pilot stage Oxygen enrichment: Commercial
12	3.5.2.	Post-combustion carbon capture using absorption technologies	Pilot stage
13	3.5.3.	Calera process	Pilot stage
14	3.5.4.	CO_2 sequestration in concrete curing technology	Development stage
15	3.5.5.	Carbonate looping technology	Development stage
16	3.5.6.	Industrial recycling of CO_2 from cement process into high-energy algal biomass	Demonstration stage
17	3.5.7.	Bio-technological carbon capture	Prototype stage
18	3.5.8.	Capturing the CO_2 resulting from limestone precalcination	Research stage
19	**3.6.**	**Use of nanotechnology in cement and concrete production**	Research stage

Because the nature of emerging technologies is a constant and rapid change, the information presented in this report is also subject to change. If readers are aware of a new technology that is not presented in this report or have updated information about a technology that is described in this report, please contact the authors of the report.[1]

2. Description of Cement and Concrete Production

Portland cement was invented in Britain during the late 19th century and named for its resemblance to stone from the Isle of Portland off the British coast. It is the most commonly used type of cement worldwide (PCA 2012) and is the fundamental constituent of concrete. The original Portland cement was made by heating a combination of finely ground limestone and clay

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[1] Ali Hasanbeigi: ahasanbeigi@lbl.gov; Lynn Price: lkprice@lbl.gov

that hardened when combined with water. Cements that harden when combined with water are known as hydraulic cements (PCA 2012).

The general process by which cement is manufactured today entails quarrying and crushing or grinding of the raw materials – commonly limestone, chalk, and clay – which are then combined and passed through a kiln in the form of either a dry powder or a wet slurry. Kiln temperatures range from 1,450°C. The heat fuses the raw materials into small pellets known as clinker. The cooled clinker is combined with gypsum and ground into the fine powder known as Portland cement. The American Society for Testing and Materials (ASTM) defines several types of Portland cement with different properties as well as several blended hydraulic cements that are made by combining materials such as Portland cement, fly ash, natural pozzolana (a siliceous volcanic ash), and blast furnace slag (PCA 2012). The subsections below describe the process by which cement is produced in more detail, with a focus on the energy and CO_2 emissions impacts of cement production processes.

2.1. Cement Production Processes and Energy Use

Mining and Quarrying

As noted above, the most common raw materials used in cement production are limestone, chalk, and clay, with limestone or chalk forming the majority of the ingredients in cement. These materials are usually extracted from a quarry adjacent or very close to the cement plant. Limestone provides calcium oxide and some of the other oxides, and clay, shale, and other materials provide most of the silicon, aluminum, and iron oxides required for the manufacture of cement. Approximately 5 percent of CO_2 emissions from cement production are associated with quarry mining and transportation (WWF 2008).

Raw Material Grinding and Preparation

Grinding raw materials for cement is an electricity-intensive step generally requiring about 25 to 35 kilowatt-hours (kWh)/t (t) raw material. Grinding differs according to the type of process used in clinker production. In dry processing, the raw materials are ground into a flowable powder in horizontal ball mills, vertical roller mills, or roller presses. Materials might be dried using waste heat from the kiln exhaust or clinker cooler hood, or auxiliary heat from a stand-alone air heater. The moisture content in the dry feed is typically around 0.5 percent but can range from 0 to 0.7 percent. When raw materials are very moist, as is the case in some countries and regions, wet processing may be preferable. In the wet process, raw materials are ground in a ball or tube mill with the addition of water to produce a slurry whose water content ranges from 24 to 48 percent but is typically 36 percent (Worrell and Galitsky 2004).

Clinker Production

Clinker production is the most energy-intensive stage in cement production, accounting for more than 90 percent of total cement industry energy use and virtually all of the fuel use. Kiln systems evaporate the inherent water in the raw meal, calcine the carbonate constituents (calcination),[2] and form cement minerals (clinkerization). The main type of high-heat or pyroprocessing kiln used today is the dry rotary kiln. A dry rotary kiln uses feed material with low moisture content (0.5 percent). The first dry kiln process was developed in the U.S. and did not involve preheating.

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[2] Calcination is the process of heating a substance to a high temperature that is below the substance's melting for fusing point, to change the substance's physical or chemical constitution.

Later developments added multi-stage suspension preheaters (cyclones) or shaft preheaters. More recently, precalciner technology was developed in which a second combustion chamber is added between the kiln and a conventional pre-heater that allows for further reduction of kiln fuel requirements. The typical fuel consumption of a dry kiln with four, five, or six-stage preheating can vary between 2.9 and 3.5 gigajoules (GJ)/t clinker, and almost all the process-related CO_2 emissions from cement production are associated with calcination during clinker production. Once the clinker is formed in the rotary kiln, it is cooled rapidly to minimize the formation of glass and ensure the maximum yield of alite (tricalcium silicate), an important component for the hardening properties of cement. The main cooling technologies are the grate cooler or the tube or planetary cooler. In the grate cooler, which is most common today, the clinker is transported over a reciprocating grate through which air flows perpendicular to the clinker flow (Worrell and Galitsky 2004).

Finish Grinding

To produce powdered cement, the nodules of clinker are finely ground in ball mills, ball mills combined with roller presses, roller mills, or roller presses. At this stage, 3 to 5 percent gypsum is added to control the setting properties of the cement. The amount of electricity used for raw meal and finish grinding depends strongly on the hardness of the materials (limestone, clinker, pozzolana, etc.) and the desired fineness of the cement as well as the amount of additive. Blast furnace slag is harder to grind and thus requires more grinding power. Traditionally, ball mills are used in finish grinding, but many plants use vertical roller mills too. Modern state-of-the-art approaches utilize a high-pressure roller mill or horizontal roller mill (e.g., Horomill®). Finished cement is stored in silos; tested; and bagged or shipped in bulk on bulk cement trucks, railcars, barges, or ships (Worrell and Galitsky 2004). Figure 2 shows the steps of the cement production process using the new suspension preheater and precalciner (NSP) kiln.[3]

2.2. CO_2 Impact of Cement Production

The production of 1 metric ton (t) of cement releases an estimated 0.73 to 0.99 t CO_2/t cement depending on the clinker-per-cement ratio and other factors. A major difference between the cement industry and most other industries is that fuel consumption is not the dominant driver of CO_2 emissions from cement production. As noted above, more than 50 percent of the CO_2 released during cement manufacture, or approximately 540 kg CO2 per t of clinker (WBCSD 2009), is from calcination in which limestone ($CaCO_3$) is transformed into lime (CaO) in the following reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

The rest of the CO_2 emitted during cement manufacture is the result of burning fuel to provide the thermal energy necessary for calcination to occur. Kilns in which calcination takes place are heated to around 1,450°C. Typically, energy accounts for 30 to 50 percent of cement production costs. Also, an average 100 to 110 kWh of electricity is consumed per t of cement. The share of CO_2 emissions from electricity use is, on average, 5 percent of the total CO_2 emissions in the cement industry. Depending on the energy source and the efficiency at which it is used in the local electricity mix, this figure can vary from less than 1 percent to more than 10 percent. As

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[3] This description of the cement production process is partially excerpted from Worrell and Galitsky (2004).

noted above, some 5 percent of CO_2 emissions are associated with quarry mining and transportation (WWF 2008).

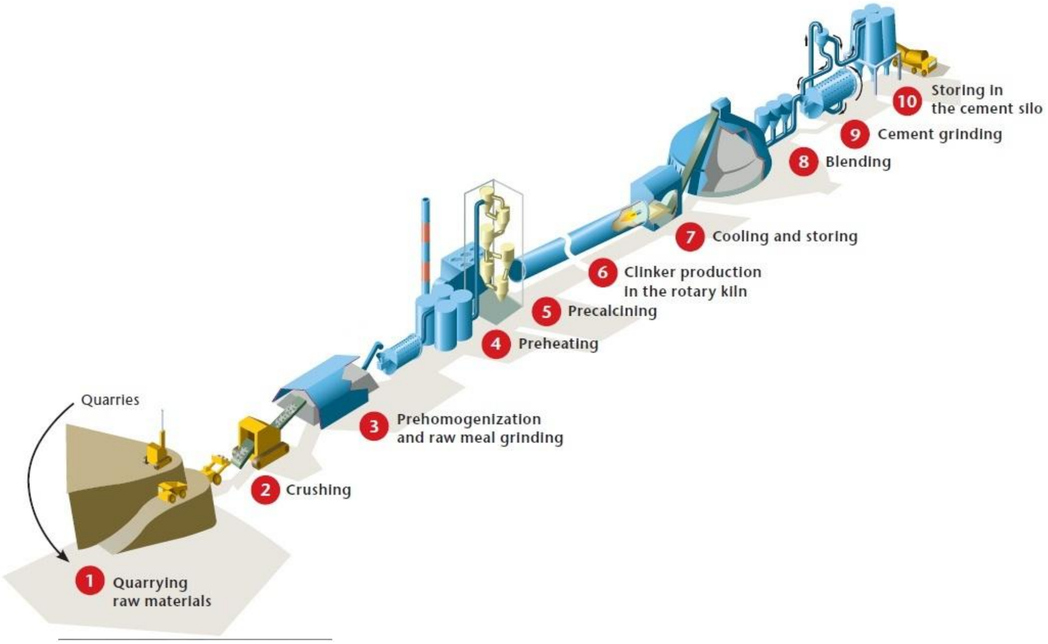

Figure 2. Steps in the cement production process using the new suspension preheater and precalciner kiln (WBCSD/IEA 2009a)

2.3. Concrete Production Process

Concrete is a mixture of paste and aggregates in a simple form. The paste, composed of Portland cement and water, coats the surface of the fine and coarse aggregates. Through a chemical reaction called hydration, the paste hardens and gains strength to form the rock-like mass known as concrete (PCA 2012). Typically, a mix is about 10 to 15 percent cement, 60 to 75 percent aggregate and 15 to 20 percent water. Entrained air in many concrete mixes may also take up another 5 to 8 percent. Figure 3 below shows the example of the share of each competent in concrete production.

Figure 3. The share of each component in concrete production
Source: PCA 2012

Concrete is produced in four basic forms, which are ready-mixed concrete, precast concrete, concrete masonry, and the cement-based materials represent products that defy the label of "concrete," yet share many of its qualities. Each of these products has unique applications and properties. In all cases, the production of cement used in concrete production accounts for the largest share of energy and carbon footprint of the concrete produced.

3. Emerging Energy-efficiency and CO_2 Emission-reduction Technologies

The subsections below describe emerging technologies to reduce energy consumption and CO_2 emissions in the different steps of the cement production process, as well as emerging alternative raw materials and products for cement and concrete production.

3.1. Emerging Grinding Technologies

High-activation grinding is the main emerging grinding technology described below; other emerging technologies are mentioned briefly.

3.1.1. High-Activation Grinding

Description:
One strategy for conserving materials and reducing energy use in cement production is to increase the amount of elements other than Portland cement in blended cement products. However, increased use of other elements can result in a final product that is slow to develop compressive strength. One solution that has been researched to improve compressive strength development is using high-energy milling to mechanically increase the reactivity of some of the blended constituents, i.e., fly ash and slag (Kumar et al. 2006). Mechanical activation or enhanced reactivity of fly ash or blast furnace slag in cement results from the combined effects of increased surface area and physiochemical changes produced by vibratory or attrition milling (Kumar et al. 2007).

Kumar et al. (2007, 2008) studied mechanically-induced reactivity of blast furnace slag and fly ash. They found that up to 65 percent of the clinker in blended cement could be replaced with milled fly ash. The strength of the resulting product was comparable to that of commercial cement containing only 20 to 25 percent fly ash. The increased reactivity and reduced water requirements of attrition- and vibratory milled fly ash are attributed to the fact that, with these milling techniques, the small (<1 micrometer [µm]) cenospheres of the fly ash retain their original shape. In contrast, grinding fly ash in a ball mill destroys most of the cenospheres. Because the cenospheres remain intact in mechanically-activated fly ash, the resulting hydrated cement demonstrates lower porosity and improved strength compared to a product made with ball-milled fly ash. Kumar et al. (2008) also studied the use of mechanically activated granulated blast furnace slag (GBFS) used in place of 50 to 95 percent of the clinker in Portland slag cement. Test results showed that Portland slag cement containing 80 to 85 percent mechanically activated GBFS was much stronger than typical commercial Portland slag cement, which contains 35 percent slag. Both 1-day and 28-day strength were found to increase (Kumar et al. 2008).

The EMC Cement Company produces energetically modified cement (EMC) and pozzolana using a commercialized technology based on mechanical activation concepts. EMC's plant began operating near Jewett, Texas in September, 2004 with an initial production capacity of about 150,000 t/year, which can be increased to meet demand. Waste fly ash from a power plant is conveyed directly to the EMC production facility (EMC Cement 2012).

Energy/Environment/Cost/Other Benefits:

- No waste material; the grinding process does not pollute air or water.

- Process is enclosed, with required dust protection features.
- Energy consumption is 30 to 50 kWh/t product.
- Twelve workers can operate a plant producing approximately 150,000 tons per year (EMC Cement 2011).
- For every t of clinker replaced by additives from mechanical activation grinding, the avoided energy uses are approximately:
    - ✓ thermal energy: 3.0 to 6.5 GJ/t clinker
    - ✓ electricity: 60 to 100 kWh/t clinker (European Commission 2010)
- The electricity used for mechanical activation ranges from 30-50 kWh/t product (EMC Cement 2012) and should be deducted from aforementioned savings.
- Other avoided emissions (from clinker production and kiln fuel use) include sulfur dioxide (SO_2) and nitrogen oxides (NOx).

Block Diagram or Photo:

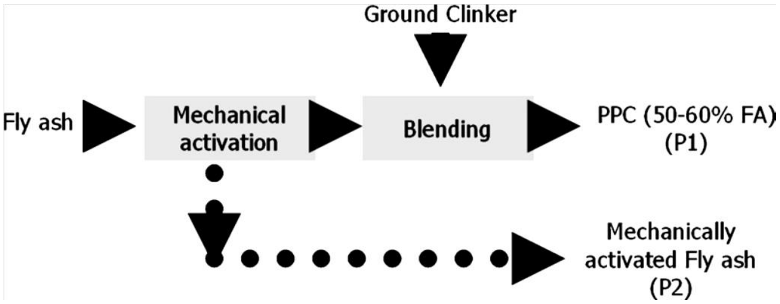

Figure 3. Schematic of possible process for producing Portland pozzolanic cement containing a high volume (50 - 60%) of fly ash (Product P1) and mechanically activated fly ash (Product P2) (Kumar et al. 2007)

Commercial Status*:*
Semi-commercial

References for Further Information:
Kumar et al. (2006, 2007, 2008); EMC Cement (2011); Schneider et al. (2011); Schneider (2008)

Other Emerging Grinding Technologies:
Ultrasonic comminution efficiently transfers to the raw material the energy needed for crushing, by means of acoustic ultrasonic pulses that are generated by two counter-rotating disks with special aerodynamic surfaces. The small-pulse durations exert pressure waves that pulverize the particles. Ultrasonic comminution was introduced in 2003 and has only been tested at a model scale for slag grinding. There are currently proposals for additional research, and scaling up to industrial dimensions is under consideration. Plasma comminution is another emerging grinding technology. It is performed in a liquid and uses shock waves. It has been tested on semiconductor materials (Schneider et al. 2011; Schneider 2008).

3.2. Emerging Kiln Technologies

3.2.1. Fluidized Bed Kiln

Description:

A fluidized bed kiln (FBK) burns raw materials into powder with granules 1.5 to 2.5 millimeters (mm) in diameter. FBK uses a new technology known as granulation control/hot self-granulation (NEDO 2008), which agglutinates part of the raw material powder to form a core and attaches other raw material powder around the core. A FBK replaces the traditional rotary kiln with a stationary vertical cylindrical vessel (reactor) where the raw materials are calcined in a fluidized bed. An overflow at the top of the reactor regulates the transfer of clinker to the cooling zone. FBKs have improved heat recovery rates compared to conventional rotary kilns (burn to 1,400°C and cool to 100°C in a two-stage cooler) (European Commission 2010).

The advantages of a FBK are anticipated to be lower capital costs, lower operating temperatures, fewer NO_x emissions, lower overall energy use, and ability to accept a wide variety of fuels. However, it is difficult to scale up the current FBK demonstrations to the required 5,000 to 6,000 t/day (tpd) clinker capacity (Worrell and Galitsky 2004). Early FBK technologies were not commercially successful because of high clinker recycling rates. Today, FBK development is in progress in Japan and the U.S. A FBK with a clinker capacity of more than 1,000 tpd was being erected in China in 2009 but it is not clear whether or not it is in operation now (CSI/ECRA 2009).

Based on a feasibility study of a plant with a clinker capacity of 3,000 tpd as well the actual operation history (from 1986 to1995 by Sumitomo Osaka Cement Co. Ltd, Japan) of a 200-tpd clinker capacity plant, FBKs could achieve the following compared to a conventional rotary kiln: 1) reduction of heat use and CO_2 levels by 10 to 12 percent, 2) a NO_x emission level of 380 milligrams (mg)/Normal cubic meter (Nm^3) or less, 3) maintenance of current SO_x emissions levels, and 4) reduction of construction cost and installation area by 30 percent (European Commission 2010).

Energy/Environment/Cost/Other Benefits:

- FBK energy use is expected to be 10 to 15 percent lower than that of conventional rotary kilns.
- NO_x emissions are reduced to 0.77 kg/t clinker, compared to 2.1 to 2.6 kg/t clinker for conventional kilns, because of lower combustion temperatures in the FBK (Worrell and Galitsky 2004).
- Future FBK fuel consumption is estimated at 2.66 to 3.1 GJ/t clinker. This might be less than that of conventional rotary kilns but not of modern precalciner rotary kilns, which have demonstrated fuel use of 2.7 to 2.8 GJ/t clinker (Worrell and Galitsky 2004). CSI/ECRA (2009) reports that the FBK reduces thermal energy use by up to 300 megajoules (MJ)/t clinker but increases the electricity used by approximately 9 kWh/t clinker (CSI/ECRA 2009).
- FBKs might produce clinker with lower alkali content than is found in clinker from conventional rotary kilns.

- An FBK needs less space and has greater flexibility with respect to raw material feed than conventional rotary kilns do (Worrell and Galitsky 2004).

Block Diagram or Photo:

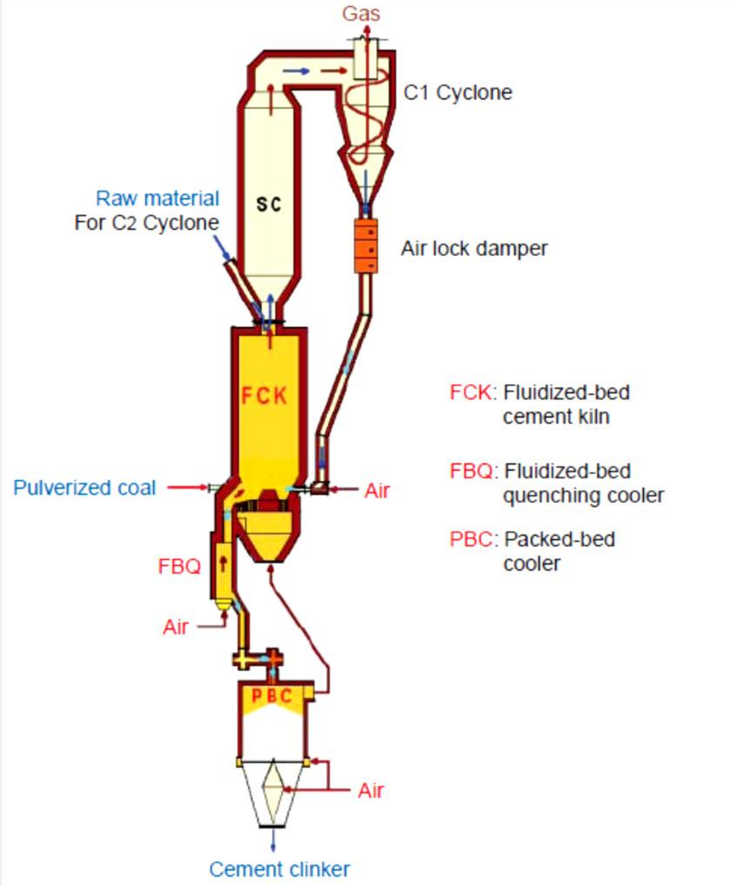

Figure 4. Block diagram of fluidized-bed cement firing kiln system (NEDO 2008)

Commercial Status*:*

Demonstration stage

References for Further Information:

Worrell and Galitsky (2004); NEDO (2008); CSI/ECRA (2009)

3.3. Emerging Technologies for Alternative Raw Materials

One strategy for reducing the energy consumed in and/or CO_2 emissions from cement production is to use alternatives to traditional raw materials. Alternative raw materials and/or industrial byproducts may include steel slag, carbide slag, and calcareous oil shale. Emerging technologies enable the use of these alternative raw materials as well as production of cement with a reduced lime saturation factor.

3.3.1. Use of Steel Slag as Raw Material for the Kiln - CemStar® Technology

Description:

For steel manufacturing, calcium oxide or lime (CaO) is added to molten steel at 1,650° C to remove impurities such as silica, magnesium, aluminum, and other oxides. These impurities float to the top and are poured away as slag (Perkins 2000). The CemStar® process was first developed in 1994 by Texas Industries (Midlothian, Texas). This process uses electric arc furnace slag as input to the cement kiln in place of limestone (Worrell et al. 2008). During the kiln pyroprocess, ¾-inch- to 1-inch-diameter slag is added to the feed end of the kiln as a component of the raw material mix. Because of its lower melting point (1,260° C to 1,316° C), the slag does not require additional fuel in the kiln to form clinker with other raw feed components. Moreover, mineralizers already present in the slag help catalyze clinker formation. In addition, the exothermic reaction of converting dicalcium silicate into tricalcium silicate, which happens when slag is exposed to the high temperature, releases supplementary heat into kiln, resulting in even higher efficiency of the cement manufacturing process (Perkins 2000).

The CemStar® process eliminates the need to grind the slag because it allows the addition of 2-centimeter (cm) slag lumps directly to the kiln (using large lumps has traditionally led to poor clinker formation). Depending on the location of the slag injection the CemStar® process might also save heating energy (calcination energy is estimated to be 1.9 GJ/t clinker). Because there is already calcined lime in the slag, the CemStar® process results in reduced CO_2 emissions from calcination. The lower combustion energy conditions and flame temperatures also lead to a decrease in NO_x emissions (Worrell et al. 2008).

Traditional clinker production expansion methods are typically very costly and time consuming, requiring significant resources and disrupting continuous facility operations. CemStar® offers significant production and operational advantages including improved production rates of clinker, minimal capital investment requirements, no additional fuel consumption, and stable kiln operations. CemStar® technologies can be installed with minimal disruption in continuous kiln operation (Perkins 2000). For example, Texas Industries has licensed its patented CemStar cement production process to Rio Grande Portland Cement Company in Mexico (TXI 1998).

Energy/Environment/Cost/Other Benefits:

- CemStar® technology increases clinker production by up to 15 percent compared to the conventional process.

- CemStar® technology allows replacement of 10 to 15 percent of clinker by electric arc furnace slag.
- Using 10 percent slag would reduce energy consumption by 0.19 GJ/tonne, CO_2 emissions by roughly 11 percent, and NO_x emissions by 9 to 60 percent, depending on kiln type and plant specific conditions (Worrell et al. 2008; Perkins 2000).
- Equipment costs are mainly for handling materials and vary from $200,000 to $500,000 per installation. Total investments are approximately double the equipment costs. CemStar® charges a royalty fee.
- Cost savings result from increased income from additional clinker produced without increased operation and energy costs.
- Cost savings also come from reduced iron ore purchases because the slag helps to meet iron needs in the clinker.
- In 1999, the U.S. Environmental Protection Agency (U.S. EPA) awarded special recognition to the CemStar® process in the U.S. as part of the ClimateWise program (Worrell et al. 2008).

Block Diagram or Photo:
Not Available

Commercial Status*:*
Semi-commercial

References for Further Information:
Worrell et al. (2008); Perkins (2000)

3.3.2. Non-carbonated Raw Material for Cement Production – Use of Carbide Slag

Description:

Carbide slag, also known as calcium carbide residue (CCR), is an unavoidable solid-waste byproduct of the industrial production of ethyne, polyvinyl chloride, polythene alcohol, and other products. A large amount of carbide slag from industrial production causes serious pollution in the surrounding environment, especially in water. Because there are no other appropriate disposal methods, carbide slag is currently disposed of in landfills.

In conventional cement production, limestone is decarbonated in the pyroprocessing stage (main reaction: $CaCO_3 \rightarrow CaO + CO_2$) to produce CaO (the main content of clinker) and CO_2; this accounts for more than half of the CO_2 emissions during clinker production. To decrease the CO_2 emissions, CCR can be used to partially replace limestone as a raw material. Calcium hydroxide [$Ca(OH)_2$], the main content of CCR, produces CaO and water (H_2O) during pyroprocessing (e.g., in a cement kiln) without CO_2 emissions (main reaction: $Ca(OH)_2 \rightarrow CaO + H_2O$). Thus, using CCR will substantially reduce CO_2 emissions from cement production (UNFCCC 2008a).

Using CCR in cement kilns entails the following steps:

1) CCR dehydration and transportation
2) Grinding and storage
3) Raw material homogenization
4) Clinker burning
5) De-dusting (UNFCCC 2009)

In the first stage, wet CCR is dehydrated, reducing its moisture from 90 percent to the value required according to the moisture content of the other raw materials and kiln type. For the NSP rotary kiln, moisture is reduced to approximately 12 to 14 percent (UNFCCC 2009). For the semi-dry kiln, moisture is reduced to only 65 percent (UNFCCC 2008b). Because the semi-dry kiln is an older technology that is not promoted anymore, we focus on the use of CCR in NSP rotary kilns. For the NSP rotary kiln, wet CCR is dehydrated by pressure filtration and a spin dryer and transported to the grinding system by a belt conveyor. After grinding, which can be done in a vertical roller mill, the raw material in the CCR is homogenized before being fed to the NSP kiln. A large-scale electric de-duster should be installed on precalcination and cooling systems. (UNFCCC 2009).

Energy/Environment/Cost/Other Benefits:

- The type and quality of the clinker produced by CCR are unchanged compared to clinker produced by traditional methods.
- Using CCR will avoid significant CO_2 emissions. In a cement plant in Sichuan Province, China, CCR was used to produce 600,000 tons of clinker per year. The resulting annual CO_2 emissions reduction was reported to be equal to 224,540 tCO_2 resulting in CO_2 reduction of 374 kg CO_2/t clinker.
- When CCR is used instead of limestone, fuel consumption can be reduced because some chemical reactions that would take place if limestone was used will not take place if CCR is used.

- The capital cost to implement this technology in two NSP kiln cement plants in China is reported to be between US$2.9 and US$4.3 Million (1 US$= 6.83 Chinese yuan).
- Use of CCR in the cement industry mitigates the risk of pollution to environments, especially water resources and surrounding landfills (UNFCCC 2008a, 2009).

Block Diagram or Photo:

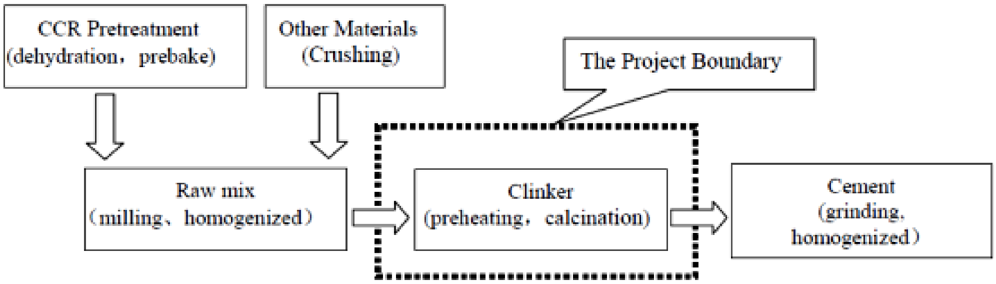

Figure 5. Flow chart of cement production process using CCR (UNFCCC 2009)

Commercial Status:
Semi-Commercial

References for Further Information:
UNFCCC (2008a, 2008b, 2009)

3.3.3. Cement with Low Lime Saturation Factor

Description:

The lime saturation factor (LSF) in ordinary Portland cement clinker typically ranges between 90 and 102, with average LSFs of up to 97. Higher LSFs are preferred for fast-setting ordinary Portland cements with high compressive strength. Producing Portland cement with very high LSFs (above 100) has several negative consequences. One is increased CO_2 emissions from calcination of greater amounts of $CaCO_3$ in the raw meal, which requires higher burning temperatures. The higher temperatures also mean the clinker granules have denser micro-structure and are therefore more difficult to grind. With regard to resource use, larger volumes of pure limestone are required to achieve higher LSFs. Finally, LSFs higher than 102 will result in large amounts of free lime, which does not contribute to development of compressive strength and can affect the soundness of the final product.

Portland cement with a lower LSF entails fewer CO_2 emissions from calcination because there is less limestone in the raw meal. Better combustibility of the raw meal means lower burning temperatures, which saves energy. Kiln capacity can also be slightly increased. Additionally, lower LSFs can mean reducing the amounts of valuable pure limestone in the raw meal. A main disadvantage of Portland cement with a low LSF is the reduced alite content and lower compressive strength compared to Portland cement of equal fineness but with a higher LSF. Though compressive strength can be increased to a limited degree by grinding the cement more finely, it is difficult to estimate the electric energy required for the additional grinding. Although less dense clinker with low LSF burned at relatively low temperatures might be easily grindable, additional energy is required to achieve a higher fineness, which is necessary to achieve compressive strength equal that of Portland cement with a higher LSF; the finer the required texture, the more energy required for grinding (CSI/ECRA 2009).

Because a reduction in LSF automatically results in an increased belite content, cement with lower LSFs is sometimes called “belite cement.” Belite cements are produced at the industrial scale and have reasonably good properties (early strength, compressive strength, etc.). Belite cement can be composed of limestone, burnt clay, volcanic ash, pyrite ash, and gypsum. Reactive forms of belite can be stabilized by rapid cooling, hydraulic activity, and strategies to improve physical-mechanical properties, resulting in a low-energy cement. Mechanical activation of belite has shown promising results to improve the hydration properties of the cement, but the long required grinding time is a disadvantage.

Campillo et al. (2007) analyzed the potential of nanomaterials to improve the initial compressive strength of belite cements. Different nanoparticles were added to belite cement, and the resulting microstructure modifications and mechanical properties were studied. Results indicated that the addition of nanoparticles could improve the initial compressive strength of belite cement so that it was competitive with Portland cement (Campillo et al. 2007). Other approaches to improve the mechanical strength of belite cements include use of hydrothermal techniques to produce material with a very high specific area (Kacimi 2009).

Energy/Environment/Cost/Other Benefits:

- CO_2 emissions from calcination are reduced in low-LSF cements because of the lower limestone content in the raw meal compared to the raw meal for cements with higher LSF.
- Energy consumption:
  - Thermal energy consumption decreases by 100 MJ/t clinker for an assumed decrease in LSF of 10 (with no production increase assumed).
  - Electric energy increases by 10 to 20 kWh/t cement for an assumed decrease in LSF of 10 (CSI/ECRA 2009).
- CO_2 emissions:
  - Indirect CO_2 emissions increase because of increased electricity use.
  - Direct CO_2 emissions decrease because of reduced fuel use and reduced emissions from calcination.
- Other raw materials used in place of limestone are usually inexpensive and may be waste products.
- For longer hardening periods (~90 days), compressive strength of belite cements is greater than that of ordinary Portland cement.
- Early hydration of belite cements is slower than that of ordinary Portland cement. Blending belite cements with ordinary Portland cement to accelerate the initial rate of hydration may produce composite cement suitable for use for many purposes (Popescu et al. 2003; Kacimi et al. 2009).

Block Diagram or Photo:

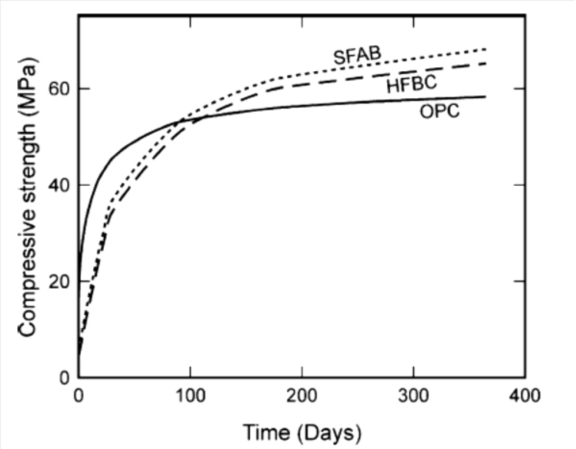

Figure 6. Development of compressive strength of ordinary Portland cement, high ferro-belite clinker, and sulphoferroaluminate-belite clinker cements (Popescu et al. 2003)

Commercial Status:

Semi-commercial

References for Further Information:

CSI/ECRA (2009); Popescu et al. (2003); Kacimi et al. (2009); (Campillo et al. 2007)

3.3.4. Calcareous Oil Shale as an Alternative Raw Material

Description:

Calcareous oil shale can be used as an alternative feedstock and partial fuel substitute in clinker production. If oil shale is burned separately, the resulting ash can be used as an additive in finish grinding. Partially decarbonated oil shale can also be used to reduce CO_2 emissions from the calcination process. Oil shale may have caloric value that will contribute to the energy requirements in the precalciner and/or the kiln. To be used as a feedstock, oil shale must be ground to <90 µm (Hilger 2003). Oil shale can reportedly be used for 8 to 10 percent of the raw meal in the kiln. Oil shale has already been used in some cement plants in Germany and Russia (U.S. EPA 2010; ECRA 2007).

Energy/Environment/Cost/Other Benefits:

- Energy use could be reduced by 74 MJ/t cement if oil shale is used to make up 8 percent of the raw meal in cement production.
- Assuming that oil shale replaces 8 percent of the raw meal, an investment of $1/t cement would be required to install a feed system. Operating costs would increase by $0.08/t cement assuming the shale source is close to the cement manufacturing facility.
- The reduction in CO_2 emissions from using oil shale is directly related to the amount of limestone feedstock replaced by the shale and the caloric value of the shale (U.S. EPA 2010).

Block Diagram or Photo:

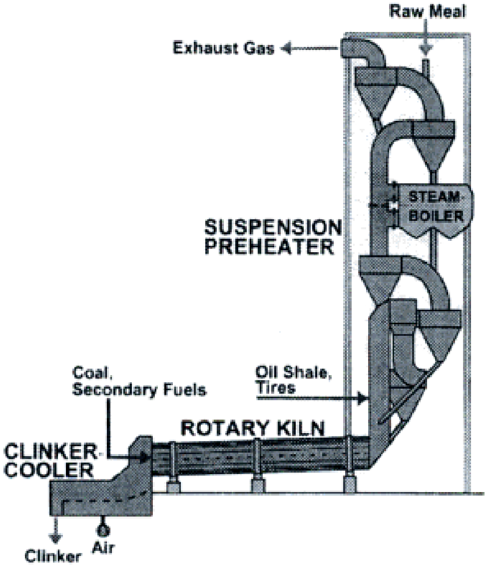

Figure 7. NSP rotary kiln using oil shale (Hilger 2003)

Commercial Status:

Pilot stage

References for Further Information:

Hilger (2003); U.S. EPA (2010); ECRA (2007)

3.4. Emerging Alternative Cement Products

The subsections below describe emerging products based on fly ash, recycled materials, magnesium oxide, and geopolymer that can be employed as alternatives to traditional Portland cement.

3.4.1. Cement/Concrete Based on Fly Ash and Recycled Materials

Description:

Using alternative binders in place of Portland cement in concrete reduces the energy consumption and greenhouse gas impacts associated with concrete production. Using an alternative concrete made with fly ash as the binder and pulverized glass as the aggregate further reduces the environmental impacts of concrete production.

Fly ash is a byproduct of coal burning that can have cementitious characteristics similar to those of Portland cement. The binding properties of fly ash depend on the type of coal burned and nature of the combustion process that produces the ash. Fly ash usually replaces no more than 25 percent of the Portland cement in concrete. Better understanding of the binding capacities of different types of fly ash might reveal additional possibilities. If the use of fly ash in concrete could be increased, the greenhouse gas footprint of concrete could be reduced. Increasing the amount of fly ash used in concrete would put to practical use large amounts of unused fly ash (39 million tons of fly ash is unused each year in the U.S. according to data from 2004). Ongoing research is focused on developing high-volume-fly-ash concretes. However, these products still use a significant amount of Portland cement.

Concrete has also been made using fly ash as the binder and pulverized glass as the aggregate. Aggregate typically accounts for 70 to 85 percent, by weight, of the material used in concrete. Mining of natural aggregates for the large volumes of concrete produced globally significantly disrupts virgin land. In place of natural aggregates, pulverized post-consumer glass can be used in concrete. Post-consumer glass is readily available in the U.S. which generated 13.2 million tons of glass in 2006, of which only 22 percent was reused (Roskos et al. 2011).

In 2008, Montana State University/Western Transportation Institute performed research using 100-percent fly ash concrete with glass aggregate. This fly-ash-and-glass concrete was used successfully to construct both structural and nonstructural elements of a building. However, further research is required on this new material’s fundamental engineering properties (Cross et al. 2005). The study identified 96 plants throughout the U.S. as potential sources of ash that could be used as the sole binder for concrete (Roskos et al. 2011).

Using fly ash as the binder and recycled materials as aggregate has a double benefit: it reduces the need to dispose of waste fly ash in landfills as well as the demand for mined aggregate and thus the impacts of mining.

Several existing companies produce cement or precast concrete and other building materials from recycled industrial wastes. One company is RecoCement, which has developed a technology to produce cement made entirely from recycled materials, primarily fly ash. RecoCement products have been tested and produced in small batches by an independent laboratory; the products show satisfactory compressive strength. The company is considering leasing land near the Port of Milwaukee WI, USA to build a $7-million manufacturing plant for this material (RecoCement 2011).

CERATECH is another company that produces cement from fly ash. The company states that its product is successfully used by the U.S. Department of Defense, industrial facilities, state departments of transportation, port authorities, airports, and others (CERATECH 2012). CalStar Products, Inc. also has an innovative technology that uses recycled fly ash as a primary component in architectural facing bricks and durable pavers (CalStar Products 2012).

Energy/Environment/Cost/Other Benefits:

- Recycling fly ash to produce concrete avoids the need for landfill disposal of this industrial byproduct.
- Use of fly ash reduces or eliminates the need to mine virgin raw materials for Portland cement production and provides a constructive use for waste fly ash.
- Increasing use of fly ash will significantly reduce the energy use needed for cement and concrete production.
- Increasing use of fly ash can significantly reduce the greenhouse gas footprint of concrete production by eliminating CO_2 emissions from energy use and calcination in cement production.
- Using recycled materials as aggregate in concrete diverts these materials from landfills and reduces the need for mined aggregate. Pulverized post-consumer glass is a recycled material that can be used as concrete aggregate.

Block Diagram or Photo:
Not Available

Commercial Status*:*
Semi-commercial

References for Further Information:
Roskos et al. (2011); Cross et al. (2005); RecoCement (2011); CERATECH (2012)

3.4.2. Cement and Construction Materials based on Magnesium Oxide

Description:

Before Portland cement came into widespread use in the 20th century, magnesium oxide (MgO)- and magnesium chloride-based cements were popular. Today, magnesium-based cements are reported to have compressive strengths ranging from 9,000 to 45,000 pounds per square inch (psi) and tension strengths of more than 800 psi, which is many times stronger than conventional concrete. Combined with clays and cellulose, magnesium oxide forms cement that can breathe water vapors electromagnetically. Clay in magnesium oxide also balances and enhances moisture movement, allowing cement that is made with it to continuously expel moisture, which prevents rotting (Swanson n.d.).

Several entities are producing or have produced MgO-based cements and construction materials that have several environmental benefits. One is Novacem Company, which is developing a new cement production system based on MgO and special mineral additives that lock atmospheric CO_2 into its construction materials. The Novacem process uses magnesium silicates instead of limestone, which eliminates the CO_2 emissions that are normally associated with raw materials processing (calcination). Because the Novacem production system operates at a low temperature, it can take advantage of fuels that have low energy content or carbon intensity (e.g., biomass or municipal solid waste), which further reduces carbon emissions. Carbonates are added to modify the hydration of MgO, which allows the cement to develop compressive strength even when no CO_2 is present. The properties of this alternative cement product are currently being optimized; so far, its performance is acceptable for several applications (e.g., masonry products). Special carbonates that are required for manufacturing the product have a negative carbon footprint because they are produced by carbonating part of the manufactured MgO, and they use atmospheric/industrial CO_2 for this purpose. Novacem claims that the production process to make 1 t of Novacem cement absorbs up to 100 kilograms (kg) more CO_2 than it emits, making it a carbon-negative product. In addition, because all hydration reactions are reversible, Novacem products can be recycled and used to make new products. Novacem plans to open a pilot plant in 2012 with industry partners. The first entry of the product to the market is expected in 2014-2015 (Novacem 2012).

Argonne National Laboratory and others have licensed several firms to market magnesium-based cements under the name “Ceramicrete.” Ceramicrete has many applications ranging from treatment of hazardous waste to consumer products including construction and structural materials requiring high compressive strength, and sealants and coatings. Similar to the process of making cement, the process of forming Ceramicrete requires mixing MgO powder and soluble phosphate powder with water using commercially available equipment. Wet materials are pumped, gunned, or sprayed. The result is a nonporous material that has compressive strength greater than that of concrete. Ceramicrete expands slightly when it sets and so forms an excellent seal, in contrast to conventional cements, which contract (ANL 2003).

Eco-Cement, developed by TecEco, incorporates reactive magnesia and wastes, and can be used to create concretes that absorb CO_2 and water from the atmosphere. These concretes can be recycled back into Eco-Cement, which is either carbon neutral or negative (i.e., it sequesters carbon) if carbon is captured during its manufacturing. To make Eco-Cement, magnesite is heated in a kiln to approximately 600 to 750^{o}C. Grinding in the hot area of the kiln improves the efficiency of the product. The heating process produces reactive MgO powder that is then added to a predetermined but variable amount of hydraulic cement such as Portland cement; supplementary cementitious materials like fly ash can also be used. The final blended powder is Eco-Cement. When mixed with water and aggregates such as sand, gravel, and waste materials (e.g., ash, plastic, sawdust, slag), Eco-Cement is ready for pouring into concrete, pressing into blocks, or other uses. Because Eco-Cement is less alkaline than other hydraulic cements like Portland cement, reducing the incidence of delayed reactions that would reduce the strength of the concrete, it can include more waste (TecEco 2012).

Energy/Environment/Cost/Other Benefits:

- For every ton of ordinary Portland cement replaced by Novacem cement, about 0.75 ton of CO_2 could be captured and stored indefinitely (Novacem 2012). Carbon can also be captured during manufacture of Eco-Cement (TecEco 2012).
- Ceramicrete expands slightly when it sets and thus forms an excellent seal, in contrast to conventional cements, which contract.
- Specialty applications for Ceramicrete can take advantage of its low porosity, nonflammability, strength, and other physical properties.
- Ceramicrete makes beneficial use of common waste materials.
- No formation energy is required to manufacture Ceramicrete (ANL 2003).
- Eco-Cement is less alkaline than other hydraulic cements like Portland cement, so Eco-Cement can include more waste (TecEco 2012).

Block Diagram or Photo:

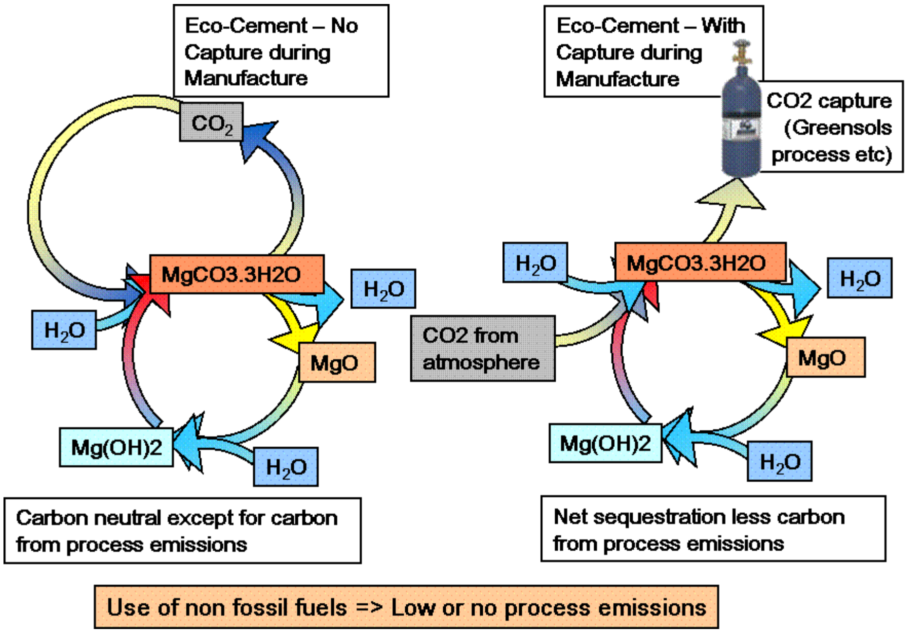

Figure 8. Eco-Cement CO_2 release and capture during manufacturing (TecEco 2012)

Commercial Status: Pilot stage

References for Further Information:

Novacem (2012); TecEco (2012); Swanson (n.d.); (ANL 2003)

3.4.3. Geopolymer Cement

Description:

Geopolymer materials fit in the category of current innovative technology for the construction industry. In contrast to Portland cement, geopolymers rely on minimally processed natural materials or industrial byproducts as binding agents. Potential energy and CO_2 savings from the use of geopolymers are significant. Geopolymer cements that are used as binders are composed of a reactive solid component and an alkaline activator. Reaction with the alkaline agent causes a three-dimensional, inorganic, alumosilicate polymer network to form, which contributes to the high compressive strength of the hardened product. Materials suitable for a geopolymeric polycondensation[4] are alumosilicates, which can be found in nature (metakaolin, natural pozzolana) or industrial wastes (fly ash, GBFS) (CSI/ECRA 2009). Geopolymers are manufactured at relatively low temperatures, with calcining of aluminosilicates occurring at 750°C. However, no energy consumption data are available for this process (APP 2009).

Until now, geopolymers have been produced only for demonstration purposes and used only for non-structural applications such as paving (CSI/ECRA 2009). Other probable applications of geopolymers are bridges, and structural retrofits using geopolymer-fiber composites. Geopolymer technology is most advanced in precast applications, which can relatively easily handle sensitive materials such as high-alkali activating solutions and because of the controlled high-temperature curing environment that many geopolymer systems require (U.S. DOT 2010).

Few techniques have been proposed for mass production of geopolymers. The first and only industrial production plant was built in Australia. It is important to note that properties of geopolymer cements depend heavily on the raw materials from which they are made, the chemical composition of the final product, and other features that can affect the properties of concrete such as compressive strength development and crack formation. Another limitation is that reactive components of geopolymers, i.e., fly ash and slag, are industrial waste products whose availability might be limited in some regions. In addition, the highly alkaline conditions under which geopolymers are produced raise an operational safety concern. Production quantities and costs for the alkaline activator (e.g., sodium silicate) are important considerations as well(CSI/ECRA 2009).

Pyrament®, a North-American geopolymer application with blended Portland-geopolymer cements, is used successfully for rapid pavement repair (U.S. DOT 2010). Blue World Crete Company produces a geopolymer that combines a proprietary binding agent with materials containing alumina silicate (Blue World Crete 2012). A link to a short list of geopolymer manufacturers is given below.

Energy/Environment/Cost/Other Benefits:

- Potential energy and CO_2 savings from the use of geopolymers are significant.

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[4] Any condensation reaction, of a monomer having two functional groups, which leads to the formation of a polymer.

- Expected CO_2 emissions for geopolymers are about 300 kg CO_2/t product. This estimate does not take into account emissions from production of the activators, such as sodium silicate, for which no data are available (CSI/ECRA 2009).
- Major geopolymer systems rely on minimally processed natural materials or industrial byproducts as binding agents.
- The use of industrial byproducts/wastes in the production of geopolymers creates a constructive use for these materials.

Block Diagram or Photo:

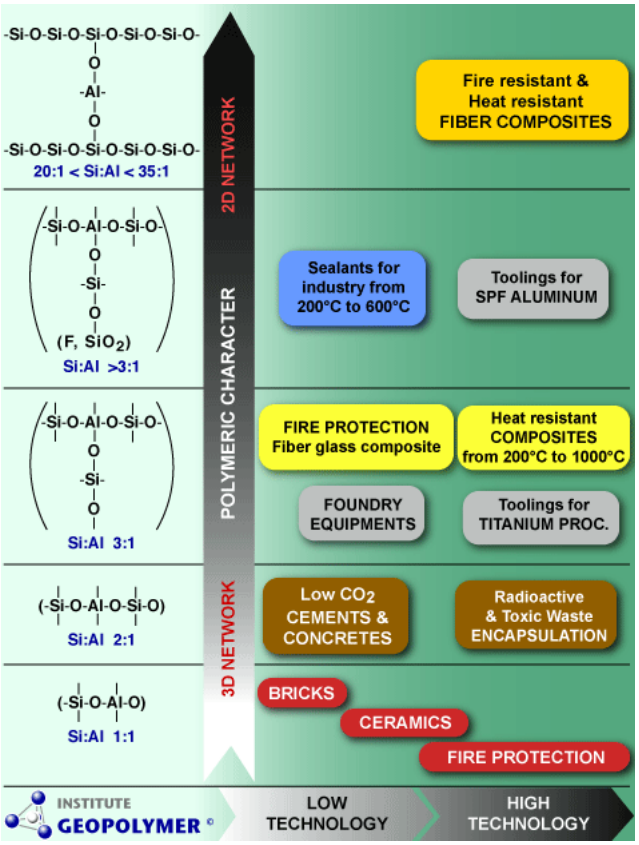

Figure 9. Chemical structure and applications of geopolymers (Geopolymer Institute 2012)

Commercial Status:
Demonstration stage

References for further information:
Geopolymer Institute (2012); CSI/ECRA (2009); Blue World Crete (2012)

A short list of companies that are manufacturing and selling geopolymers can be found at: http://www.geopolymer.org/about/business-fellows . This list is not exhaustive.

3.4.4. Celitement: A hydraulic binder based on calcium hydrosilicates

Description:
Developed at the Karlsruhe Institute of Technology (KIT), Celitement is a new family of cementitious binders. It is based on a new class of amorphous hydraulic calcium hydrosilicates. Hardening proceeds through formation of Calcium Silicate Hydrate phases (C-S-H) comparable to those from OPC hydration. Suitable raw materials for the production of Celitement include carbonates, e.g. marl or limestone and a wide range of natural and secondary silicates e.g. natural sand, slags, glasses and fly ash. Carbonates are calcined before processing. The carbonate fraction in the raw material varies in the range from 30 to 40%. In the most simple case quicklime and quartz sand are used. About one half of the raw material, which includes all the calcined lime, is hydrothermally treated in an autoclave at temperatures around 200°C. Calcium silicate hydrates are formed similar to the processing of autoclaved aerated concrete. In a second step the synthesised calcium silicate hydrates are mixed and milled together with the remaining siliceous materials. During milling hydrogen bonds, which stabilize the autoclaved products, are destroyed and new amorphous calcium hydrosilicates are formed around cores of non reactive co-milled silicates. Since newly formed C-S-H-phases are the only hydration product of Celitement, the heat of hydration is significantly reduced (Stemmermann et al. 2010; Celitement 2012). At present a pilot plant is constructed with a production capacity of 100 kg/d. Celitement GmbH indicates that in 2014 a first plant is scheduled to enter commercial production (Stemmermann et al. 2010).

Energy/Environment/Cost/Other Benefits:
Celitement GmbH claims the followings about the Celitement binder (Stemmermann et al. 2010; Celitement 2012):

- It is similar in mixing, setting and hardening to standardized cements based on OPC.
- The production of Celitement on an industrial scale could save up to an estimated 50% CO_2-emission and primary energy as a result of significant reduction in carbonate content of the raw material. In addition, only about half of the raw material is thermally processed.

Block Diagram or Photo:

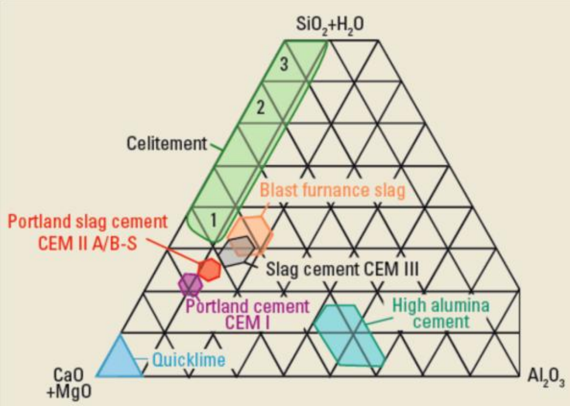

Figure 10. Composition of various hydraulic binders in a projection on the (CaO + MgO) – Al_2O_3 – (SiO_2 + H_2O) system (Stemmermann et al. 2010)

Commercial Status:
Development stage

References for further information: Stemmermann et al. (2010); Celitement (2012)

3.5. Emerging Carbon Capture Technologies for the Cement Industry

Introduction

During cement production, CO_2 is emitted mainly from fuel combustion and limestone calcination. Three basic technologies to capture CO_2 are pre-combustion capture, oxy-fuel combustion, and post-combustion capture (see Figure 11) (ECRA 2007).

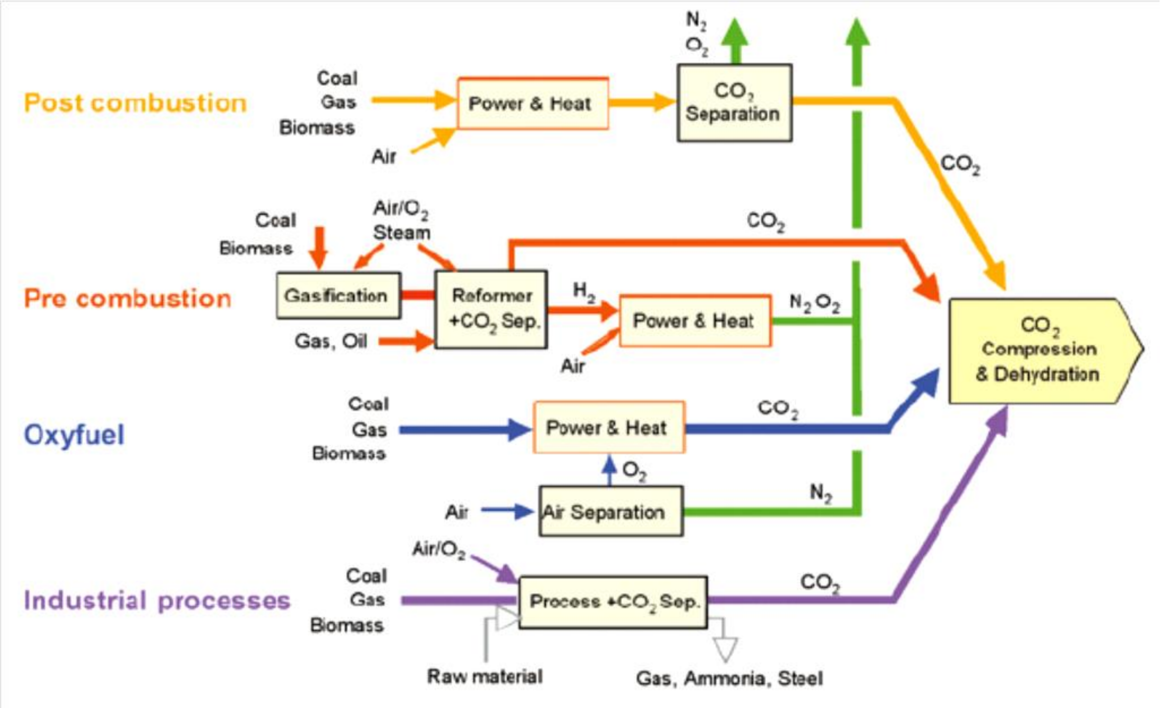

Figure 11. CO_2 capture technologies (ECRA 2007)

Note: Capture from industrial process streams means application of the abovementioned techniques in the steel industry, cement industry, manufacture of ammonia, alcohols, etc.

Carbon capture and storage (CCS) is an emerging technology for the cement industry designed to capture and compress CO_2 emissions into liquid form that can be permanently stored deep underground. Because the majority of CO_2 emissions from cement production originate from limestone calcination, pre-combustion technologies do not significantly decrease CO_2 emissions of cement plants; therefore, this CO_2 capture technology is not suitable for the cement industry. It is more appropriate to consider CO_2 capture technologies in the context of cement production process. Oxy-fuel technology uses oxygen instead of air in cement kilns, which results in a pure CO_2 exhaust stream. Oxy-fuel technology is currently being demonstrated in small-scale plants. Further research is required to make this technology a viable option for the cement industry. Post-combustion technologies are end-of-pipe mechanisms that do not need to be fundamentally altered for the clinker-burning process, so these technologies are appropriate for new kilns as well as retrofits (WBCSD/IEA 2009a).

Carbon capture technologies for the cement industry might not be commercially available until 2020. Some pilot projects have begun, for example in California and the UK. Rough estimates of 20 to 35 Mt/year overall maximum CO_2 emission reduction are made based on 80 percent efficiency and 10 to 20 large kilns (average 6,000 tonnes per day) that are assumed be implemented between 2015 and 2020 globally (WBCSD/IEA 2009a).

Barker et al. (2009) assess costs for building new cement plants with post-combustion and oxy-fuel technologies in the UK. The study assumed construction of a dry-process cement plant with a five-stage preheater and precalciner and a cement output of 1 Mt/y. For the Oxy-combustion technology, the costs were estimated to be €40/t of CO_2 avoided for a 1 Mt/year (yr) cement plant in Europe and €23/t for a 3 Mt/yr plant in Asia. These costs are about the same as the cost of the Oxy-combustion technology installed at a typical coal-fired power plant. In contrast, the estimated costs of post-combustion capture are substantially higher, equal to €107/t CO_2 for a 1 Mt/yr European cement plant and €59/t for a 3Mt/yr Asian plant. These costs are substantially higher than the cost of the post-combustion capture at power plant, mainly because of lower economies of scale and the need to install flue-gas desulphurization, NOx reduction, and a steam generating plant for post-combustion capture technology.

Barker et al. (2009) state that using oxy-combustion only in the precalciner will avoid approximately 61 percent of the CO_2 emissions that result from traditional cement production. Implementing oxy-combustion in both precalciner and kiln could come close to achieving 100 percent avoidance of onsite CO_2 emissions, but significant technical uncertainties remain about this approach. Oxy-combustion requires a sharp increase in onsite power consumption compared to the traditional process. This increase results mainly from oxygen production and CO_2 compression and purification. If we factor in the CO_2 emissions from power generation, the overall reduction in CO_2 emissions attributable to oxy-combustion installed only in the precalciner decreases to from 61 to 52 percent (Barker et al. 2009).

3.5.1. Oxygen Enrichment and Oxy-fuel Technologies

Description:

The U.S. cement industry has used oxygen-enriched combustion since the 1960s. Using oxygen-enriched combustion air increases energy efficiency, production capacity, and allows fuels with low calorific value to be used in place of fossil fuels. This increases kiln flame temperatures while reducing CO_2 emissions. Short-term experiments have demonstrated a kiln capacity increase of 25 to 50 percent when combustion air is enriched with 30 to 35 percent oxygen (by volume). Oxygen enrichment has not yet been applied for purposes of reducing CO_2 emissions. Enriched combustion air might reduce kiln fuel use and thus CO_2 emissions, but additional power is required to produce oxygen, so it is not clear whether there would be a net reduction in total energy use.

Oxy-fuel technology is another emerging candidate for CO_2 capture in new cement kilns. This technology is currently still being researched (ECRA 2007 and 2009).

Oxy-fuel technology differs from oxygen enrichment in that oxygen enrichment does not replace air but injects oxygen into the combustion zone along with combustion air. In contrast, oxy-fuel technology replaces the air with an oxygen stream, using pure oxygen instead of air for fuel burning. Because this eliminates the nitrogen that would normally be in the air that is traditionally used for fuel burning, fuel requirements and flue gas volumes are reduced. When the oxygen stream is fed to the kiln, the resulting kiln exhaust gas contains up to 80 percent of the CO_2 concentration from the fuel burning. This fraction of the exhaust stream is transported to a CO_2 separation, purification, and compression facility (U.S. EPA 2010).

Technical issues associated with use of oxy-combustion (oxy-fuel technology) at a cement plant include: the high flame temperatures (3,500°C) produced by this process which are too hot for proper operation of a cement kiln and the need for recycling a portion of the flue gases back to the combustion zone to provide the necessary dilution; heat-transfer characteristics that are influenced by changing the atmosphere within the combustion chamber; deterioration of kiln walls at higher oxygen levels; clinkering process chemistry under different atmospheres need further investigation; costly removal of contamination from the CO_2-rich exhaust gas resulting from excessive air infiltration; power consumption increases of 200 to 240 kWh/t O_2 for oxygen delivery using an air separation unit (Barker et al. 2009).

Energy/Environment/Cost/Other Benefits:

- Oxygen enrichment technology reduces fuel use by 100 to 200 MJ/t clinker but increases electricity use by 10 to 35 kWh/t clinker compared to fuel and electricity use in conventional processes (CSI/ECRA 2009).
- Short-term experiments have reported a 25- to 50-percent increase in kiln capacity with oxygen enrichment at 30 to 35 percent (volume) in combustion air (CSI/ECRA 2009).
- With oxy-fuel technology, overall energy requirements drop by 75 to 84MJ/t cement despite an increase of 92 to 96 kWh/t cement that is attributable primarily to operation of the CO_2 separation, purification, and compression facility as well as the oxygen production (U.S. EPA 2010).

- With oxy-fuel technology, reduction in CO_2 emissions from reduced fuel combustion ranges from 454 to 726 kg CO_2/t cement; however, this would be partially offset by CO_2 emissions increasing by between 50 and 68 kg CO_2/t cement because of increased electricity use (U.S. EPA 2010).
- Using oxy-fuel technology only in the precalciner avoids approximately 61 percent of CO_2 emissions from the process. Using the technology in both precalciner and kiln could avoid almost 100 percent of CO_2 emissions although greater technical uncertainties are associated with this approach (Barker et al. 2009).
- The additional investment costs for oxy-fuel technology in a new facility are estimated to range from $495 to $540 million, and operational costs would increase by $10 to 13/t cement for a facility producing 2.2 million ton /yr. Costs related to transport and storage of CO_2 are not included (U.S. EPA 2010).

Block Diagram or Photo:

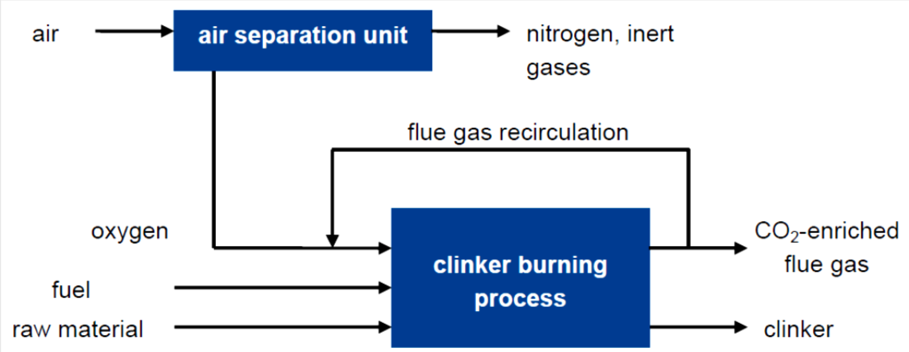

Figure 12. Oxy-fuel technology with flue gas recirculation (ECRA 2009)

Commercial Status:
Oxy-fuel technology: Pilot stage
Oxygen enrichment: Commercial

References for further information:
ECRA (2007 and 2009); U.S. EPA (2010); Barker et al. (2009); CSI/ECRA (2009)

3.5.2. Post-combustion Carbon Capture Using Absorption Technologies

Description:

Solvent scrubbing has been used to separate CO_2 in chemical industry exhaust streams (Bosoago et al. 2009). Post-combustion carbon capture takes advantage of this commercially mature technology and applies a common solvent, monoethanolamine (MEA), for CO_2 scrubbing. Because of the high cost of this solvent, it has to be regenerated and reused, an energy-consuming process that results in additional CO_2 emissions. SO_2, NO_2, and oxygen play an important role in solvent degradation mechanisms. Therefore, the SO_2, NOx, and particulate matter concentrations in flue gases need to be reduced to a minimum before the flue gases go through the solvent scrubbing CO_2 capture system (CSI/ECRA 2009).

Barker et al. (2009) evaluated several technical issues associated with post-combustion amine scrubbing using MEA in a new cement plant. These issues include: the concentration of SO_2 in the flue gas for post-combustion capture with amines since amines react with acidic compounds to form salts that will not dissociate in the amine stripping system, problems of solvent degradation associated with NO_x in the flu gas, the need to limit dust levels to maintain efficiency of the CO_2 capture process, the need for large amounts of steam for solvent regeneration, maintenance of excess oxygen in the process since the clinker must not be generated in reducing conditions, maintenance of the mandatory temperature range for CO_2 absorption levels (flue gas must be cooled from about 110°C to about 50°C), and the influence of acidic components that may reduce the efficiency of the MEA absorption process. Other concerns surrounding amine use include high costs, energy use for sorbent regeneration, and the potential for degraded solvents to become hazardous wastes (Barker et al. 2009). On the other hand, Bosoaga et al. (2009) highlights the advantage of higher concentration of CO_2 in the flue gas of cement plants over power plants, thus demanding less power for CO_2 compression.

An extensive study by the International Energy Agency (IEA) proposes that cement plants make major changes to implement absorbent technologies. These changes include: addition of a solvent scrubber and regenerator as well as a compressor to increase the pressure of CO_2 emissions for transport by pipeline, high-efficiency flue gas desulphurization and de-NO_x to meet flue gas purity requirements, and a combined heat and power plant to provide steam for regeneration of the solvent. The IEA performed a techno-economic analysis of these changes for a new dry-feed-process cement plant located in the UK, with a five-stage preheater and production capacity of 1.1 million tons of cement/yr. The analysis showed that total fuel (coal) consumption for power generation increased by 207.2 MW, and net power consumption from the grid decreased by 13.1 MW (because of onsite electricity generation) compared to fuel and power consumption of a similar cement process without the CO_2 capture system. This takes into account excess electricity generation of 2.9 MW by the combined heat and power plant. Avoided CO_2 emissions were 594,000 tons/yr, or 653,200 tons/yr, taking into account the import and export of electricity, which showed 74-percent and 77-percent reductions, respectively. The CO_2 savings would have been lower if fuels were not coal. Capital costs increased by \$443M, and operating costs, taking into account the export of excess electricity generation for the steam plant, increased \$95.7 M/yr (U.S. EPA 2010).

Absorption technologies are currently only being used at a pilot scale in the energy sector. Demonstration plants are in the planning phase (ECRA 2009), with the first industrial application expected around 2020. With modifications, these technologies should then be available for the cement industry (CSI/ECRA 2009). Availability of a transport (pipeline) grid and storage sites are also important factors necessary to support this CO_2-capture technology.

Energy/Environment/Cost/Other Benefits:

- When post-combustion absorption technologies are used, thermal energy consumption increases by 1,000 to 3,500 MJ/t clinker, and electricity consumption increases by 50 to 90 kWh/t clinker. Overall, primary energy consumption will be high, likely more than 3 MJ per kg CO_2 avoided.
- Direct CO_2 reduction potential from a carbon-capture system is up to 750 CO_2/t clinker. Indirect CO_2 emissions increase by 25 to 60 kg CO_2/t clinker because of increased electricity consumption.
- A rough prediction is that an investment of $130 to $443 million will be needed for this technology, and operations will cost $13 to 96/t cement, excluding the cost of CO_2 transport and storage (CSI/ECRA 2009; EPA 2010).

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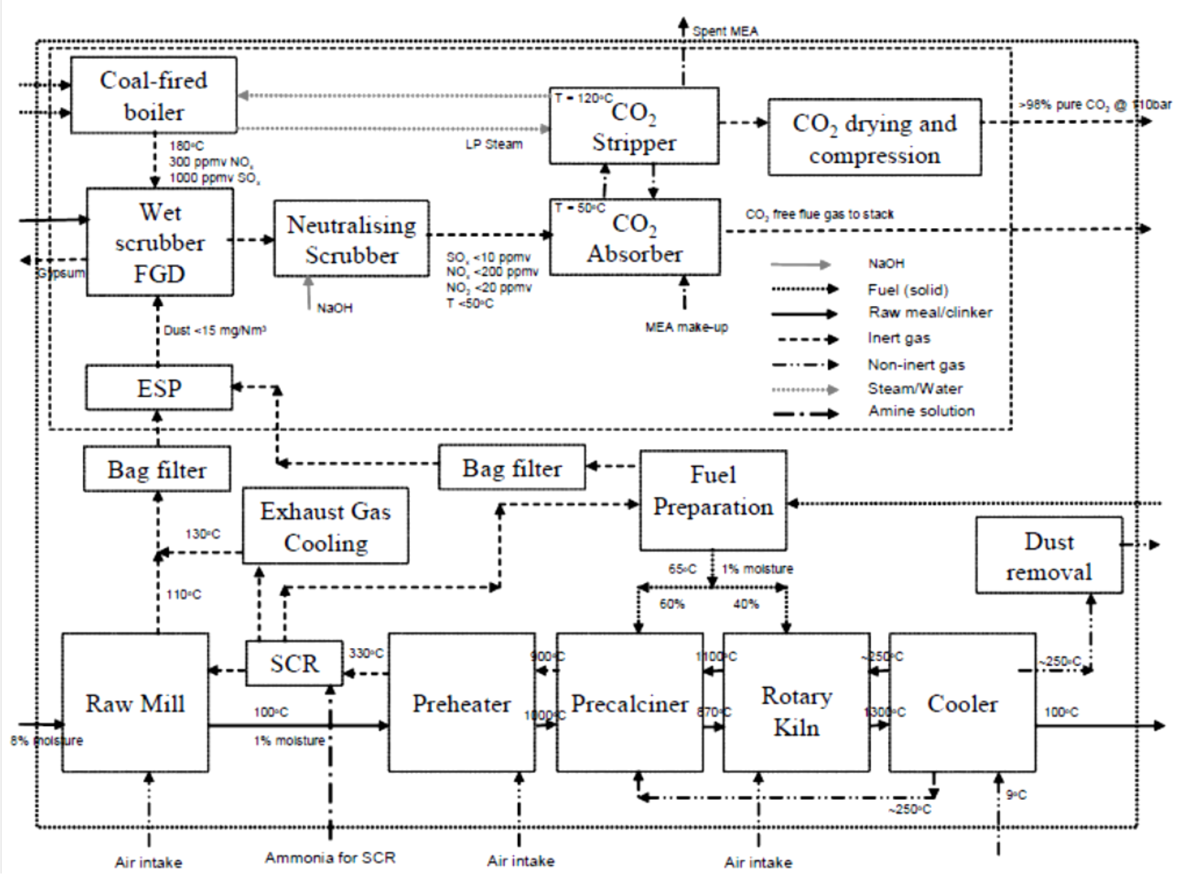

Figure 13. A cement plant with post-combustion CO_2 capture system (Barker et al. 2009)

Commercial Status:

Pilot stage

References for Further Information:

CSI/ECRA (2009); ECRA (2009); U.S. EPA (2010); Barker et al. (2009); Bosoaga et al. (2009)

3.5.3. Calera Process

Description:

The Calera process captures power-plant CO_2 and stores it as a carbonaceous material. Using a process known as “mineralization via aqueous precipitation,” the Calera process converts gas into stable solids such as metastable calcium, magnesium carbonate, and bicarbonate minerals. The process requires a high pH and thus is most economic when power plants are located near sources of suitable brines, which are extracted from geologic formations, as well as alternative sources of alkalinity and minerals. Calera cement is similar to Portland cement and aggregate but can differ by site based on the inclusion of trace components. After processing, the solid materials produced by the Calera process can be used in various construction applications. Calera has another proprietary high-efficiency electrochemical process called “alkalinity based on low energy” which uses only salt and electricity to produce NaOH and HCl ($NaCl + H_2O \rightarrow NaOH + HCl$) (Calera 2012).

Co-producing electricity with the Calera carbon capture process could reduce power plant emissions by up to 90 percent, with offsetting CO_2 emissions of 10 to 30 percent from the Calera process (CO_2 emissions associated with the energy use by Calera process). It is possible that Calera supplementary cementitious material could replace 20 percent of ordinary Portland cement in concrete, significantly decreasing concrete’s carbon footprint. Challenges associated with the Calera process include dependence on brines extracted from geologic deposits; the need for alternative natural alkalinity resources and/or minerals near the power plant; increase in energy use by Calera process (energy penalty); production of more calcareous material than needed in the current market; potential impact on water balances and hydrology from extraction and reinjection of brines; and the need for environmentally acceptable management of the brines and bicarbonate solutions that must be pumped from and returned to geologic formations as part of the process (Bren 2011).

Calera has a demonstration project at Moss Landing, California that is capable of capturing 30,000 tons per year of CO_2, which is equivalent to a 10-MW electric (MWe) natural gas power plant (Calera 2012). Other Calera demonstrations are planned in California and Wyoming in the USA as well as in China and Australia during the next few years.

Another company, Skyonic Corporation, has developed SkyMine® technology, which is a carbon mineralization process that removes CO_2 from industrial waste streams through cogeneration of carbonate and/or bicarbonate materials. A demonstration facility is under construction at Capitol Aggregates, Ltd. cement plant in San Antonio, Texas. This plant is predicted to capture 75,000 t of CO_2 from flue gasses and mineralize the carbon emissions to produce 143,000 t of baking soda, which could be used in industrial applications including as feedstock for bio-algae fuels (Parsons Brinckerhoff and GCCSI 2011).

Energy/Environment/Cost/Other Benefits:

- Using less cement and more supplementary cementitious material from the Calera process could reduce CO_2 emissions from concrete production. Calera claims that its process requires less additional energy than many other carbon capture and storage processes if off-peak and low-carbon energy sources are utilized for manufacturing the required alkalinity.

- Calera technology focuses not only on capturing CO_2 that would otherwise be released into the atmosphere but also on recycling this CO_2 for concrete production. This is an advantage compared to some other CCS technologies (e.g., post-combustion absorption) in which CO_2 would be stored underground, a technique whose safety and efficacy are still in question.
- In addition to capturing CO_2, the Calera technology can capture SO_2 and other acid gases, mercury, and other heavy metals (e.g., silver, arsenic, barium, cadmium, chromium, lead, and selenium) and can safely isolate them in calcium carbonate precipitate (Bren 2011).

Block Diagram or Photo:

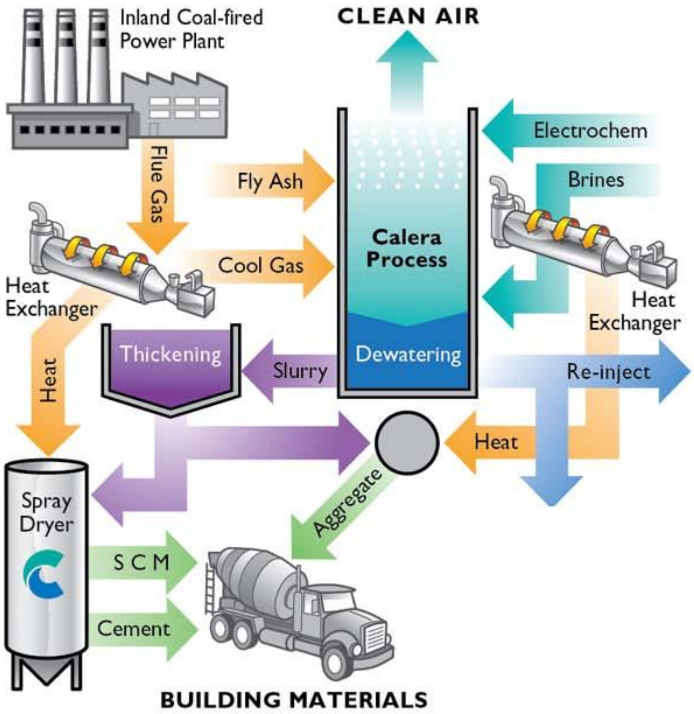

Figure 14. Calera process (Calera 2012)

Commercial Status:
Pilot stage

References for Further Information:
Calera (2012); Bren (2011)

3.5.4. CO_2 Sequestration in Concrete Curing

Description:

CarbonCure, Inc. of Canada has developed a concrete curing process that captures CO_2 emissions from their plants as well as neighboring plants and permanently storing the CO_2 in precast concrete products. The capture is accomplished by exposing those products to CO_2-rich flue gases during the concrete curing process. This CO_2 sequestration method had been attempted in the past but was deemed undesirable because of energy required to produce high pressures in the curing chambers. CarbonCure claims that their process can operate at atmospheric pressure without the need for curing chambers. Though this process remains unproven, industry experts believe it holds great potential if successful (Hamilton 2008). Currently, design and industrial testing are in progress to reduce installation and operation risks of the process. The first demonstration plant is projected to start operation in 2012 (CarbonCure 2012).

Carbon dioxide is naturally reabsorbed in concrete products over hundreds of years through natural chemical reactions. In the CarbonCure process, freshly mixed concrete is exposed to a stream of CO_2-rich flue gas, which speeds up the reactions between the gas and the calcium-containing minerals in cement. As an added benefit, no heat or steam is required, which saves energy and prevents additional CO_2 emissions (Hamilton 2008). The process produces only water and heat as byproducts. With 5 billion tons of concrete consumed per year worldwide, of which 10 percent is estimated to be precast concrete, there is potential to capture 60 Mt per year of CO_2 through concrete curing if this technology is proven and commercialized. However, sequestration of CO_2 through concrete curing would be exclusively confined to precast concrete plants, and the precast concrete that sequesters carbon is not likely to be favored by the market over existing products. Thus, the product's competitiveness compared to conventionally cured concrete will be determined by the cost savings, reduced curing time, and monetary value of the CO_2 abated through the process (Parsons Brinckerhoff and GCCSI 2011).

Shao et al. (2010) examine the feasibility of this technology and the CO_2 absorption capacities of masonry block, paving stone, cement board, and fiberboard. Capacities were based on the cement content of the products studied and ranged from 6.3 to 18.9 percent within different conditions (Shao et al. 2010).

Researchers at McGill University are also developing a curing process for the precast concrete industry in which CO_2 is used as a reactant to increase the rates of compressive strength gain in the concrete, to reduce energy consumption levels, and to improve the durability of precast concrete products (NETL 2011; Kashef-Haghighi and Ghoshal 2010).

Energy/Environment/Cost/Other Benefits:

- CarbonCure, Inc. claims the following benefits from implementation of carbon curing technology:
    - 38 percent energy savings compared to conventional precast concrete curing
    - 17 percent reduction in product greenhouse gas emissions compared to conventional precast concrete
    - 10 percent cement savings compared to conventional precast concrete curing

  - 20 percent less product waste
  - Meets the American Society for Testing and Materials (ASTM) and the Canadian Standards Association (CSA) industry quality standards
  - Profitable within first year
  - Less than a day to install the equipment, which means easy retrofit with minimal disruption to existing processes
  - Capital cost: $8,000 (CarbonCure 2012).
- Use of CO_2 accelerates the curing process and enables it to take place at lower temperatures (Parsons Brinckerhoff and GCCSI 2011).

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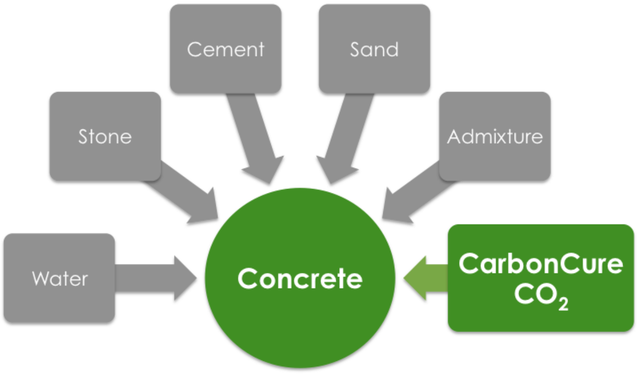

Figure 15. Schematic of CarbonCure process (CarbonCure 2012)

Commercial Status:
Development stage

References for Further Information:
Parsons Brinckerhoff and GCCSI (2011); CarbonCure (2012); NETL (2011); Kashef-Haghighi and Ghoshal (2010)

3.5.5. Carbonate Looping Technology

Description:

Amine scrubbing carbon capture technology uses a significant amount of additional energy that can be reduced by using lime (CaO) as a regenerable sorbent. After reacting with CO_2 for a number of cycles , CaO loses its ability to react with CO_2 and usually becomes waste. However, the exhausted (spent) sorbent could partially replace the main raw material in cement manufacturing, $CaCO_3$. Because the spent sorbent would not need to be calcined in the kiln (releasing CO_2 to form CaO), using it as a replacement for limestone in cement would reduce CO_2 emissions from calcination, which accounts for more than 50 percent of total CO_2 emissions from the cement production process. This process is also known as a "looping cycle" or "carbonate looping" technology (Dean et al. 2011).

Abanades (2008) describes the fundamentals of the carbonate looping process, and Pathi et al. (2011) created a model of a simple carbonate looping process based on the average conversion of calcined limestone. The model is used to study the influence of average conversions of limestone in the carbonator on the flow rates of various streams within the looping process, and to study the energy necessary for calciner reactivation. In addition, the model is used to study the carbonate looping process as implemented in the cement pyroprocess.

The European Cement Research Academy (ECRA) has estimated that modern anthracite- and lignite-fired power plants emit 750 or 950 grams(g) CO_2 /kWh, respectively. An 800-MWe power generation plant discharges approximately 620 or 780 tpd of degraded CaO sorbent (the sorbet has a lifetime of 30 cycles). For a mid-sized plant producing 3,000 tpd of clinker, use of precalcined CaO could meet approximately one-third of the raw material needs. This looping technology would be feasible if the cement plant and the power plant both function in close cooperation, ideally, next to each other in an operational link. (Hollingshead and Venta 2009).

Energy/Environment/Cost/Other Benefits:

- In addition to the benefit of the CO_2 captured by the calcium looping system, use of the spent precalcined CaO as the raw material for cement production would reduce cement plant CO_2 emissions by more than 50 percent.
- Reusing spent sorbent reduces the waste stream.
- Using spent sorbent instead of limestone for the cement production conserves natural limestone resources.

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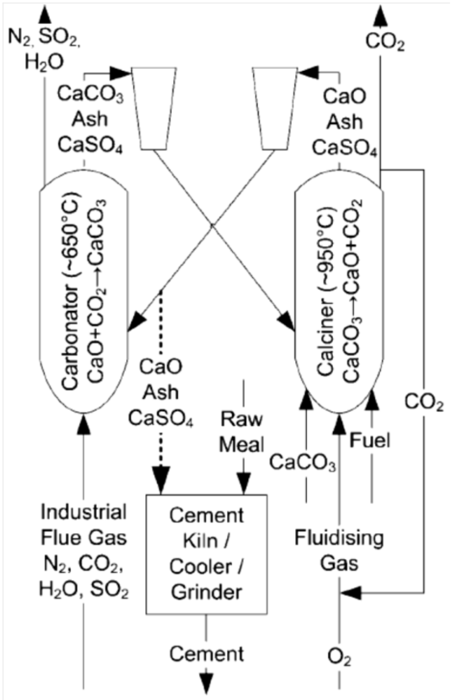

Figure 16. Flow diagram of calcium-looping CO_2 capture and cement manufacture (Dean et al. 2011)

Commercial Status:
Development stage

References for Further Information:
Dean et al. (2011); Pathi et al. (2011); Hollingshead and Venta (2009)

3.5.6. Industrial Recycling of CO_2 Emissions into High-energy Algal Biomass

Description:

Concentrated CO_2 streams produced by cement or power plants could be used to cultivate algae. Due to algae's sensitivity to impurities, the recycled CO_2 would have to undergo a cleaning process before being used for this purpose. Currently, closed algal cultivation systems for biofuel production have moved from the research phase to pilot and demonstration projects. Because of algae's potential as a feedstock for biodiesel production, food products, and chemicals, several large global companies, including BP, Chevron, Virgin, and Royal Dutch Shell, have invested research funding in this area (APP 2008).

Commercial-scale systems range from 10 to 100 hectares and are estimated to absorb between 500 and 55,000 t CO_2 per system per year. Algae biomass fuels are predicted to become the largest biofuel class by 2022 when they will account for an estimated 37 percent of all biofuels produced. However, large land areas are required for algae cultivation, so the potential for this technology could be limited in areas with high land prices (Parsons Brinckerhoff and GCCSI 2011). Similar to existing agricultural systems, algal cultivation requires large quantities of nutrients, which makes it CO_2 intensive. The technical and reliability barriers to this technology are expected to be overcome within 3 to 5 years, and commercial deployment is expected in 5 to 10 years (APP 2008).

The Cement Task Force of the Asia Pacific Partnership (APP) initiated a project on high- yielding algae culture, with bench-scale development of a cement emissions bioreactor followed by a pilot project and then a commercial-scale demonstration. The current status of the project is not clear. APP predicted 1.2 billion tons per year of algal biomass fuel produced using this technology. The ACC Ltd. Cement plant in India will implement the pilot plant after testing is completed at the Indian Institute of Technology. The total fund for the project was about \$10 million (APP 2008). Another case study by Pond Biofuels, a Canadian company, captures CO_2 and other emissions from a cement plant to create nutrient-rich algae slime. The algae are grown at a facility next to the cement plant to be harvested, dried, and then used as fuel in the plant (Pond Biofuels 2012).

Algenol is a U.S. company planning to develop a \$850-million algae plant in the Sonora Desert. Approximately 6 Mt of CO_2 per year would be reused to produce 3.8 million cubic meters of ethanol. Solazyme is another company taking advantage of the microbial fermentation process, fermenting algae on a large scale without the need for sunlight, to produce algae oil. A third company, MBD Energy, uses algae to recycle captured industrial flue-gas emissions and produce algae oils suitable for manufacture of high-grade plastics, transport fuel, and livestock feed (APP 2008).

Energy/Environment/Cost/Other Benefits:

- On average, about 1.8 tons of CO_2 will be utilized per ton of dry algal biomass produced.
- This technology has significant potential for large-scale reuse of $CO_{2.}$
- Existing crude oil refineries can use algal oil.
- Local use of CO_2 emissions avoids the need for transportation and storage.

- Algae cultivation systems can avoid competing with terrestrial food crops, a challenge that has restricted development of first-generation biofuels.
- Sewage wastewater can be utilized as a source of nutrients for this technology.
- The yield of an algae cultivation system is forecast to be 10 times greater per land area than the yields of terrestrial vegetable oil crops.
- This technology could offer a carbon negative pathway in which carbonization is used to produce fuel (Parsons Brinckerhoff and GCCSI 2011).

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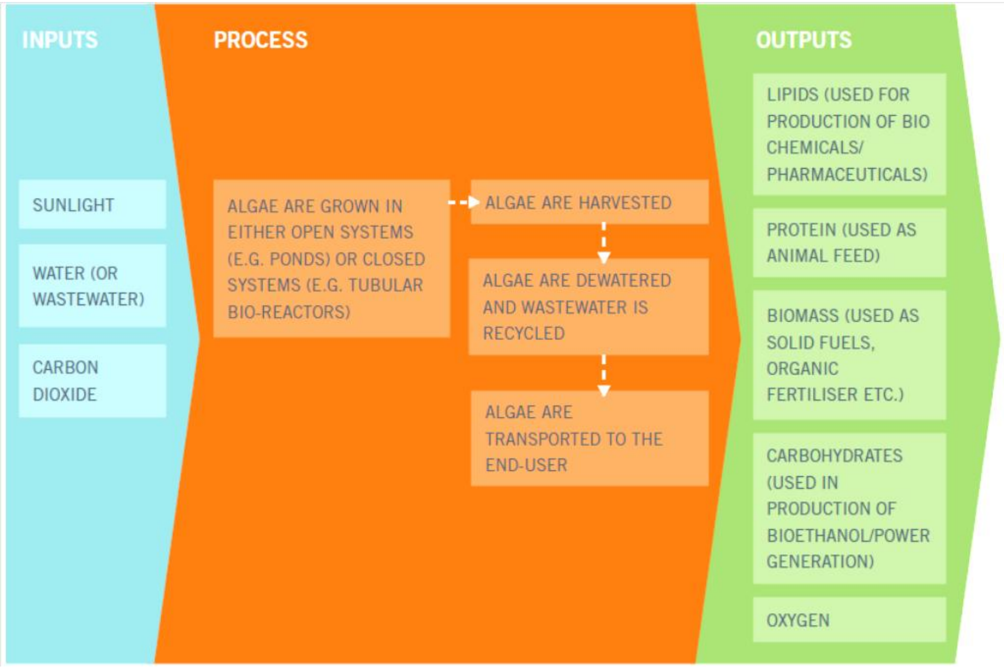

Figure 17. Algae cultivation overview (Parsons Brinckerhoff and GCCSI 2011)

Commercial Status:
Demonstration stage

References for Further Information:
Parsons Brinckerhoff and GCCSI (2011); APP (2008); Pond Biofuels (2012)

3.5.7. Bio-Technological Carbon Capture

Description:

CO_2 Solution, Inc. has taken a biomimetic approach to efficiently capture CO_2 using the natural power of a biocatalyst (enzyme) and carbonic anhydrase, which are substances that manage CO_2 during respiration in mammals. In this technology, the biocatalyst and carbonic anhydrase are used within a reactor to create an “industrial lung” that captures CO_2 from industrial flue gases. After the waste CO_2 is captured, pure CO_2 is produced with the help of the enzyme and then stored underground and/or used in enhanced oil recovery. This technology can be applied to coal-fired power generation, oil sands, and other CO_2-intensive industries such as cement and steel. Prototypes tested at Alcoa Inc.'s aluminum smelting facility in Quebec, Canada demonstrated the full functionality and stability of the enzyme under real-world conditions (CO_2 Solution 2012).

This patented process has three phases. First, flue gas containing CO_2 enters the reactor where it is dissolved or captured in an aqueous solution. CO_2 is then converted into a bicarbonate ion (HCO_3-) in the presence of the enzyme. This bicarbonate-ion-enriched solution from the reactor is regenerated either by production of pure CO_2 for underground storage, enhanced oil recovery or other industrial uses; or by production of solid carbonate for various industrial uses. The capture solution is reused in another cycle.

Traditional post-combustion CO_2 capture methods are based mainly on amine solvents, which are energy intensive and require high temperatures to strip CO_2 for underground capture and storage. CO_2 Solution, Inc. claims that the enzyme can materially lower the cost of carbon capture by allowing a reduction in the size of the absorber equipment and reducing process energy requirements (CO_2 Solution 2012).

Energy/Environment/Cost/Other Benefits:

According to CO_2 Solution, Inc. their carbon capture technology showed the following benefits at prototype scale (CO_2 Solution 2012):

- Use of the enzyme increased CO_2 removal by 30 percent for a given quantity of solvent solution compared to conventional solvent scrubbing technology.
- Use of the enzyme lowers capital and operating costs by allowing a reduction in the size of the absorber column and reducing total energy requirements.
- When stripping CO_2-rich solvent (desorption), the enzyme can reduce energy consumption by increasing the CO_2 transfer rate. This is significant because, in conventional technology, the desorption stage is a major contributor to the cost of the total CO_2 capture process.

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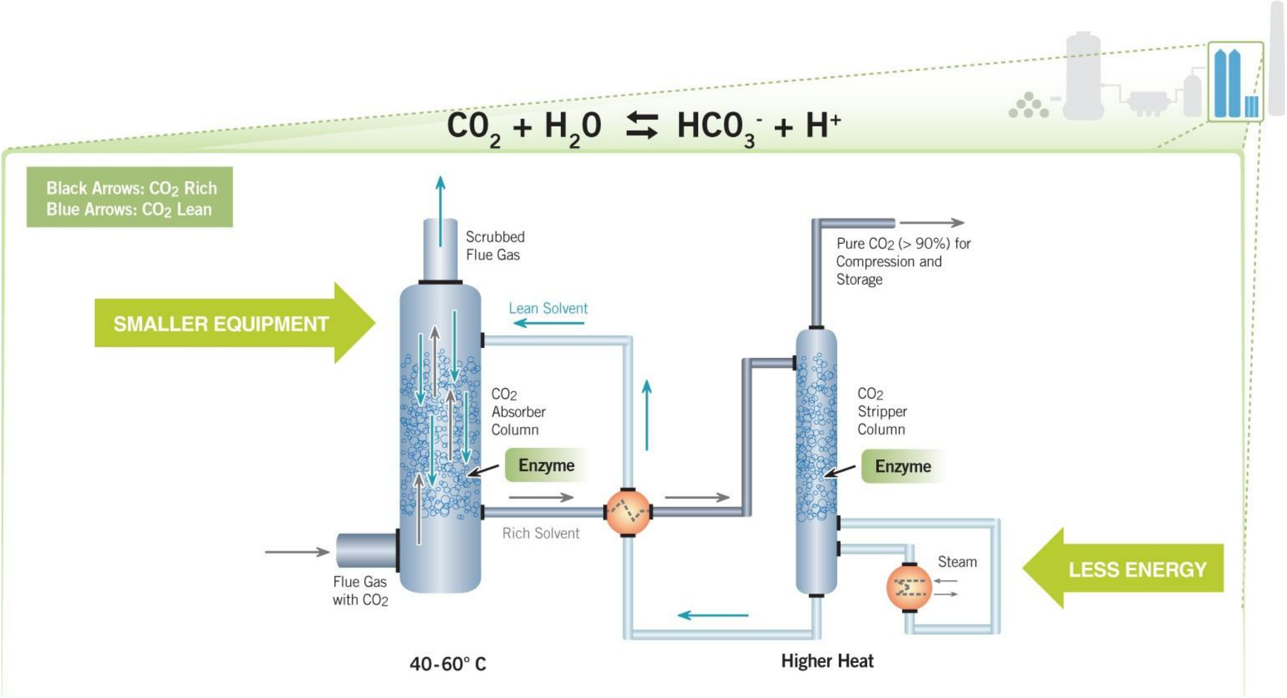

Figure 18. CO_2 Solution Inc. bio-technological CCS system (CO_2 Solution 2012)

Commercial Status:
Prototype stage

Reference for Further Information:
CO_2 Solution (2012)

3.5.8. Capturing CO_2 Emissions from Precalcination of Limestone

Description:

A typical NSP kiln cement plant operates by feeding limestone ($CaCO_3$) to a precalciner that produces CaO by dissociating CO_2 from $CaCO_3$ at high temperatures. Thus, in addition to other products of combustion and excess combustion air, the flue gas from the precalciner contains CO_2 as a result of the calcination of $CaCO_3$ and combustion of the fuel. As a result, the total CO_2 produced in the precalciner is diluted within a larger exhaust stream, making capture of the CO_2 difficult (U.S. EPA 2010).

Rodriguez et al. (2008) investigated a novel process using superheated CaO to separate the calcination and combustion reactions into independent chambers. The heat necessary to run the calciner is provided by a stream of high-temperature CaO particles that circulates between a fluidized bed combustor and a fluidized bed calciner. As a result of this arrangement, the exhaust stream from the calciner consists primarily of CO_2. The CO_2 can then be collected and compressed in preparation for storage. Because more than 50 percent of the CO_2 released in the cement manufacturing process is from calcination, this technology could avoid significant CO_2 emissions from cement plants.

Aspen HYSYS simulations by Rodriguez et al. (2011) have demonstrated that this process is theoretically feasible. However, no pilot plant has been built based on this system yet. This technology would be more economical in new plants because retrofits would involve removal of existing preheaters and precalciners (if present) and construction of the fluidized beds, cyclones, heat exchangers, and compressors associated with the CO_2 capture process (Rodriguez et al. 2011).

Energy/Environment/Cost/Other Benefits:

- This technology could, theoretically, capture more than 45 percent of the CO_2 released in the cement manufacturing process and avoid about 38 percent of the CO_2 emitted in cement manufacturing (including the CO_2 generated by producing the electrical energy needed for the limestone precalcination process itself).
- The cost has been estimated to be about 12 $/t of avoided CO_2 (Rodriguez et al. 2011).

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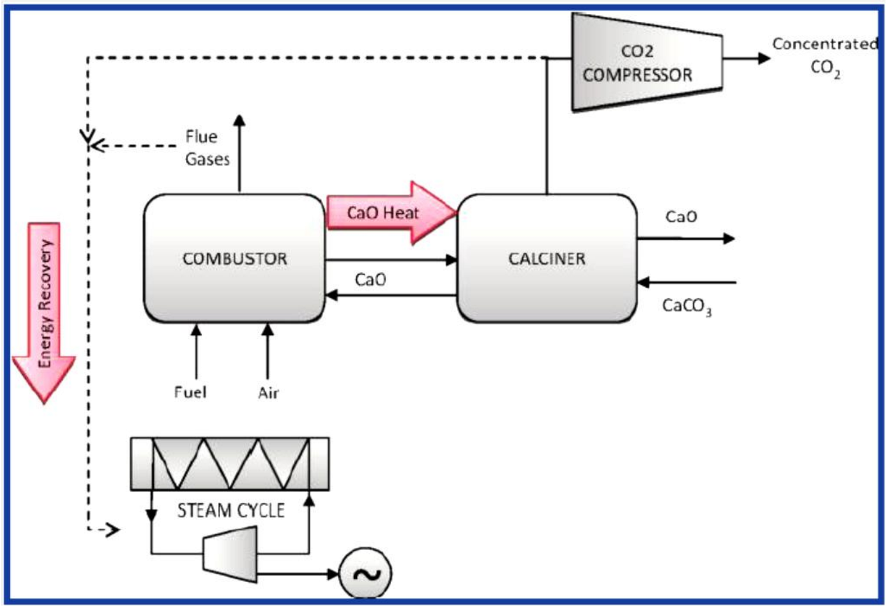

Figure 19. Schematic of the proposed precalciner for obtaining a CO_2-concentrated stream from the calcination of $CaCO_3$ (Rodriguez et al. 2011)

Commercial Status:
Research stage

References for Further Information:
Rodriguez et al. (2008 and 2011)

3.6. Nanotechnology in Cement and Concrete Production

Description:
Nanoscience and nanotechnology are the study and application of extremely tiny particles that can be used in other fields of science, such as chemistry, biology, physics, materials science, and engineering (National Nanotechnology Initiative 2012). Nanostructures can be integrated into larger systems. Concrete is a macro-material strongly influenced by the properties of its components and hydrates at the nanoscale (Sobolev and Gutierrez 2005; Raki et al. 2010). Nanoscience and nanotechnology are being applied to develop cement, alternate cementitious binders, and concrete with improved performance and reduced environmental footprint. To date, research areas are as follows (WBCSD 2012; Selvam et al. 2009; Taylor et al. 2007):

- Development of nanocements and eco-friendly, high performance cements/binders manufactured with lower clinker content
- Improvement in cement and concrete performance through incorporation of nanoparticles and chemical admixtures
- Better understanding of cementitious materials through nanoscale investigations of cement hydration reactions and hydration products to achieve cements and concretes with tailored performance
- Development of activators/ catalysts for low-temperature clinkerization
- Use of nanoparticles to reinforce cementitious matrices for improved flexibility and toughness
- Application of photocatalytic titanium dioxide nanoparticles for self-cleaning concrete surfaces
- Development of cement-based nanocomposites for various applications

Energy/Environment/Cost/Other Benefits:

- Research has shown the potential for improving concrete properties by modifying the structure of cement hydrates through the addition of nanoparticles and nanotubes, and controlling the delivery of admixtures (Raki et al. 2010).
- Nanoparticles, such as silicon dioxide, were found to be a very effective additive to polymers and concrete, producing high-performance and self-compacting concrete with improved workability and strength compared to traditional products (Sobolev et al. 2006).
- Incorporating nanoparticles allows the increased use of supplementary cementitious materials, reducing the energy need compared to the production of Ordinary Portland Cement.

Block Diagram or Photo:

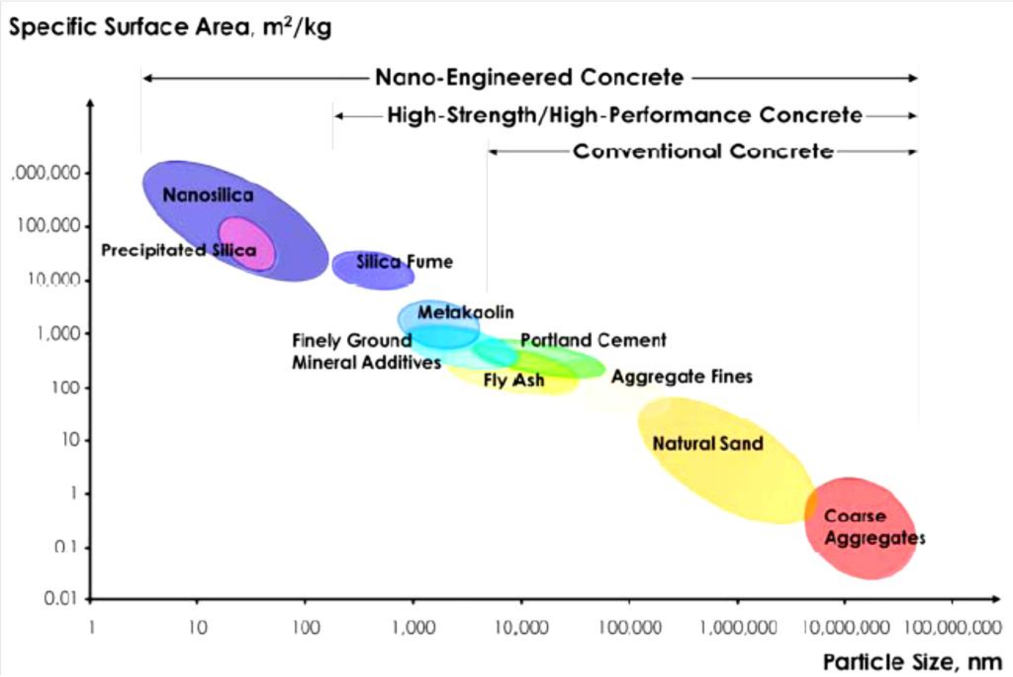

Figure 20. Particle size and specific surface area scale related to concrete materials (Sobolev and Gutierrez 2005)

Commercial Status:
Research stage

References for Further Information:
National Nanotechnology Initiative (2012); Selvam et al. (2009); Taylor et al. 2007); Sobolev et al. (2006)

Summary and Conclusions

This report describes 19 emerging energy-efficiency and CO_2 emissions reduction technologies for cement and concrete production. The information presented for each technology was collected from various sources, including manufacturers.

All the emerging energy-efficiency and low-carbon technologies presented in this report are alternatives to conventional production of cement and concrete or production of the conventional raw materials used in manufacturing cement or concrete. It is likely that no single technology will be the best or only solution but instead that a portfolio of technologies should be developed and deployed to address the increasing energy use and CO_2 emissions of the cement industry.

As can be seen from the information presented in this report, most of the technologies have energy (CO_2) penalty associated with their operation. Therefore, further research is needed to improve and optimized these technologies in order to minimize their energy penalty. In addition, for some technologies, there was not much information available except from the technology developer. Conducting independent studies and validation on the fundamentals, development, and operation of these emerging technologies can be helpful to private and public sectors as well as academia.

Shifting away from conventional processes and products will require a number of developments including: education of producers and consumers; new standards; aggressive research and development to address the issues and barriers confronting emerging technologies; government support and funding for development and deployment of emerging technologies; rules to address the intellectual property issues related to dissemination of new technologies; and financial incentives (e.g., through carbon trading mechanisms) to make emerging low-carbon technologies, which might have a higher initial costs, competitive with the conventional processes and products.

It should be noted that the purpose of this report is solely informational.

Acknowledgments

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